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# Impact of Biochar Aging on Soil Physicochemical Properties

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**Abstract:** Biochar undergoes significant transformations in soil as a result of chemical, physical, and biological processes. These alterations can impact its initial properties, influencing both its agronomic effectiveness and its capacity for carbon sequestration. Long-term observations of biochar-aging effects in soil are limited but highly relevant, as they provide a more realistic picture of the agronomic and societal benefits of biochar than short-term studies with relatively "fresh" biochar. This study aimed to describe the aging effects of biochar and their impact on a range of soil properties at a long-term biochar experiment in Bayreuth, Germany. For this purpose, soil and biochar samples were taken 13 years after application (two variants: 1. co-composted and 2. pristine biochar) and compared with a fresh variant in which the same unaged biochar was freshly mixed with the control soil. The soil quality parameters, pH and electrical conductivity, decreased significantly ($p < 0.05$) during biochar aging. Specifically, the pH dropped from 7.4 in freshly biochar-amended soil to 6.8 in the pristine aged biochar variant and 6.9 in the co-composted aged biochar variant. Electrical conductivity decreased from 217.0 µS cm$^{-1}$ in the freshly amended soil to 81.1 µS cm$^{-1}$ in the pristine aged variant and 87.6 µS cm$^{-1}$ in the co-composted aged variant. Nitrogen retention was enhanced in the soil amended with co-composted aged biochar compared to the pristine aged biochar soil. Total nitrogen (TN) was higher at 1.94 g kg$^{-1}$ versus 1.57 g kg$^{-1}$ ($p < 0.05$), and ammonium-N ($NH_4^+$-N) was slightly elevated at 35.7 mg kg$^{-1}$ versus 33.0 mg kg$^{-1}$, although the difference was not statistically significant. The nitrate-N ($NO_3^-$-N) content was significantly lower in all biochar-amended soil variants compared to the control soil. Total carbon (TC) levels decreased during biochar aging in all soil variants. However, the reduction was significantly lower in the co-composted aged biochar soil (25.0 g kg$^{-1}$) compared to the pristine aged biochar soil (20.5 g kg$^{-1}$, $p < 0.05$). This study identified multiple aging effects on biochar following 13 years of exposure in loamy soil. Importantly, the results showed that compared to the amendment of pristine biochar, co-composting did not diminish the TC of the treated soil, and more N could be retained, 13 years after amendment. In fact, co-composting prior to soil application is recommended to fully realize the potential agronomic benefits.

**Keywords:** biochar aging; soil health; carbon sequestration; long-term field experiment



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## 1. Introduction

Soils are the basis of a functioning food system and source of income for eight billion humans worldwide. Besides providing economic value and nutrition, soil fulfills several other services and ecosystem functions, such as biomass and fiber production, regulation of water, and nutrient cycles. Moreover, soils fulfill an enormous habitat function by hosting

25% of global biodiversity [1] and are thereby the foundation of the food chains nourishing aboveground species, thus humanity [2]. In addition, soils are the most important terrestrial C sink, storing 3500–4800 Pg of C [3], whereas terrestrial vegetation and the atmosphere store only around 800 Pg C each. Therefore, it is of great importance to not just consider soil as an economic resource and means for our global food system but also being a key in climate change mitigation.

Since ancient times, humans have used different forms of organic soil amendments (OSAs) [4], the most common forms being straw, slurries, manures, and compost. Examples of more modern forms are biogas digestates, sewage sludge biosolids, and biochar. These amendments not just contain nutrients but also varying amounts of C-rich organic compounds. Therefore, the application of OSAs is often used as a way to increase soil organic carbon (SOC) [5,6]. However, these different OSAs have different mean residence times (MRTs) in soil and usually (with the exception of biochar) have to be regularly reapplied to maintain the SOC stock increase in the soil.

Biochar is the product of the thermochemical conversion of organic biomass under minimized oxygen supply, also known as pyrolysis. One must distinguish biochar from other carbonaceous material produced from pyrolysis. In contrast to char or charcoal, biochar is specifically produced for the purpose of being applied to soil [7]. Biochar contains highly aromatic C compounds and only small amounts of N (most of them being polycyclic and not available for plants) and is therefore, in contrast to other common types of OSAs, highly stable against microbial decomposition. Biochar's MRT is estimated to be 556 $\pm$ 483 years as suggested by a recent meta-analysis [8], which underlines its high SOC sequestration potential. The wide variation in the mean MRT is mainly because of two factors. Firstly, the original studies included in the meta-analysis reported a broad range of MRTs, with estimates up to 891 years. And secondly, because both field and incubation studies were included in the literature assessment. The observation time of incubation studies is shorter than the actual decomposition time of biochar; thus, the MRT must be extrapolated with a high uncertainty and often does not reflect real field conditions. Long-term field observations of biochar stability are therefore urgently needed.

While biochar resides in soil, several reactions with its immediate surrounding environment take place. These processes do not just affect biochar dissipation but lead to physical, chemical, and biological alterations of the biochar particles. Physical alterations include changes in particle size, porosity, and surface area, and chemical alterations affect mostly surface properties [9]. Surface alterations due to biochar aging are often linked to the sorption of soil organic matter (SOM), leading to increased surface polarity, decreased specific surface area (SSA), and increased surface charge. The process of SOM sorption depends on pH, with a lower pH generally leading to increased SOM sorption [10]. SOM sorption can, moreover, block pores and thereby prevent microbes and minerals from penetrating into the particle and interacting with the particle's inside [11]. Changes in the oxidation state of aged biochar are mostly biologically driven because aging leads to a colonization of soil microbes that oxidize the altered surface [12]. This then leads to the incorporation of oxygen into surface groups, which makes the surface more hydrophilic, and due to more negative charges, there is a high potential for positive ion retention.

The field aging of biochar leads to multiple processes occurring simultaneously and sequentially. Aging methods and experiments aiming to imitate these processes artificially are less time-intensive than field aging techniques but do not represent the multiple facets of the aging of biochar and their agronomic implications. Field aging experiments are often carried out with a limited duration [9,13,14], and none of them have observed field aging processes on a decadal scale. However, it is critical to understand how aging dynamics impact biochar's environmental effects and its agronomic benefits on longer time scales. Since aged biochar better reflects what biochar mineralization would look like in hundreds and thousands of years [12], understanding its process is particularly interesting for long-term SOC sequestration and carbon dioxide removal.

The co-composting of biochar particles before application does not only "load" the biochar with nutrients, thereby making the soil more fertile, but it also mimics the natural aging process of SOM sorption and coating formation. This affects the stability of particles against microbial decomposition, due to the microbial preference to utilize organic substrates on particle surfaces that require less activation energy for metabolization [9]. Co-composting also enhances the natural oxidation of biochar particles [11], which as already explained, increases the surface cation exchange capacity (CEC) and thereby nutrient availability for plants, consequentially leading to higher crop yields [15]. Studies comparing co-composted and pure biochar have found that co-composting increases plant growth but has no negative effect on the long-term stability of biochar [16,17]. Whether the advantageous effects of co-composting on soil and biochar properties are limited to only a few years after amendment or if they persist in the long-term is still unknown.

This study aimed to investigate the impact of long-term biochar aging on soil and biochar characteristics after long-term exposure to environmental conditions in a loamy soil under a temperate climate in Bayreuth, Germany. The first objective was to resample the biochar-amended soil after 13 years of aging and create an un-aged reference by mixing unamended control soil with the original biochar, which was sealed for 13 years. The second objective was to analyze a variety of soil and biochar properties such as pH, EC, SOM, soil nutrients, and soil C in order to describe the soil health status as a function of biochar aging. The third objective was to analyze if pristine aged biochar and co-composted aged biochar impact the soil differently in the long-term.

Our working hypotheses are as follows:

1. Biochar aging leads to significant changes in soil chemical and physical properties;
2. Co-composted biochar increases soil fertility more than pristine biochar.

## 2. Material and Methods

### *2.1. Sampling, Site Characteristics, and Amendment Properties*

To test the hypotheses of this study, a long-term biochar field experiment established in 2010 and located at Donndorf, a village close to Bayreuth, Germany, was sampled. Table 1 summarizes the main characteristics and properties of the experimental site and the used amendments. A more detailed description of its experimental design can be found in Cooper et al. (2020) [18].

In this experiment, three of the ten treatments from the original Latin rectangle field experiment design (Figure S1) were selected. The Latin rectangle structure ensures treatment independence, as each treatment appears only once per row and column. The following treatments were applied: pristine biochar at a rate of 31.5 Mg ha$^{-1}$, co-composted biochar combined with 70 Mg ha$^{-1}$ compost at the same biochar rate, and an untreated control. Each treatment included five field replicates, with the application occurring in May 2010. The commercial biochar (CarbonTerra, Wallerstein, Germany) was made from pine wood chips and produced in a gasification system via slow pyrolysis at 550 °C for 36 h followed by a second step of high-temperature pyrolysis at 800 °C for 2 h. The compost was produced by BKE Bio-Kompost and Disposal/GmbH & Co., Bayreuth, Germany and derived from green litter. The biochar–compost mixture was set up on 17.05.2010 at the "Bindlacher Berg" composting site, before being transported to the field experiment site on 21.05.2010 after four consecutive days of co-composting. The experiment site was under farming cultivation in each of the following years. More details of the farming activities can be found in Cooper et al. (2020) and Gross et al. (2024) [17,18].

Soil sampling took place in March 2023 before summer sowing. Prior to this, mustard was planted in the fall of 2022 as a cover crop. Samples were collected from five field replicate plots. These plots had been treated with either pristine biochar, co-composted biochar, or left untreated as a control. Biochar amendments were incorporated to a depth of 10 cm using a rotary tiller in 2010. We assumed vertical particle migration with time, and therefore, soil samples in 2023 were taken from a depth of 0–30 cm and combined into composite samples for each treatment group. For clarity, we will refer to the soil treated

with aged pristine biochar as "A_BC_S", the soil treated with aged co-composted biochar as "CC_BC_S", and the untreated soil as "Control_S".

**Table 1.** Main site characteristics and soil, biochar, and compost properties at the beginning of the field experiment in Bayreuth.

| | **Bayreuth Field Experiment** |
|---|---|
| **Site characteristics** | |
| Latitude | 49°56′01.7″ |
| Longitude | 11°31′17.1″ |
| Mean annual precipitation [mm] | 507 |
| Mean annual temperature [°C] | 8.2 |
| Current use | Organic cropland |
| Tillage depth [cm] | 0–10 |
| Soil properties [0–30 cm] | |
| Soil type | Cambisol |
| Soil texture | Sandy loam |
| Sand [%] | 62 |
| Silt [%] | 12 |
| Clay [%] | 26 |
| Initial SOC [%] | 1.6 |
| pH | 5.4 |
| **Biochar properties** | |
| Feedstock | Pine wood |
| Pyrolysis temperature [°C] | 550–800 (two stages) |
| Total carbon [g $kg^{-1}$] | 843 |
| Total nitrogen [g $kg^{-1}$] | 4 |
| Black carbon [g $kg^{-1}$ C] | 795 |
| C/N | 239 |
| H/C [atomic ratio] | 0.11 |
| pH [$CaCl_2$] | 8.77 |
| Ash [g $kg^{-1}$] | 90 |
| CEC [mmolc $kg^{-1}$] | 72.7 |
| WHC | 249.4 |
| **Compost properties** | |
| Feedstock | Green litter |
| Total carbon [g $kg^{-1}$] | 186 |
| Total nitrogen [g $kg^{-1}$] | 10 |
| C/N | 18.8 |
| H/C [atomic ratio] | 1.41 |
| pH [$CaCl_2$] | 6.99 |
| Ash [g $kg^{-1}$] | 66.1 |
| CEC [mmolc $kg^{-1}$] | 304.3 |
| WHC [%] | 203.8 |

For a better elucidation of the impact of biochar aging on soil properties, we prepared a reference soil by mixing 6 kg of the material from the control site with 472.5 g fresh biochar used as an amendment at the beginning of the field experiment (F_BC_S) in 2010 (Table 1). This mixture was calculated to replicate the conditions found in the top 30 cm of field soil at the start of the experiment. Given that biochar can undergo aging in the presence of oxygen, the used biochar was stored in sealed plastic buckets to prevent oxidation.

### *2.2. Soil and Biochar Analysis*

The control soil (Control_S) and the biochar-treated soils (F_BC_S, A_BC_S, and CC_BC_S) were analyzed for the following parameters: pH, electrical conductivity (EC), water holding capacity (WHC), soil organic matter (SOM), total carbon (TC), total nitrogen (TN), total phosphorus (TP), soluble phosphorus, available inorganic nitrogen ($NH_4^+$-N and $NO_3^-$-N), specific surface area (SSA), total pore volume, and pore radius. In addition, the biochar (F_BC) used to prepare the fresh biochar-amended soil for this study was also

analyzed for pH, EC, and WHC, as well as SSA, total pore volume, and pore radius. It is important to underline that this is the same biochar that was used in 2010 for treating the soil, referred to in this study as A_BC_S. Furthermore, SSA, pore volume, and pore radius were also determined in two additional biochar samples, A_BC and CC_BC; these biochar samples were separated from a small amount of aged biochar-treated soils, A_BC_S and CC_BC_S, respectively.

The pH of the soils and biochar was measured in triplicates (CRISON pH Basic 20) in 1:10 ($w/v$) soil:MiliQ water after being stirred for 30 min and left to rest for another 30 min, following the method described by Campos et al. (2020) [19]. After pH measurements, the supernatant was filtered, and electrical conductivity (EC) was determined using a conductivity meter (CRISON ECmetro Basic 30) [20].

The water holding capacity (WHC) of amended and un-amended soils and biochar was determined in 6 replicates by weighing the water retained in 2 g of each material after saturation and subsequent settling for 2 h, in accordance with de la Rosa et al. (2014) [20]. Maximal WHC was calculated as the ratio of the weight of retained water to the dry weight of the sample expressed in percentage.

SOM content was determined according to the loss-of-ignition method based on the gravimetric weight change associated with the high-temperature oxidation of organic matter. After initial oven drying at 105 °C overnight, the samples were ignited in a muffle furnace for 6 h at 550 °C. The percentage weight loss during the ignition step is the reported SOM (% wt. loss).

Total carbon (TC) and total nitrogen (TN) contents were determined in duplicates by conducting dry combustion using a Flash 2000 elemental micro-analyzer (Thermo Scientific, Bremen, Germany). Total phosphorus (TP) was determined in triplicates following controlled acidic digestion with ultrapure nitric and hydrochloric acid (DigiPREP Block Digestion Systems (SCP Science)) via analysis by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Varian, Santa Clara, CA, USA).

Soluble phosphorus content was obtained in triplicates. Previously dried soil, passed through a 2 mm sieve, was mixed with activated carbon (about 6% w:w) in falcon tubes. Extraction was carried out according to the Olsen method [21] with a sodium bicarbonate extraction solution at a solid-to-solution mass ratio of 1:20, by shaking for 30 min in a bottle shaker. Supernatants were filtered twice, through folded filters (general filter) and Whatman No. 2 filters in succession, and measured by spectroscopy with a Bran–Luebbe autoanalyzer.

Available inorganic nitrogen ($NH_4^+$-N and $NO_3^-$-N) was quantified after the extraction of the samples with 1 M KCl ($w/w$ 1:50) for 1 h at 180 rpm, centrifuged for 5 min at 4000 rpm, and filtered through Whatman No. 2 filter paper [22]. The ionic content was measured in the supernatant by colorimetric assays via Omega SPECTROstar (BMG LABTECH GmbH, Ortenberg, Germany). The $NO_3^-$-N content of the extract was measured using the salicylic–sulfuric acid method [23], and $NH_4^+$-N was determined with an adapted protocol from the colorimetric method described by Greweling and Peech (1960) [24].

Specific surface area (SSA) and pore volume were determined via adsorption–desorption analysis of $N_2$ at 77 K using an Autosorb iQ Surface Area Analyzer (Quantachrome Instruments, Boynton Beach, FL, USA). Prior to measurement, samples were degassed in a vacuum at 378 K to remove surface adsorbates. SSA was calculated from the adsorption branches using the Brunauer–Emmett–Teller method (BET). The total pore volume was determined by applying the desorption isotherm of the Barrett–Joyner–Halenda (BJH) model. The average pore radius was estimated as a ratio of the total pore volume and SSA.

### *2.3. Statistical Analyses*

Statistical analyses were performed with Microsoft Excel and the software Past 4.03. To determine the significant differences of soil properties due to biochar treatments, a one-way ANOVA was used. Differences were considered statistically significant at $p < 0.05$. After finding a significant result in the ANOVA, a post hoc Tukey's honestly significant difference (HSD) test was employed to compare all possible pairs of means. Pearson's correlation

was used in order to assess the linear relationships between the analyzed parameters (pH, EC, WHC, SOM, TC, TN, $NO_3^-$-N, $NH_4^+$-N, total P, soluble P, SSA, total pore volume, and pore radius). The analysis was performed on three observations; where duplicates were analyzed, the missing values were replaced by mean imputation. For the significance testing, $p < 0.05$ was set as the criterion. Principal component analysis (PCA) was conducted on the entire dataset to evaluate the influences of treatments on soil parameter variation. R [25] was used for visualization.

## 3. Results and Discussion

### *3.1. Aging Effects on pH and EC*

The freshly added biochar led to a significant increase ($p < 0.05$) in soil pH (Figure 1). This initial pH increase is due to the "liming effect" of biochar and the release of calcium and other alkaline cations. However, as biochar ages, its acid-neutralizing effect diminishes, leading to a decrease in soil pH. Decreasing biochar pH after aging in soil is a well-known and described phenomenon [9]. With increasing time and biochar aging, basic species such as carbonates and hydroxides dissipate, which could explain the lower soil pH [26]. Another explanation could be the surface oxidation of biochar [26,27] and the increase in carboxylic groups during aging due to partial biochar oxidation [28].

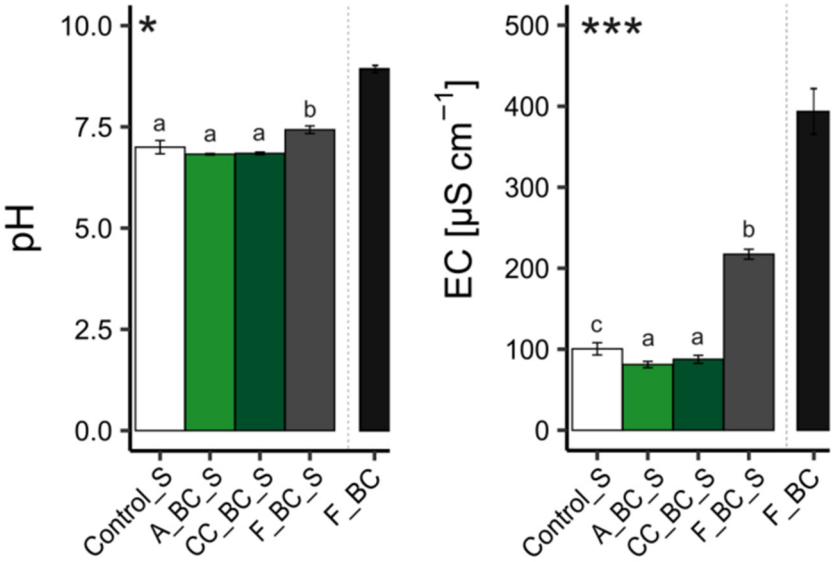


**Figure 1.** Soil and biochar pH (**left**) and electric conductivity (EC) values (**right**) of the different treatments (Control_S is the control soil; A_BC_S is the aged biochar-amended soil; F_BC_S is the fresh biochar-amended soil; CC_BC_S is the co-composted biochar-amended soil; F_BC is fresh biochar, stored and sealed for 13 years). Each bar represents the mean of three replicates. Error bars indicate the standard deviation. Asterisks indicate the level of significance (* $p < 0.05$; *** $p < 0.001$). Different letters indicate significant differences between the treatments.

The EC of biochar in soil is responsible for the exchange of ions and therefore is a critical property for soil fertility. Fresh biochar increased soil EC, indicating a higher concentration of soluble salts in the soil (Figure 1). The aged biochar treatments showed lower EC levels, indicating a reduction in soluble salts and ions, which might be due to leaching [29,30] and microbial activity. Moreover, an increase in oxidation and O-functional groups on the surface of biochar, typical of biochar aging, leads to decreasing EC [31].

### *3.2. Aging Effects on TC, SOM, and Soil Nutrients*

The fresh mixing of un-aged biochar with the control soil after 13 years ("F_BC_S") increased TC significantly ($p < 0.05$) (Figure 2). Aging resulted in a significant decline in TC levels when comparing fresh biochar-amended soil, which showed ~three- to fourfold

more TC, with both aged biochar soil treatments, A_BC_S and CC_BC_S. The CC_BC_S treatment had significantly more TC than the pristine A_BC_S treatment (Figure 2). The SOM difference between the variants followed a similar pattern, with F_BC_S showing the highest content and both aged variants showing significantly lower values ($p < 0.05$). However, the SOM decline during aging was not as drastic as TC, and both aged variants showed no significant difference. During aging, biochar particles tend to sorb organic matter components from their surrounding soil material, resulting in organic coatings on the particle surface and reduced SOM loss or increased SOM stabilization. This SOM coating strongly affects biochar physical–chemical properties and influences the stability of the aromatic "backbone" [11]. The co-composting of biochar facilitates this natural process of coating formation and could therefore explain the higher TC levels compared to the pristine biochar treatment. However, the threefold-declining TC content of CC_BC_S and A_BC_S compared to the F_BC_S treatment cannot be explained by aging alone. Gross et al. (2024) found a clear indication of the vertical transport of biochar particles from the topsoil to subsoil occurring in the Bayreuth experiment and laterally between the experiment plots [17]. Although these biochar particles disappear from the topsoil and lead to declining TC contents, they still have agronomic and ecological implications. Wang et al. (2023) found that vertically translocated biochar particles contribute to subsoil SOC sequestration and higher subsoil pH [32]. Biochar transport to different parts of the soil profile eventually depends strongly on soil and environmental properties [33] and needs further evidence from agronomic field trials with contrasting agricultural practices [34].

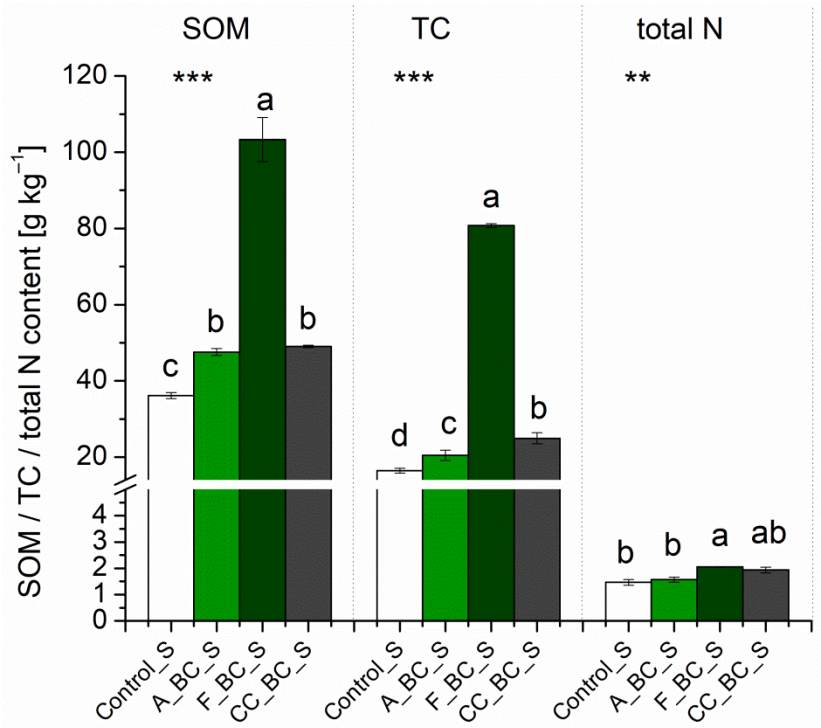


**Figure 2.** Soil organic matter (SOM), total carbon (TC), and total N content of the four different treatments (Control_S is the control soil, A_BC_S is the aged biochar-treated soil, F_BC_S is the fresh biochar-treated soil, CC_BC_S is the co-composted biochar-treated soil). Each bar represents the mean of three replicates. Error bars indicate the standard deviation. Asterisks indicate the level of significance (** $p < 0.01$; *** $p < 0.001$). Different letters indicate significant differences between the treatments.

In the aged biochar treatments, especially the co-composted treatment, TN levels were higher than in the treatment which received fresh biochar. The addition of fresh biochar decreased plant-available N (Figure 2). Fresh biochar added to soil can lead to the immobilization of N [15,35,36], which is more likely if the biochar's C/N is very

high [37] and it was added without additional fertilizer as a co-amendment or without a pre-treatment with nutrients, such as co-composting. Mixing biochar with compost has been shown to prevent N immobilization. According to our results, aging led to a significant increase in $NH_4^+$-N compared to the freshly added biochar (F_BC_S) (Figure 3). The co-composted treatment thereby showed the highest $NH_4^+$-N. The presence of biochar led to significantly lower $NO_3^-$-N levels compared to the control soil (Figure 3), which could be related to a more negative charge on the biochar surface and thus less $NO_3^-$-N capture. Kammann et al. (2015) demonstrated that the co-composting of biochar can enhance nitrate capture [16]. They explained their surprising finding with the development of acid and basic functional groups and organomineral complexes on the biochar surface. Total P and the soluble P fractions showed no significant differences between the treatments (Figure 4).

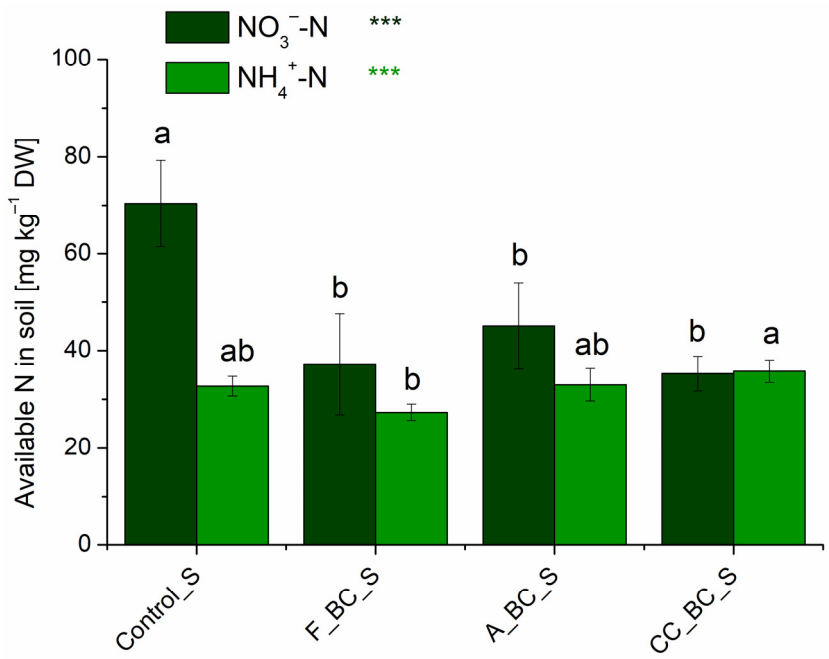


**Figure 3.** Nitrate-N ($NO_3^-$-N) and ammonium-N ($NH_4^+$-N) content of the four different treatments (Control_S is the control soil, A_BC_S is the aged biochar-treated soil, F_BC_S is the fresh biochar-treated soil, CC_BC_S is the co-composted biochar-treated soil). Each bar represents the mean of three replicates. Error bars indicate the standard deviation. Asterisks indicate the level of significance (*** $p < 0.001$). Different letters indicate significant differences between the treatments.

### *3.3. Aging Effects on SSA and WHC*

Sorption of SOM to biochar surfaces during aging influences the SSA and eventually the hydraulic properties of the particle. $N_2$ BET SSA in both the soil and biochar of the co-composted variant was lower than in the other treatments (Table 2). This decrease in SSA reduces surface reactivity and sorption. However, the sorption of SOM could produce a more negative surface charge and thus a higher potential for positively charged cations for sorption. Moreover, it intercepts compounds and organisms from penetrating into the biochar particle through pores and thereby prevents the aromatic core from potential degradation. According to our findings, biochar additions reduced the soil WHC. Limited pore access after the sorption of SOM to the biochar surface can potentially negatively affect the WHC. However, this argumentation cannot explain the lower WHC in the "F_BC_S" treatment, which was prepared by mixing the un-aged biochar with control soil sampled after 13 years. Considering that the biochar was added without milling, the pore size distribution is likely to be shifted to larger pores that allow preferential flow and decrease the water retention in the soil–biochar mixture. This is likely to be supported by the hydrophobicity of fresh biochar. Whereas these impacts may be of minor

importance in undisturbed soils, they can create artefacts during the determination of WHC in a laboratory.

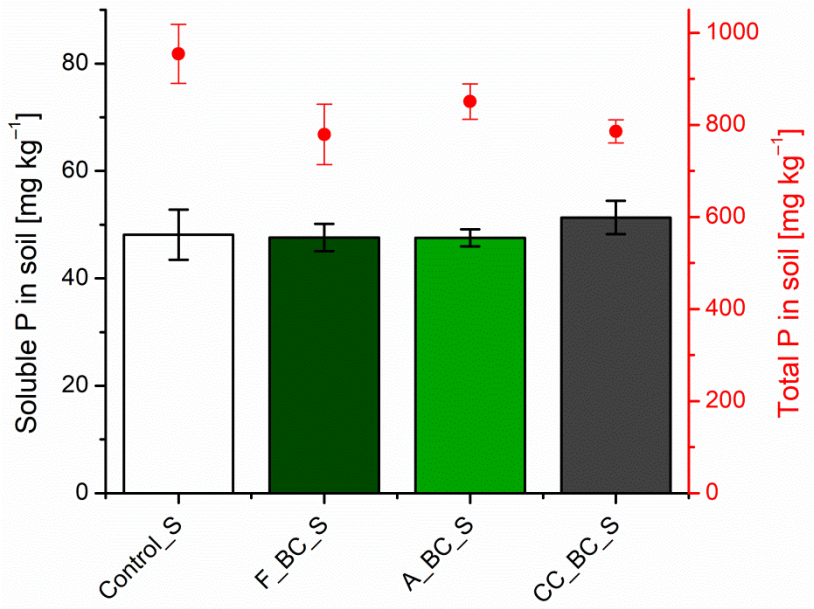


**Figure 4.** Soluble P and total P content of the four different treatments (Control_S is the control soil, A_BC_S is the aged biochar-treated soil, F_BC_S is the fresh biochar-treated soil, CC_BC_S is the co-composted biochar-treated soil). Each bar represents the mean of three replicates. Error bars indicate the standard deviation.

**Table 2.** Specific surface area, pore size and volume, and water holding capacity (±standard deviation) of the soil and biochar particles of four different treatments.

| | Soil | | | | Biochar | | |
|---|---|---|---|---|---|---|---|
| | **Control_S** | **F_BC_S** | **A_BC_S** | **CC_BC_S** | **F_BC** | **A_BC** | **CC_BC** |
| **Parameter** | | | | | | | |
| SSA * [m$^2$ g$^{-1}$] | 5.3 | 18.1 | 3.1 | 2.8 | 445.1 | 100.2 | 89.8 |
| Total pore volume [cm$^3$ g$^{-1}$] | 0.022 | 0.027 | 0.015 | 0.014 | 0.241 | 0.071 | 0.064 |
| Pore radius [Å] | 80.8 | 29.8 | 94.1 | 99.6 | 10.8 | 14.1 | 14.2 |
| ** WHC [%] | 41.6 ± 4.1 | 31.5 ± 3.5 | 30.3 ± 2.8 | 25.9 ± 2.9 | 152.8 ± 7.2 | n.a. *** | n.a. *** |

* specific surface area, ** water holding capacity, *** not analyzed.

### *3.4. Principal Component Analysis*

Principal component analysis reduced the dimensionality of the dataset, which included 13 variables/soil properties determined in four soil variants, to two major axes (Figure 5a), with the first principal component, PC1, accounting for 59.4%, and the second principal component, PC2, accounting for 24.6% of the variance in the dataset. Together, they explain 84% of the total variance, suggesting that these two compounds capture most of the variability in the data. The analysis separated the soils by the applied soil treatments into distinct clusters. The cluster representing fresh biochar-treated soil (F_BC_S) was separated from the other clusters along the PC1 axis, suggesting that fresh biochar significantly alters soil properties, distinguishing this soil from the other treatments and the control. The other three clusters can be found at approximately the same position on the PC1 axis but were spread out along the PC2 axis. This indicates that over time, the effect of pristine biochar and co-composted biochar on soil properties might diminish, and the biochar-amended soil eventually becomes more similar to the un-amended soil. Further, the separation of the two aged soils, treated with pristine biochar and co-composted biochar,

could indicate that the interactions between compost and biochar during co-composting may have led to a modified impact of biochar on the soil properties.

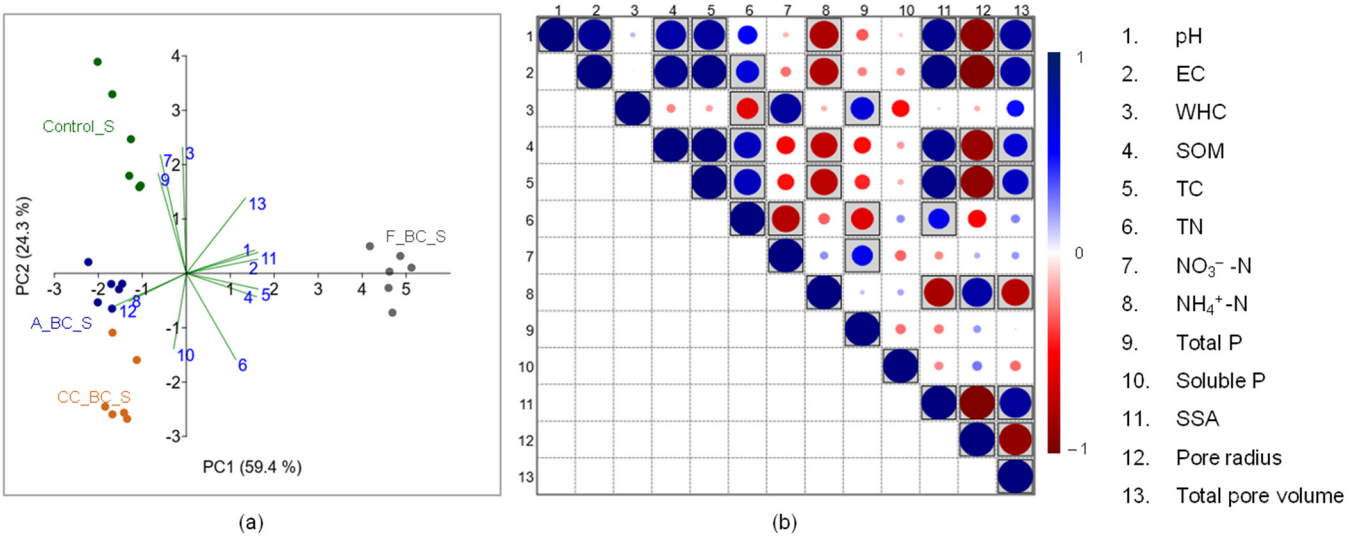


**Figure 5.** Statistical analysis (**a**) principal component analysis (PCA) biplot and (**b**) Pearson's correlation of the soil properties (pH, electrical conductivity (EC), water holding capacity (WHC), soil organic matter (SOM), total carbon (TC), total nitrogen (TN), available inorganic nitrogen in nitrate ($NO_3^-$-N) and ammonium ($NH_4^+$-N) forms, total phosphorus (Total P), soluble phosphorus (Soluble P), specific surface area (SSA), pore radius and total pore volume) obtained for the four different treatments (Control_S is the control soil, A_BC_S is the aged biochar-treated soil, F_BC_S is the fresh biochar-treated soil, CC_BC_S is the co-composted biochar-treated soil). Correlations with a $p < 0.05$ are boxed in the Pearson's correlation graph.

The vectors representing the individual soil properties are tagged in Figure 5 with the numbers 1–13. The vectors for available nitrogen content in the $NH_4^+$ form (8) and pore radius (12) point to the two aged soils, showing a positive long-term effect of biochar treatment on the $NH_4^+$-N content in soil. This positive correlation between the pore radius and $NH_4^+$-N indicates the higher mobility of these ions in larger pores. This could explain why in F_BC_S, which has a significantly smaller average pore radius than the other soils (Table 2), we observed a significantly lower $NH_4^+$-N content (Figure 3). On the other hand, the vectors representing total P (9) and available N in the $NO_3^-$ form point toward the control soil, showing no significant correlation with any of the treatments. The surface area (11), pH (1), and EC (2) vectors point to the fresh biochar-treated soil, suggesting that biochar treatment has an immediate effect on these properties, the strength of which decreases over time. In addition, Pearson's correlation was performed to determine the strength and direction of the linear relationships between the soil properties (Figure 5b). Each dot in the figure represents a correlation between two variables (soil properties), with blue and red representing positive and negative correlations, respectively. The intensity of the colors and the size of the dots indicate the strength of the correlation: larger dots with a more intense color show a strong correlation, and smaller dots less intense in color indicate a weak correlation between the two variables. The boxed dots show statistically significant correlations ($p < 0.05$). The results show a strong positive correlation between pH (1) and EC (2), indicating a common influence on these two parameters. Both of these parameters showed a significant positive correlation with TC (5), SSA (11), and pore volume (13) and a negative correlation with $NH_4^+$-N (8) and pore radius (12). The higher TC content stemming from biochar addition could possibly have a positive correlation with pH and EC as a result of the presence of ionizable functional groups as well as basic cations on the biochar. The negative correlation of pH and EC with some of the N species indicates that soil acidity and salinity need to be considered during nitrogen management in soil. Total P

(9) and soluble P (10) showed no strong correlation with any other parameter, indicating soil treatments did not influence P content significantly. TC (5) and SOM (4) correlated positively with SSA (11) and negatively with pore radius (12). These correlations conformed well with the correlations observed in the PCA biplot.

## 4. Conclusions

Our findings demonstrate that the application of biochar, even after 13 years of aging, still has significant positive effects on physical and chemical soil properties, although the magnitude decreases with time in the soil. Whereas some soil properties such as soil pH and EC showed decreasing effects with aging time, the ability to retain nitrogen increased, especially if the biochar was co-composted before being applied. Given the enhanced benefits of co-composted biochar compared to untreated biochar, co-composting should be strongly considered as a pre-treatment before biochar application to soils. The strongly declining TC cannot be explained by aging effects alone but is due to an interplay of biochar degradation and transport. Future studies will have to verify the proportion of biochar stability loss, vertical and lateral transport, and the impact of such transport dynamics on soil quality.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agronomy14123007/s1, Figure S1: Design and treatments of the Bayreuth biochar field experiment.

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