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# Impact of Pyrolyzed and Unpyrolyzed Animal Manures on Soil Properties, Carbon Sequestration, and Clover Productivity in Andisol

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**Abstract:** The use of organic waste in agricultural soil can enhance crop yields, improve waste management, and boost soil carbon (C) sequestration. However, more field data are required to fully understand the impacts of pyrolyzed and unpyrolyzed animal manures. The objectives of this study were (i) to analyze the impact of two pyrolyzed and unpyrolyzed manures on soil properties, soil C storage, and clover productivity and (ii) to examine the biochar's movement through the soil profile. Poultry litter (PL), dairy manure (DM), poultry litter biochar (PLBC), and dairy manure biochar (DBC) were applied at rates of 8 t ha$^{-1}$ in a field experiment with red clover (*Trifolium pratense* L. var. Quiñequeli) in an Andisol. We monitored changes in soil chemical properties, foliar properties, and crop yield after three clover cuttings. To examine the movement of biochars through the soil profile, we set up a lab experiment where field conditions were simulated. PLBC, DBC, and PL increased soil pH by 0.5 (6.44), 0.28 (6.22), and 0.25 (6.19) units, respectively. Soil available P increased in both pyrolyzed and unpyrolyzed PL treatments (by 8.53 mg P kg$^{-1}$, on average). Clover yields only increased in treatments with amendments that provided more available P and increased the pH. The addition of DBC increased soil total C (30.3%). Both biochars added to the soil surface exhibited little movement through the soil profile (2 to 4 cm). In this study, the pyrolysis of manures emerged as an option for reducing waste volume from the farming industry. Manure biochars proved useful at low rates for enhancing crop yields (PLBC) and storing C in the soil (DBC).

**Keywords:** biochar; dairy manure; poultry litter; amendments; soil nutrition

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## 1. Introduction

Organic carbon (OC) is a significant indicator of soil quality and plays a crucial part in both crop yield and the reduction in the impacts resulting from climate change [1]. The regulation of OC commonly hinges on the equilibrium between carbon inputs and outputs (for instance, $CO_2$ and $CH_4$ emissions and/or carbon loss through erosion). However, this balance in farming soils is susceptible to disturbances induced by climate change. However, this can be mitigated by implementing appropriate management methods such as the application of biochar or manure [2].

The agriculture and livestock sectors can contribute to reducing global warming by 2050; they have the potential to mitigate between 2.3 and 9.6 Gt $CO_2$ eq yr$^{-1}$ [3]. The practice of using manure as a soil enhancer has been thoroughly investigated for its eco-friendly benefits in agriculture, with evidence suggesting that it can boost soil OC levels and crop productivity if sustained over a certain period [4–6]. Manure C retention coefficients between 12% [6] and 45% [7] have been reported depending on the time interval of the study. However, the effects of manure application on soil greenhouse gases (GHG) could offset the net C gains [8] because manure can be rapidly mineralized to $CO_2$. Nevertheless, considering the increasing demand for crops, it is important to evaluate the potential use of organic fertilizers in agricultural systems to increase yields [9]. The application of manure as a soil amendment and organic fertilizer can improve the physical, chemical, and biological properties of the soil [10]. In theory, manures are returned to the Earth, enabling plants to tap into their nutrient contents [4,11]. Meanwhile, the swift expansion of global livestock production has created an overwhelming volume of waste [4,5,12]. Hence, it is crucial to devise strategies for reusing and minimizing waste. For example, transforming manure into manure biochar through pyrolysis can be a strategic move for nations with significant animal and farming sectors [7,13–15].

Biochar is a carbon-rich material derived via pyrolysis, a process that converts organic substances such as agricultural byproducts or animal waste [2,16]. This material can be added to soil for ecological or agronomic purposes. Biochar interacts with the soil matrix, modifying its chemical [7,14,17–19], physical [20], and biological properties [13,20,21]. The pyrolysis method transforms OC into an insoluble aromatic structure, making biochar resilient to both abiotic and biotic degradation [22–25]. Although the carbon half-life of biochar in soil is speculated to be several hundred to a few thousand years [2,26], a minor portion can be carbon-labile [16,19,25]. Nonetheless, recent investigations have indicated that less carbon mineralization occurs in pyrolyzed manures compared to their original feedstocks [7,27]. The use of biochar as a soil amendment has also received increasing attention because of its agronomic benefits [28,29]. For example, biochar application has been shown to impact sorghum [17], rice [30–32], and corn yields [33]. However, in a recent review by [29], no results were found on crop yields in temperate latitudes, while [28] found that the increase in crop yield depends on (i) biochar doses, (ii) biochar feedstock, (iii) soil type (Andisols were not included), and (iv) the use or not of positive controls (i.e., chemical fertilizer). In particular, manure biochars have a liming potential and can provide nutrients such as phosphorous (P), potassium (K), calcium (Ca), nitrogen (N), and magnesium (Mg) to soil and plants [14,17,34–37], while their effect on soil carbon contents can be lower than others biochars [17,38].

In order to recommend sustainable practices in agricultural systems, it is crucial to simultaneously examine the impact of organic amendment on crop yield, C sequestration, soil quality, and the environment. The major objective of this research was to assess the impact of pyrolyzed and unpyrolyzed amendments (PL, PBC, DM, and DBC) on soil C storage and red clover (*Trifolium pratense* L. var. Quiñequeli) productivity in an Andisol. In addition, we examine the biochar's movement through the soil profile.

## 2. Materials and Methods

### *2.1. Experimental Site*

The study was established under field conditions in the experimental station "El Nogal" of the University of Concepcion, located in Chillan, Ñuble Region, Chile (36°35′45.2″ S 72°04′49.7″ W; altitude: 139 m above sea level (masl)). The soil in the area is predominantly composed of Humic Haploxerands (Andisol) [39], which are developed from modern volcanic ashes that originated during quaternary volcanic activity [40]. The main properties of the topsoil (0–10 cm) are as follows: pH in $H_2O$ (5.96); total C (3.3%); total N (0.23%); Olsen P (44.2 mg kg$^{-1}$); exchangeable P (1.82 cmol kg$^{-1}$); available N (15.6 mg kg$^{-1}$); ammonium (4.0 mg kg$^{-1}$); nitrate (17.1 mg kg$^{-1}$); and bulk density (0.8 Mg m$^{-3}$) and sand, silt, and clay contents of 22%, 51%, and 27%, respectively. The experimental station, under a Mediterranean climate, receives approximately 875 mm of annual precipitation, primarily during winter (May to September). In this study, the plots were irrigated twice a day from December to February (average temperature of 28.5 to 29.5 °C), maintaining soil moisture above 60% throughout the experiment to avoid soil dryness.

### *2.2. Feedstock and Biochars*

Biochar feedstock was obtained from poultry litter and dairy manure collected from the Ñuble region in Chile. The poultry litter consisted of poultry manure along with other waste products from poultry production, such as eggshells. The initial samples of dairy manure and poultry litter had a high moisture content, exceeding 60%. As a result, they were left to air-dry (maximum temperature of 25 °C and air humidity below 60%) in a sheltered outdoor area for a fortnight until the moisture content was reduced to 20%.

Subsequently, the manure samples were sieved through a 5 mm mesh size and stored. Biochars were generated via a slow pyrolysis process in a batch system, which involved heating to peak temperatures of 600 °C for a period of 2 h. The gases were not released into the environment during the pyrolysis. All gases generated in the process were condensed and collected as bio-oil; no biogas was produced. The amendments, namely, poultry litter (PL), dairy manure (DM), poultry litter biochar (PLBC), and dairy manure (DBC), were standardized, sieved to a particle size of less than 250 µm, and preserved in desiccators at 25 °C for future application. The specifics of these amendments are outlined in Table 1.

**Table 1.** Chemical characteristics of feedstock and biochars.

| Treatments | TC (%) | TN (%) | Corg (%) | $H{:}C_{org}$ * | pH | $NO_3^-$ N (mg kg$^{-1}$) | $NH_4^+$ N (mg kg$^{-1}$) | $P_2O_5$ (%) | $K_2O$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| PL | 16.2 | 1.2 | - | - | 8.7 | 612.9 | 157.3 | 4.83 | 1.37 |
| DM | 30.5 | 1.2 | - | - | 8.21 | 47.3 | 101.4 | 0.43 | 0.3 |
| PLBC | 11.5 | 0.6 | 6.84 | 0.07 | 10.5 | 2.27 | 9.6 | 2.26 | 1.34 |
| DBC | 38.0 | 1.4 | 36.96 | 0.28 | 10.7 | 3.53 | 5.1 | 0.39 | 1.14 |

* Atomic ratio.

The material derived from poultry litter exhibited a low OC percentage (6.84%), and as such, it does not qualify as biochar based on the International Biochar Initiative (IBI) guidelines [41]. Despite this, for ease of comparison and to simplify discussions between treatments, it will be referred to as poultry litter biochar (PLBC) in this context.

### *2.3. Experimental Treatments and Sampling*

Prior to sowing, a seed germination analysis was conducted. For this purpose, 400 seeds of red clover (*Trifolium pratense* L. var. Quiñequeli) were used without disinfecting. These seeds were placed in Petri dishes (Ø90 × 15 mm) with sterile absorbent paper and distilled water, then stored in a germination chamber at 21 °C. Seed germination was evaluated periodically according to the method in [42]. A 95% germination rate was determined, a value that facilitated the adjustment of the sowing dosage to be used in the study. The soil was prepared similar to a conventional system, with a disk plow and a harrow. To evaluate the effect of the amendments on soil properties, forage yield, and forage composition, 18 plots were established under field conditions (0.7 × 0.7 m with buffer zones of 0.7 m wide between plots). The rate used for each amendment was 8 t·ha$^{-1}$; this rate was calculated by fixing an amendment/soil ratio of 1% [7,14,17] using the soil bulk density (0.8 g cm$^{-3}$). The following treatments were applied in triplicate: (1) soil as control, Soil; (2) NPK fertilizer, Soil_F; (3) poultry litter, PL; (4) dairy manure, DM; (5) poultry litter biochar, PLBC; and (6) dairy manure biochar, DBC. Before seeding, each amendment was spread over the soil surface and combined up to a soil depth of 10 cm. The same soil disturbance was simulated in the Soil control and Soil_F plots (without amendments).

The seeds were sown manually (continuous stream) at a dosage of 15 kg·ha$^{-1}$, equivalent to 1.5 g m$^{-2}$ at 1–2 cm deep and spaced 7–8 cm between rows. In the Soil_F treatment, the equivalent to 80 kg $P_2O_5$ ha$^{-1}$ was added at the start of the experiment as triple superphosphate (TSP), 50 kg $K_2O$ ha$^{-1}$ as muriate of potassium, and 14 kg N ha$^{-1}$ as urea.

The cultivation spanned across three months (December to February) in the plots, with three harvests taking place every 25 days. The method of harvest involved cutting the forage at a 5 cm height from the soil level. The cut forage was then dried in an oven set at

60 °C, and the resulting dried biomass was utilized for yield calculation (t $ha^{-1}$). Upon the completion of the three harvests, forage and soil samples (from the top 0–10 cm of the soil) were collected from each plot. These samples were analyzed to study the impact of the various treatments on the foliar content and the chemical properties of the topsoil.

*2.4. Analyses of Chemical Composition in Soil Amendments, Soil Samples, and Foliar Content*

Biochars and manures were characterized using analytical methods developed for biochar and compost [23]. Biochar elemental contents (total C, N, and H) were determined via dry combustion using an elemental analyzer (Elementar Analysen systeme GmbH, Hanau, Germany). Soil samples were characterized as described by [43]. Initial soil bulk density was measured following the volumetric ring method. Soil total C and N were analyzed via dry combustion using a C, N analyzer (Truspec CN, LECO, St. Joseph, MI, USA). Soil pH was determined in a 1:2.5 ($w/v$) ratio of soil–water extracts. The nitrate and ammonium were extracted according to [44] and were determined via colometry using a UV-Vis spectrophotometer. Olsen P was extracted with 0.5 M $NaHCO_3$ (pH 8.5) and measured colorimetrically using a spectrophotometer (Thermo Spectronic model Genesys TM 5, Vernon Hills, IL, USA). Soil available K was determined using an atomic absorption spectrophotometer (Unicam, Solaar 9000, Cambridge, UK). The content of foliar N analysis was conducted using the semi-micro Kjeldahl method and direct nesslerization using a UV-Vis spectrophotometer [45]. Foliar P and K were determined using the calcination method. In this study, only the foliar values of the last clover cutting were measured.

*2.5. Simulation of Biochar Movement in the Upper Layer of Soil*

To assess the transportability of biochars, soil from the test field was inserted into PVC tubes (159 $cm^3$, diameter 5.5 cm, depth 10 cm). Three treatments were implemented in triplicate (Soil, DBC, and PLBC), with the amendments being applied to the soil surface (at a rate of 8 t $ha^{-1}$) in the DBC and PLBC methods. PVC tubes were conditioned to field conditions (soil density: 0.8 Mg $m^{-3}$), and rainfalls equivalent to 800 mm $year^{-1}$ were applied. Over a 20-day period, the soil was watered via dripping. To prevent soil or biochar from leaking and to allow water to drain, the bottoms of the PVC tubes were covered with cotton gauze. After 20 days of watering, the PVC tubes were frozen (−20 °C). Once frozen, the tubes were slit lengthwise, allowing for the extraction of the frozen soil block. These frozen soil blocks were sliced every 1 cm using a custom-designed device actioned with a steel saw unit operating at a high speed [46], resulting in uniform soil layer sections that were then thawed and dried at room temperature for 72 h. To assess the movement of biochar through the soil, the total C content of each soil layer was tested via dry combustion using a CN elemental analyzer ( TruSpec CN, LECO, St. Joseph, MI, USA) and compared to soil without biochar.

*2.6. Statistical Analyses*

The experiment followed a randomized complete block design structure (n = 3). The three levels of blocks and the six levels of treatments (DM, DBC, PM, PMB, and the control) were identified as the independent variables. On the other hand, the dependent variables were the forage yield, the characteristics of the soil, and the foliar contents. We conducted a statistical analysis, which included the calculation of means, standard deviations, differences of means, and correlation analysis, with the help of R software (version 4.0.3). The normality of the collected data was confirmed through the Shapiro–Wilk test. To test differences in means, we used analysis of variance (ANOVA). If we found significant effects ($p \leq 0.05$), we further carried out mean comparisons using LSD Fisher tests ($p \leq 0.05$). Additionally, we used Pearson's r correlation coefficient to find out the correlations between the properties of the soil and forage yield.

## 3. Results

The chemical properties of the soil (as shown in Table 2) demonstrated variations based on the amendments applied, and these variations were observed for three months under field settings. The application of PLBC, DBC, and PL notably raised the soil pH from 5.94 to 6.44, 6.22, and 6.19, respectively (refer to Table 2). There was a significant increase in soil available P in treatments that used P-rich amendments and had the highest pH (PL and PLBC), leading to an average increase of 8.53 mg P kg$^{-1}$.

**Table 2.** Soil and foliar properties after three forage cuts.

| Treatment | Foliar N | Foliar P | Foliar K | Soil $NO_3^-$ | Soil $NH_4^+$ | Soil av. N | Soil av. P | Soil av. K | Soil pH | Soil N |
|---|---|---|---|---|---|---|---|---|---|---|
| **Units** | **(%)** | **(%)** | **(%)** | **mg kg$^{-1}$** | **mg kg$^{-1}$** | **mg kg$^{-1}$** | **mg kg$^{-1}$** | **mg kg$^{-1}$** | **-** | **(%)** |
| Soil | 3.98 (0.43) a | 0.34 (0.02) a | 3.44 (0.33) a | 10.27 (3.1) a | 15.50 (2.79) a | 25.77 (5.2) a | 41.77 (1.3) b | 374.1 (6.4) a | 5.94 (0.05) c | 0.22 (0.02) a |
| Soil_F | 3.71 (0.11) ab | 0.31 (0.01) a | 3.95 (0.58) a | 8.50 (1.5) a | 12.57 (3.05) a | 21.1 (1.6) a | 43.27 (4.1) b | 373.8 (72.7) a | 5.87 (0.07) c | 0.22 (0.01) a |
| PL | 3.53 (0.15) b | 0.33 (0.04) a | 3.94 (0.24) a | 9.57 (5.1) a | 10.73 (3.57) a | 20.30 (4.4) a | 50.27 (3.9) a | 379.1 (70.0) a | 6.19 (0.12) b | 0.22 (0.01) a |
| DM | 3.50 (0.10) b | 0.34 (0.03) a | 3.46 (0.27) a | 10.93 (5.8) a | 10.90 (4.96) a | 21.77 (9.2) a | 40.03 (3.2) b | 362.7 (25.2) a | 5.95 (0.06) c | 0.23 (0.01) a |
| PLBC | 3.99 (0.29) a | 0.34 (0.03) a | 3.59 (0.26) a | 10.37 (4.88) a | 11.90 (4.59) a | 22.27 (9.2) a | 50.33 (3.9) a | 408.4 (25.3) a | 6.44 (0.23) a | 0.23 (0.01) a |
| DBC | 3.42 (0.09) b | 0.320 (0.02) a | 3.76 (0.14) a | 7.57 (1.68) a | 9.87 (1.78) a | 17.4 (2.62) a | 43.90 (3.1) b | 12.3 (122.4) a | 6.22 (0.13) ab | 0.25 (0.02) a |

Different letters between treatments indicate significant differences based on LSD test ($p \leq 0.05$) (n = 3 ± S.D.).

By the end of the study, the soil mineral N and the soil available K did not exhibit any notable differences between treatments (as shown in Table 2). The soil TC concentration revealed significant variations between the unamended soil and plots treated with biochar (as illustrated in Figure 1). The DBC treatment resulted in a 1.4% increase in soil TC compared to the unamended soil, while the difference between PLBC and unamended soil was less noticeable (0.3%). There was no statistical difference in the soil TN compared to the unamended soil (Table 2).

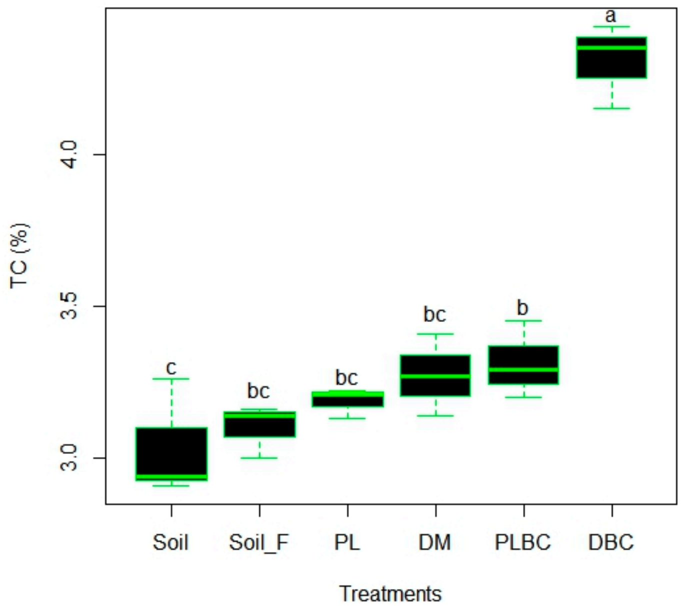



**Figure 1.** Soil total C (TC) in topsoil (0–10 cm) after three months of incorporation of amendments (n = 3 ± S. D). Different letters between treatments indicate significant differences based on LSD test ($p \leq 0.05$). The box-and-whisker plot shows the distribution of the data in the box (black color) and the green whiskers show the deviation. The green line shows the mean of the data.

After three harvests of red clover, the introduction of amendments or fertilizers did not have a substantial impact on the leaf content ($p \leq 0.05$; Table 2), with the exception of a minor yet noteworthy reduction in leaf N in the treatments involving PL, DM, PLBC, and DBC (Table 2).

However, there was a significant rise in the yield of clover ($p \leq 0.05$) with the incorporation of PL, PLBC, and mineral fertilization (on average, 68% higher than the unamended soil; refer to Figure 2d). On the contrary, treatments with DM and DBC resulted in a low forage output (on average, 9.26 t $ha^{-1}$), which was insignificantly different from the control (on average, 7.83 t $ha^{-1}$). For the initial clover harvest, the productivity response was consistent across all amendments compared to the unamended soil ($p \leq 0.05$; Figure 2a). During the second and third forage harvests, PL and PLBC showed a similar productivity response to mineral fertilization, significantly enhancing the productivity compared to the unamended soil (Figure 2b,c).

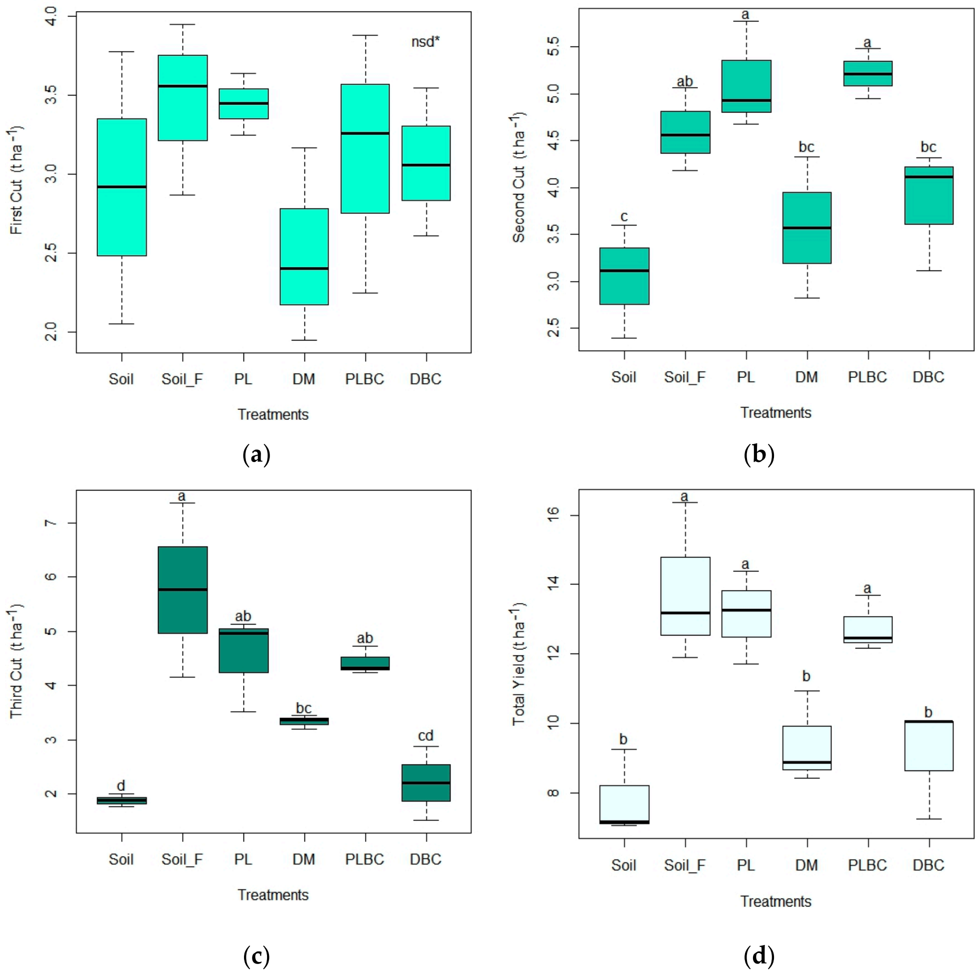



**Figure 2.** Red clover dry matter: (**a**) first cut, (**b**) second cut, (**c**) third cut, and (**d**) total red clover yield, (n = 3 ± S.D.). Different letters indicate significant differences between treatments at $p \leq 0.05$ using LSD test. nsd*: not significant differences.

Figure 3 illustrates the relationship between soil characteristics and clover production, with Pearson coefficients (r values) and significant values being displayed in Supplementary Figure S1. There was a positive correlation between the total yield of clover and the availability of P (r = 0.67, $p \leq 0.05$) as well as the pH level of the soil (r = 0.67, $p \leq 0.05$). There was also a positive correlation between the pH of the soil and the availability of P (r = 0.62, $p \leq 0.100$), which indicates a relationship between these factors. Furthermore, the strongest correlation between yield and either pH or P was observed in the second cut of clover.

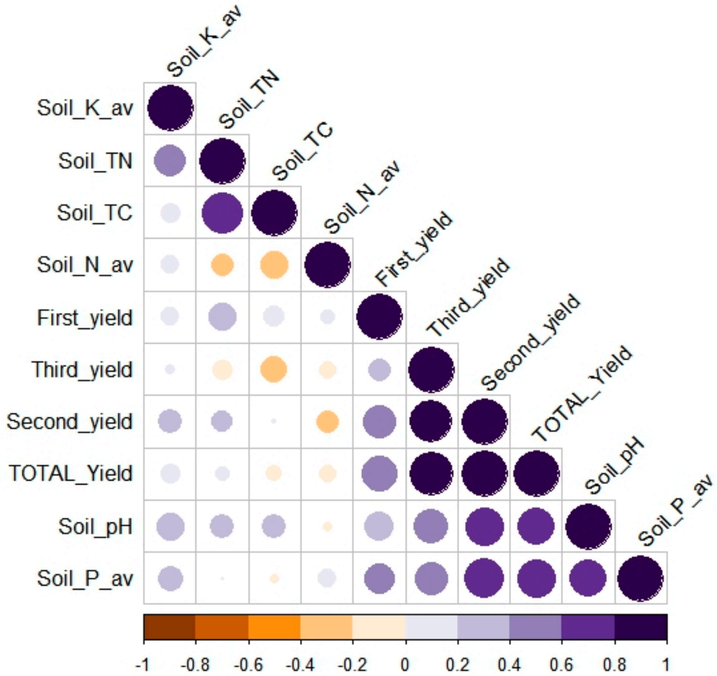
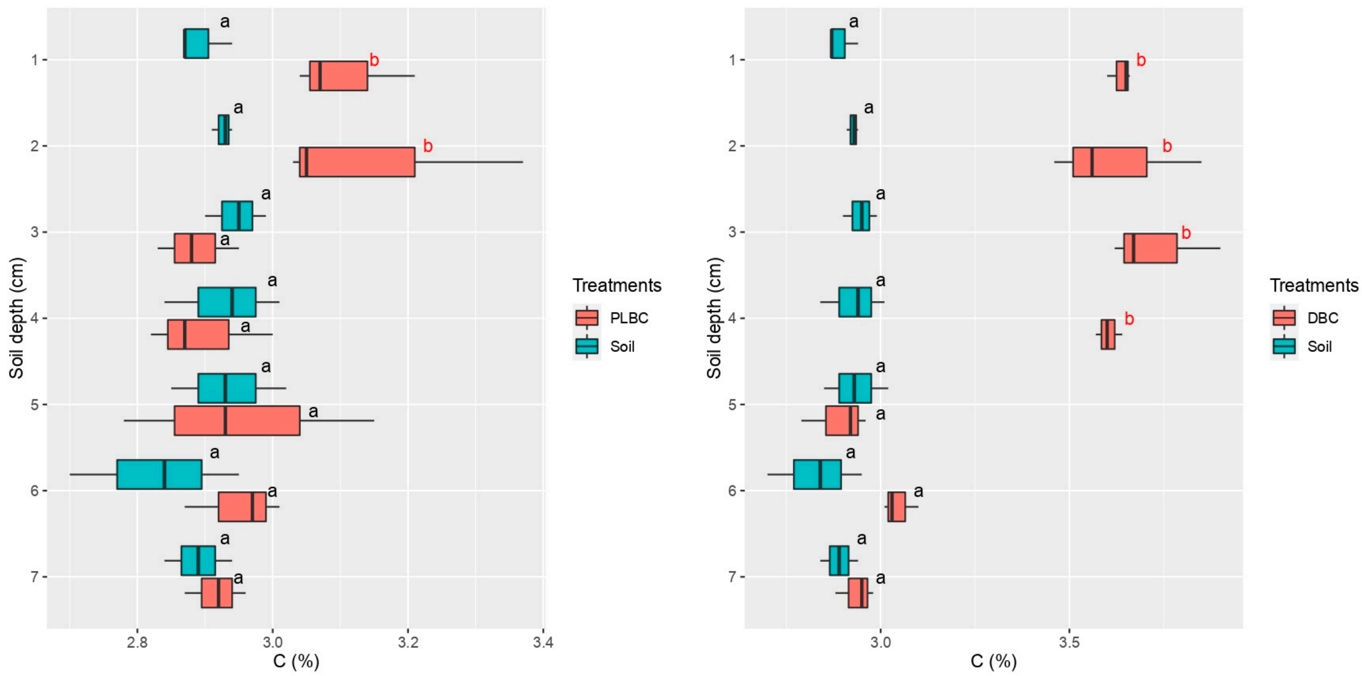



**Figure 3.** Pearson's correlation between total red clover yield and foliar and soil properties. Size and color of the circles mean significance value and Pearson's r coefficient, respectively (all Pearson's r coefficient and significance value are shown in Figure S1).

Figure 4 illustrates the displacement of biochar within the initial 10 cm of the soil profile, described as soil C content. The total C content in the soil experienced an increase in the first 2 and 4 cm of soil in the PLBC and DBC treatments, respectively. These findings illustrate the translocation of each type of biochar within the soil profile.




(**a**) (**b**)

**Figure 4.** Movement of biochar in the topsoil (0–10 cm), expressed as soil TC variation by cm in depth (n = 3 ± S.D.): (**a**) PLBB and (**b**) DBC. Different letters indicate significant differences in TC in the soil profile ($p \leq 0.05$, LSD test).

## 4. Discussion

### *4.1. Impact of Biochars and Manures on the Yield of Red Clover and Soil Characteristics*

In contrast to the original soil, both PL and PLBC considerably enhanced soil fertility and productivity, making a substantial contribution to red clover productivity and increasing soil pH and available soil P. Conversely, DBC merely increased soil pH, and DM did not influence soil attributes or clover productivity (Table 2, Figure 2). While Andosols exhibit a significant pH-buffering ability [47], this research found that biochars (PLBC, DBC) and PL elevated the soil's pH level (refer to Table 2). Biochars are basic substances, and their alkalinity is influenced by the ash content in their raw materials, as well as by their organic and inorganic bases, carbonates, and functional groups [48]. In addition, unstable feedstocks such as manures have a high potential to provide ash content due to their richer concentrations of volatile matter than wood-based biochars [49]. In this case, both raw materials had similar pH levels (averaging 8.5), which increased post-pyrolysis (averaging 10.6). Our prior research at both laboratory and field scales showed that biochars derived from manure (poultry, pig, dairy) possess high liming potential, largely due to the properties of their raw materials [7,14,17].

The modification of soil pH was a key contributor to the increase in clover yield, with a positive relationship being observed between total yield and soil pH (Figure 3). Clover is known to thrive in a range of weather conditions, yet its production is typically hampered by soil pH levels. In this research, the starting soil pH was 5.69, which rose by 0.5 to 0.75 in the PL and biochar treatments, respectively. It is well established that the ideal pH for the growth of legumes varies from 6.6 to 7.5 [50].

Volcanic soils often encounter the issue of P immobilization due to the presence of aluminum when the soil pH is low. Therefore, the alteration of soil pH in this research indirectly and directly contributes to the increase in yield by increasing the availability of soil P [35]. This was further validated by the positive correlation obtained between available P and the increase in soil pH (Figure 3). A number of researchers have found that alkaline biochars can enhance the availability of P in acidic soils [14,17,37,51], thereby boosting crop yields [17] for sorghum, [52] for broccoli, and [53] for Soybean. The studies of [37,54] have shown that biochars rich in phosphorus can serve as potential sources of available P. However, the impact of biochar applications on yield is contingent upon the increase in pH in acid soils.

In the second clover cut, both PL and PLBC demonstrated comparable productivity to mineral fertilization, while the DM and DBC fields yielded less after three cuts than the fertilizer treatment (Figure 2b–d). This outcome could possibly be attributed to the fact that PL and PLBC are abundant in phosphorus, while DM and DBC are deficient in it. In this context, [21] discovered that low-nutrient biochar, derived from willow, could enhance clover yield in unfertilized Cambisols and Andosols due to its positive impact on soil biological communities, thereby improving the nutrient cycle and nutrient availability. However, it is apparent that the capacity of biochar to enrich soil fertility is contingent on feedstock and/or pyrolysis conditions [38,55]. In this research, the pyrolysis procedure was carried out under comparable conditions (slow pyrolysis and a maximum heating temperature of 600 °C). However, the feedstocks were sourced from diverse origins and had different nutrient compositions. For example, PL had a higher nutrient content than DM, especially in terms of $P_2O_5$, $K_2O$, and available N content (Table 1). When applied at a rate of 8 t $ha^{-1}$, PL and PLBC supply more than 150 kg of $P_2O_5$ $ha^{-1}$ (Table 1), which results in high agronomic efficacy without the need for mineral fertilizer. According to an economic study by [56], P and K fertilization are major contributors to the cost of production for red clover planting. Hence, utilizing P-rich amendments, as in this instance, could considerably reduce the cost of this crop's production. Although clover yield varied significantly in this study, no significant differences were observed in the foliar properties of the crop. Here, clover foliar properties were measured only at the end of the study, which could have been a limitation.

### 4.2. Impact of Biochars and Manures on the Content of Carbon in Soil

The soil C content was found to be elevated three months after applying both types of biochar, relative to the soil that had not been amended. The greatest increase, from 3.5% to 4.4% of total C, was observed in DBC (Figure 1). The composition of biochar is largely determined by the type of feedstock used [25]. In this instance, DM has a higher C component than PL; however, both types of feedstocks resulted in highly stable biochars (evidenced by a low H/Corg ratio, i.e., less than 0.3). The primary components of biochar are typically C, H, O, and N, and the total carbon content of biochar is usually between 30 and 90%. Wood biochars tend to have a higher C content than manure biochars [17,57]. PLBC can be classified as a carbonaceous material due to its compliance with IBI requirements (C > 30%), but it is not categorized as a biochar. In this study, its application at rates of 8 t ha$^{-1}$ led to an increase in the soil's total C over a short period. The rise in soil C content following the addition of amendments can be attributed to both direct and indirect C inputs (manifested as an increase in crop dry biomass). Despite not directly contributing large amounts of C, PLBC significantly increased the primary production of clover in this instance.

Both types of biochar used in this research showed a low content of available N relative to their feedstocks. The stability of the biochar and its available C and N content are factors that influence the longevity of C in soil [14,26]. Even biochar with a high C content is not readily accessible to soil microbial communities [58] because the pyrolysis process results in the removal of functional groups containing O and H. Consequently, biochars are materials characterized by increased aromaticity, polymerization, and carbonization [59].

The alterations incorporated in our investigation had varying levels of C content (DBC > DM > PL > PLBC; Table 1), yet all contained more C than the unamended soil. Even though we did not anticipate the mineral fertilizer treatment to have an impact, it was surprising to discover that DM did not significantly boost the soil C content, even in the short term. Adding manure to soil can assist in augmenting C reserves, thereby providing potential for sequestering soil organic C [60]. In comparison to mineral fertilizer, [6] reported that manure could amass about 26% extra C in the topsoil, augmenting on average 0.12 t C ha$^{-1}$ for each ton of cumulative manure C input. However, changes in soil OC due to manure application can differ spatially based on factors such as management practices, climate, and soil type [5]. One of the reasons for such variability is that unpyrolyzed manures are high in volatile matter content and can increase soil greenhouse gas (GHG) emissions [7,15,17]. Consequently, unpyrolyzed manures have a short lifespan in the soil due to their higher labile organic matter reserves [22,25]. Our prior research has shown that using dairy and pig manures increases the rate of C decomposition, which is evident in higher soil $CO_2$ emissions and low manure C retention rates, while biochar prevents emissions ($CH_4$, $N_2O$, and $CO_2$) at both the field and laboratory scale [7,14,17].

### 4.3. Movement of Biochar in the Uppermost Layer of Soil

While conducting a literature review, we found no data regarding the movement of biochar within the soil profile. Consequently, we believe that the findings of this current study can offer valuable insights into the retention of biochar manure in volcanic soils. Our results showed that biochar, when applied to the soil surface, migrates between 2 and 4 cm into the soil profile in both the PLBC and DBC treatments (Figure 4). The ability of biochars to remain within the top few centimeters of soil, even under irrigation conditions, may be attributed to their unique properties, such as their highly porous structures, substantial surface area, and surface functional groups. These characteristics provide the biochar a significant adsorption capacity, and they are the underlying reasons for the observed improvement in soil porosity, water retention capacity, and soil structure after the application of biochar to the soil [61–63].

However, it is well-documented that biochar experiences changes over time. Studies have shown that the specific surface area of biochar tends to decrease as time passes [62,64], leading to an increase in the migration of biochar throughout the soil profile. As such, it is recommended that future research should include both short-term experiments and longterm field studies exceeding three years. The goal of these studies would be to evaluate the movement of biochar within the soil profile over various time periods and to consider the influence of roots within the soil–plant–biochar system. Furthermore, research involving repeated applications of biochar (or applications of higher amounts) should be carried out to determine the maximum quantity of biochar that soils can receive.

## 5. Conclusions

It is concluded that pyrolyzed or unpyrolyzed poultry litter residue can enhance clover yield as much as traditional mineral fertilization during the first tree cuttings. This increase in clover yield is related to the key properties of Andisols, such as their pH and P availability. Despite not affecting clover yield, dairy manure and its biochar form do raise soil pH. However, the minimal P contributions from both cow residue amendments (dairy manure and dairy manure biochar) seem to have been relevant for the crop in the volcanic soil. Pyrolysis enhances dairy manure's capability for soil C sequestration since the stabilized substance, compared to unpyrolyzed waste, had a higher amount of stable C content, which resulted in more prolonged C retention in the soil. Our lab tests revealed that both types of biochar (sourced from poultry litter and manure) moved less than 4 cm through the soil profile, even when exposed to drip irrigation. However, this finding should be approached carefully, and we recommend future field trials involving root crops and varying irrigation rates and systems.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agronomy14030592/s1, Figure S1. Pearson's r correlation coefficient and significance value between total red clover yield, foliar and soil properties. The asterisks mean *90%, ** 95% and *** 99% statistical confidence levels.

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