Interaction of pyrolysis conditions and soil texture on biochar mineralization and its effect on soil structure.

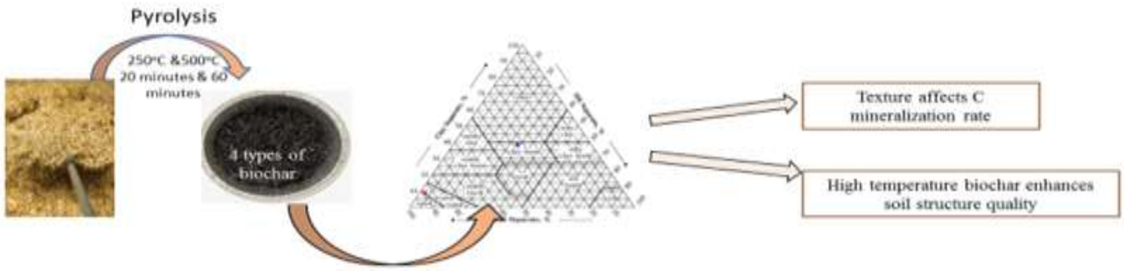
Marina Kouimtzi[1] ,Sofia Kostopoulou[1]

[1] Department of Agriculture, Faculty of Soil Science, Aristotle University of Thessaloniki, 54124 Thessaloniki,Greece

*Corresponding author:Marina Kouimtzi

E-mail: *markouimtzi@gmail.com*, tel: +306975100801

GRAPHICAL ABSTRACT



ABSTRACT

The effectiveness of biochar as a soil conditioner is depended on the feedstock type and pyrolysis conditions as these two factors determine its physical and chemical properties. Wheat straw was heated at two temperatures: a) 250^0C and b) 500^0C for two time periods: i)20 min and ii) 60 min to produce four types of wheat biochar (WB) (WB250/20, WB250/60, WB500/20 and WB500/60) that were added at two different textured soils, a sandy and a loamy one. We studied C mineralization and changes of the structural quality of the two soils. Incomplete carbonization of WB250 resulted in higher C mineralization in both soils. WB250 decomposed more intensely in the sandy soil while decomposition of WB500 was not affected by soil texture or duration of pyrolysis. Biochar addition reduced the cohesiveness of the loamy soil. WB500 enhanced the formation of smaller aggregates while pyrolysis time had no effect. None of the four types of biochar altered the aggregate size distribution of the no cohesive sandy soil. Biochar with longer pyrolysis time enhanced aggregate stability of both soils because of its higher C contents and EC that promote aggregating mechanisms. WB500/60 resulted in reduced clay dispersion in both soils.

Keywords: wheat straw, biochar, soil texture, C mineralization, aggregation

1. Introduction

In recent years, the interest for agricultural use of biochar coming from agricultural and industrial by-products has increased, in an effort to save financial and natural resources (Valili et al., 2013; Oleszczuk et al., 2012; Cruz, 2012). Biochar is produced through pyrolysis of biomass (heating under oxygen-deficiency conditions). The aim is the thermal breakdown of cellulose (240–350ºC), semi-cellulose (200–260ºC) and lignin (280–500ºC) which are all included in the raw material. The composition of the final products depends mainly on the heating rate and the working pressure of the reactor (Yang et al, 2007). The increase of the pyrolysis temperature increases carbon content and the specific surface of the biochar. During pyrolysis, almost 50% of the carbon included in the biomass initial source can be kept in the biochar produced, however, the retrieval percentages depend on the total pyrolysis procedure. The variety of the physical and chemical properties of biochar depends on the raw material, the oxygen availability and the temperatures reached during pyrolysis (Atkinson et al., 2010). According to the International Biochar Initiative (IBI), biochar is a charcoal which can be integrated into the soil for both agricultural and environmental benefits. Its porous structure makes it attractive as an adjuvant for the soil because it increases the water retention and the specific surface of the soil (Manya, 2012). The application of the biochar can lead to C sequestration (Cha et al., 2016) and can enhance soil quality. Biochar can increase microbial biomass C and the activities of enzyme (Karimi et al., 2020), reduce CO_2 emissions (Solaiman and Anawar, 2015). When biochar is added to the soil it increases the recalcitrant pool of C as its mineralization rate is much slower in comparison to fresh organic residues (Novak et al., 2009b). The decomposability of biochar in soil is affected by various factors such as the amount of added biochar, the temperature and the duration of pyrolysis, the duration of decomposition, soil pH, native SOM and clay contents (Han et al., 2021). The indirect benefits that come from the use of after-pyrolysis biomass are the increase of the microbial activity because of the decrease in the soil’s toxicity from heavy metals and increase the temporary nutrient and water retention (Zhang et al., 2013; Karami et al., 2011; Wang et al., 2015br). So, biochar can support the structural stability of the soil, intensifying the interaction of the micro-organisms and soil fragments for the formation of aggregates (Quin et al., 2014). Brodowski et al. (2006) observed that biochar in the soil can be connected to the inorganic solid phase to aggregates, which, in turn, protect it from oxidation and decomposition. Biochar in the soil can also increase the stability of the aggregates (Biederman & Harpole, 2013; Lehmann et al., 2006). According to Liu et al. (2014) the wheat straw biochar can increase the soil water-stable aggregates. Also, Du et al. (2017) reported that the addition of biochar importantly improved the formation of solid macro-aggregates in agricultural soils. Long-term biochar amendment improved soil aggregate stability and increased the SOC contents in macro-aggregates (Dong et al., 2016). Xu et al. (2019), reported that biochar can act as a cementing matter, helping microaggregates, silt, and clay components to connect into larger soil aggregates. The biochar increased the formation of macroaggregates (>0.25 mm), especially small macroaggregates (0.25–2 mm), but decreased the number of microaggregates in Mollisols (Sun et al. 2022). Furthermore, Ajayi and Horn (2016) demonstrated that biochar addition improved microstructural stability of a sandy loamy silt by increasing the particle-to-particle bonding and making the soil able to resist fragmentation and dispersion. Hammam et al (2022) observed a decrease of the dispersion ratio of a sandy and a clay loamy soil after biochar addition. On the contrary, Saffari et al. (2022) found that biochar inputs increased clay dispersion of a sandy loam soil and concluded that it was affected only by the pyrolysis temperature of biochar and not the type or the application rate. Besides, the alteration of soil solution by biochar addition influences the concentrations of exchangeable monovalent cations and leads to enhanced dispersibility (Kumari et al., 2017). The aim of this paper was the study of the effect of adding fresh and charred residues of wheat straw

(Triticum spp.) on the structural quality of two agricultural soils with different texture. The effect of a) time and temperature of pyrolysis and b) mineralization rate of carbon of the added organic material on aggregate formation, water stability of macroaggregates and clay dispersion were investigated.

2. Materials and methods

2.1. Soils

Two calcareous surface (0-15cm) soils with different texture were collected, a sandy from the region of Pirgos, Peloponnese (χ: 4372737.035 ψ: 4171097.124) and a loamy one from Trikala, Thessaly (χ: 309489.244 ψ: 437237.035). The soil samples were air-dried, grinded and passed through a 2 mm sieve. Some physicochemical properties of the soils are shown in Table 1. Soil texture was determined using the pipette method (Gee & Bauder, 1986). Electrical conductivity (EC) was determined in the saturated soil extract and pH in 1:2.5 soil/water suspension. The soil organic carbon (SOC) was determined by the wet-oxidation method (Walkley & Black, 1934) and $CaCO_3$ content by the Bernard calcimetry method.

Table 1. Chemical and physical properties of two soils.

Textural class	**Clay %**	**Silt %**	**Sand %**	**pH**	**$CaCO_3$ %**	**EC µS/cm**	**SOC %**
Loam	26	39	35	8.04	9.3	279.00	0.692
Sand	8	2	90	8.39	6.2	166.57	0.377

2.2. Biochar production

Wheat straw (WS) was collected after the harvest and was used as raw feedstock for the biochar. The plant material was cut into <5mm pieces, dried at 70^0C for 48 hours and stored under dry conditions. For biochar production, dry wheat straw was placed into metallic cylinders, which were sealed with aluminum foil in order to secure conditions of lack of oxygen during pyrolysis. Small holes were created on the foils for the gas combustion products to escape (Khadem & Raiesi, 2017).

Wheat straw samples were heated in an electrical furnace at two temperatures: a) 250^0C and b) 500^0C for two time periods: i) 20 min and ii) 60 min. The rate of temperature increase was 10^0C /min (slow pyrolysis) and the pyrolysis time (20 and 60 min) refers to the period during which the samples remained in the respective desirable temperature. In this way, four different types of wheat biochar (WB) were produced (WB250/20, WB250/60, WB500/20 and WB500/60). The final products of pyrolysis as well as dried wheat straw were ground to <2 mm and stored in dry conditions. Wheat straw and biochar subsamples were ground in a mill and were used for the determination of some chemical characteristics (Table 2). An elementary analyzer was used for the determination of N and C. EC and pH were determined electrometrically in a 1:10 (WS or WB)/deionized water suspension. The yield of WB was determined as the weight ratio of biochar to the feedstock, used for biochar production.

2.3 Experimental design

A (2 x 6) factorial experiment was organized with 2 repetitions of each treatment. The first factor was soil texture (sandy and loamy) and the second was the type of organic residue addition (WS, the 4 types of WB and a control).

0.5 gr of WB or 0.5 gr of WS was added in 50gr soil samples (1% w/w). Soil without any addition, was used as a control (C). The amended soil samples were moisturized at a moisture content equal to 60% of water holding capacity to provide optimal water content and aeration conditions for microbial activity, thoroughly mixed, placed in airtight glass vessels and weighted. The samples were incubated in stable moisture and temperature (20-23^0C) conditions for two months. Every seven days the soil samples were weighted and water was added to replace water losses during the incubation period. The microbial respiration was determined at days 1, 2, 3, 4, 7, 9, 11, 14, 17, 21, 24, 28, 35, 45 and 56 by back-titration with HCl according to Rowell (1994) in order to estimate the carbon mineralization of the four types of biochar and wheat straw in the two soils. After the end of the incubation period, the soil samples were air-dried, went through a sieve of 8mm diameter and aggregate size distribution was determined by dry sieving the <8mm aggregates in a series of sieves of 2, 1, 0.5 and 0.25mm diameter. Five aggregate size-classes were separated with mean aggregate diameter of 5, 1.5, 0.750, 0.375 and 0.125 mm. The mean weight-diameter of air-dry aggregates (MWDD), was estimated using the equation: $MWDD = \Sigma X_i W_i$ where X_i is the arithmetic mean diameter of aggregates, and W_i is the mass of aggregates of the i th size fraction expressed as a percentage of the sample mass (van Bavel, 1949). The wet aggregate stability (WAS) was determined in 2-1 mm aggregates by the modified wet sieving method and with one sieve with diameter of 0.25 mm (Nimmo & Perkins, 2002). The Eijkelkamp single-sieve wet-sieving apparatus (Giesbeek, The Netherlands) was used for the measurement and the time of sieving was 3 min. Any organic particles and biochar were determined as sand >0.25 mm (Burrell et al., 2016). Spontaneously dispersive clay (SDC) was estimated by the light transmission (T) of soil/water suspensions, as a measure of flocculation. 2g of <2mm soil were placed in polycarbonate tubes of 50ml, carefully saturated with deionized water and left to equilibrate for 30 min. Afterwards, 30 ml of water were added, the tubes were capped and turned gently upside-down for three times. Then the tubes were placed upright to allow the soil suspensions to settle for 2h and a 5 ml aliquot was taken with a pipette from 2 cm depth. The settling time and the depth were calculated according to the Stokes' law for clay particles. The aliquot was pipetted into the cuvette of the spectrophotometer and the light transmission was determined at 641 nm wavelength. Deionized water was used as the 100% T reference (Thellier & Sposito, 1989). Higher values of T correspond to decreased clay dispersibility.

2.4 Statistical Analysis

Statistical analysis was performed with one-factor analysis of variance (ANOVA). The level of significance of all the statistic tests was a=0.05. The comparisons of the means were made through the Least Significant Difference test (LSD)

3. Results and Discussion

3.1 Physicochemical characteristics of fresh and charred wheat straw

The wheat straw which is used as feedstock for biochar preparation is one agricultural waste rich in C and slightly acidic (Table 2) which is composed mainly of cellulose (35%–40%), hemicelluloses (30%–35%), and lignin (10%–15%) (Tufail et al., 2020). The yield of the produced biochar varied between 74.67% for WB250/20 and 34.16% for WB500/60 (Table 2). The high yield of WB250/20 indicates that for low temperature and duration of pyrolysis feedstock carbonization is incomplete. Zhang et al. (2015) found that at 200 ^{0}C, wheat straw lost little mass, even after 4 h, and suggest that limited pyrolysis occurs at this temperature. Also, Zhou et al. (2021) reported that at lower pyrolysis temperatures, the yield of biochar was increased due to the partial pyrolysis of the feedstock. The increase of time of residence of low temperature pyrolysis resulted in a significant decrease in the yield of WB250/60. When temperature was raised from 250 to 500 ^{0}C a further significant decrease in yield was observed but the heating duration had no effect in the yield of biochar at this temperature (Table 2). The decrease in the yield of WB with the rise of temperature is due to dehydration and thermal degradation of cellulose and lignin structure and the loss of volatiles (Chandra & Bhattacharya, 2019).

Table 2. Chemical properties of fresh wheat straw (WS) and the produced 4 types of wheat straw biochar (WB)

	N %	C %	Yield %	pH	EC μS/cm
WS	0.70a	45.00a	_	6.45c	1673a
WB250/20	0.75ab	46.62a	74.67c	6.18a	1697a
WB250/60	0.84bc	52.71b	48.36b	6.33b	2244b
WB500/20	0.91c	53.07b	36.73a	8.53e	3280c
WB500/60	1.05d	57.45c	34.16a	7.96d	3460d

Treatments followed by different letter differ significantly at a level a=0.05

Elemental analysis showed that C and N content increased with the increase of temperature and duration of pyrolysis (Table 2). No difference was observed between WS and WB250/20 for both elements. This is linked with the high yield of WB250/20 and supports the indication of incomplete carbonization. As pyrolysis duration increased from 20 min to 60 min, carbon content increased by

13.06% at 250^{0}C and by 8.25% at 500^{0}C while nitrogen content increased by 12.00% and 15.38% respectively. Carbon increase with temperature rise is attributed to the removal of volatile compounds and the development of aromatic C structures (Novak et al., 2009a). Carbon increase with pyrolysis time according to Chandra and Bhattacharya (2019) is due to the increase in the rate of loss of long chain aliphatic groups. A N enrichment relative to the original feedstock upon pyrolysis in C-rich material has been reported elsewhere and was attributed to the incorporation of N into complex structures that were resistant to heating and not easily volatilized (Li et al., 2022; Calvelo Pereira et al., 2011). The pH of both WB produced at 250 ^{0}C was acidic and showed a slight but significant reduction in relation to the feedstock. The increase of the pyrolysis temperature to 500^{0}C resulted in alkaline pH values of the produced biochar (Table 2). According to Zhang et al. (2015), the cellulose and hemicelluloses decompose around 180–250^{0}C, producing organic acids and phenolic substances that lowered the pH of the biochar produced at 250^{0}C. The pH increase of the biochar with temperature rise is mainly due to the fact that the organic functional groups such as –COOH and –OH decreased with increasing pyrolysis temperature and to the carbonates formation above 400^{o}C. The EC of the biochar increased with both the pyrolysis temperature and time (Table 2). No difference was observed between WS and WB250/20, indicating incomplete carbonization. The increase of biochar EC with temperature is attributed to the loss of volatiles from the biomass during carbonization, resulting in the accumulation of nutrients in the inert ash fraction (Chandra & Bhattacharya, 2019) and the increase of the solubility of salts and metals (Li et al., 2022). Chandra and Bhattacharya (2019) associated the EC increase with the pyrolysis time to the ionic energization of elements present in the ash fraction.

3.2 Carbon mineralization

The carbon dioxide release rate for the various treatments during the 56 days of incubation is shown in Figure 1. The CO_2 released by the control and which is due to the mineralization of the organic matter of the soil has been subtracted, so that the values should be representative of the mineralization of C of the added wheat straw and biochar. As expected, the wheat straw presented a much higher C mineralization rate compared to the treatments with biochar, in both soils as straw C content is more labile than that of biochar. C mineralization rate of the biochar at the beginning of the incubation followed the order 250/20 > 250/60 > 500/20 >= 500/60, with the effect of pyrolysis temperature being bigger than that of the pyrolysis time (Fig.1). Khadem and Raiesi, (2017) reported that C mineralization rate was significantly affected by pyrolysis temperature and soil type. High biochar C mineralization rate at the early stage of incubation and decrease of biochar C mineralization rate with the increase of pyrolysis temperature indicates an increased labile C content of the low pyrolysis biochar (Peng et al., 2011).

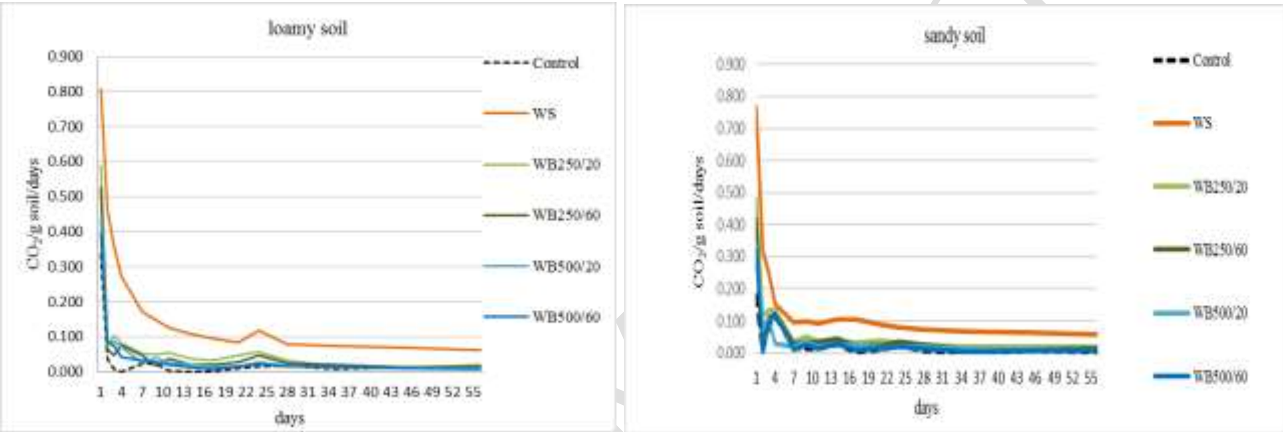


Figure 1.Carbon dioxide release rate during the 56-day incubation in both soils

The carbon mineralization for the uncharred wheat and the four biochar types took place in two phases, a rapid one in the beginning of the incubation, followed by a much slower with a stable rate, indicative of the depletion of easily degradable C pools. For all the organic materials, the maximum of mineralization was observed in the first day for both soils with the highest rate values determined in the sandy one. But, from the very second day and for the rest of the incubation period, the mineralization rate of all materials was higher in the loamy soil (Fig.1). This indicates that all 4 types of the wheat biochar comprise some labile C compounds and that low temperature biochar is richer in these compounds due to incomplete carbonization. Mukherjee et al. (2016) reported that C mineralization after biochar addition shows an initial flush as biochar comprises a small labile C pool with short turnover times (6 to 60 days) whereby 2 to 20% of the biochar C can be mineralized.

The decomposition (%) of the WS and WB in both soils, as it was calculated from the cumulative amount of CO_2-C released after 56 days minus the CO_2-C released by the control and the amount of organic C added (Wagner and Wolf, 1999) is shown in Table 3. In both soils, wheat biochar decomposed significantly slower (9.03 – 2.89%) compared to wheat straw (29.06 – 23.55%).

Table 3. Decomposition (%) of raw (WS) and charred (WB) wheat straw at the end of the incubation period.

	WS	**WB250/20**	**WB250/60**	**WB500/20**	**WB500/60**
	C decomposed (% of added C)				
Loamy soil	29.06 bC	7.03 aB	3.94 aAB	2.79 aA	2.89 aA
Sandy soil	23.55 aD	9.03 bC	5.79 bB	2.56 aA	2.52 aA

Significant difference between the two soils (lowercase letters) and for each soil among treatments (uppercase letters)

Similar percentages of biochar decomposition in comparison to the non-carbonated organic material (woodchips) are reported by Mukherjee et al. (2016), and the difference was attributed to the hardly degradable nature of biochar and its ability to be stabilized in soils in a short time. The decomposition of the biochar was affected by the pyrolysis temperature as higher temperatures resulted in lower decomposition. Pyrolysis duration affected only low temperature biochar decomposition. Among the treatments with biochar, the one with the lower pyrolysis temperature and time (WB250/20) is decomposed more intensely in both soils (Table 3). According to Hale et al., (2012) and Spokas et al., (2011) the high pyrolysis temperature plays an important role in the biochar structure as complex polycyclic aromatic hydrocarbons are created, which most probably have a toxic effect on the micro-organisms which decompose carbon. Soil texture affected decomposition of raw WS and of WB250. WS decomposed more intensely in the loamy soil while decomposition of the low-temperature biochar was significantly higher in the sandy soil. Khadem and Raiesi (2017) observed that microbial respiration was greater to low temperature biochar application in sandy soils in comparison to clayey soils and attributed the increased microbial activity to the labile C in this biochar. Decomposition of the high pyrolysis temperature biochar was not affected by soil texture.

3.3 Soil structural quality

3.3.1 Aggregate size distribution (ASD)

The cumulative aggregate size distribution and the change of the large (8-2mm) and small (2-0.25mm) macro-aggregates and of the micro-aggregates (<0.25mm) of the two soils for the different treatments is shown in Figures 2a and 2b. In the loamy soil (Fig 2a) ASD change followed the order: C=WS< WB250/20 = WB250/60 < WB500/20 = WB500/60. In relation to the control, WS addition had no significant effect on ASD while after WB additions, the percentages of the large macro-aggregates decreased significantly (Fig. 2b) and those of the smaller macro-aggregates and of the micro-aggregates increased significantly. It was observed that the biochar produced in higher pyrolysis temperature affected more intensely the ASD, but pyrolysis time had no significant effect. ASD change indicated that WB addition reduced cohesion of the loamy soil, with the effect of WB500 being the most prominent. Zong et al. (2014) found that 6% (w/w) WB addition, produced at 500 0C, reduced the mechanical strength of a clayey soil and attributed this to the dilution effect of dense soil matrix with the highly porous and less dense biochar. Also, Blanco-Canqui (2017) reported that the addition of biochar to the soil weakens the inter-particle bonds and reduces the cohesiveness of the soil.

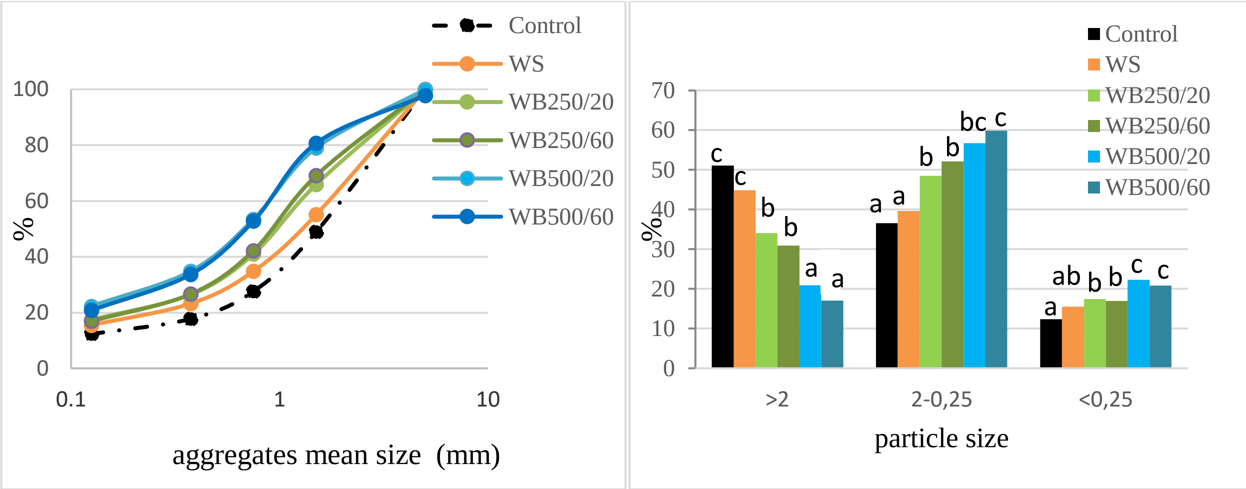


Figure 2a. Cumulative Particle Size Distribution and percentage change of the large (8-2mm) and small (2-1, 1-0.5 and 0.5-0.25mm) macro-aggregates and of the micro-aggregates (<0.25mm) of the loamy soil under various treatments

The sandy soil had no large macro-aggregates (Fig.2b). Only WS addition had an aggregating effect that resulted in the formation of large macro-aggregates. On the contrary, none of the four types of biochar affected significantly the ASD of this no cohesive soil.

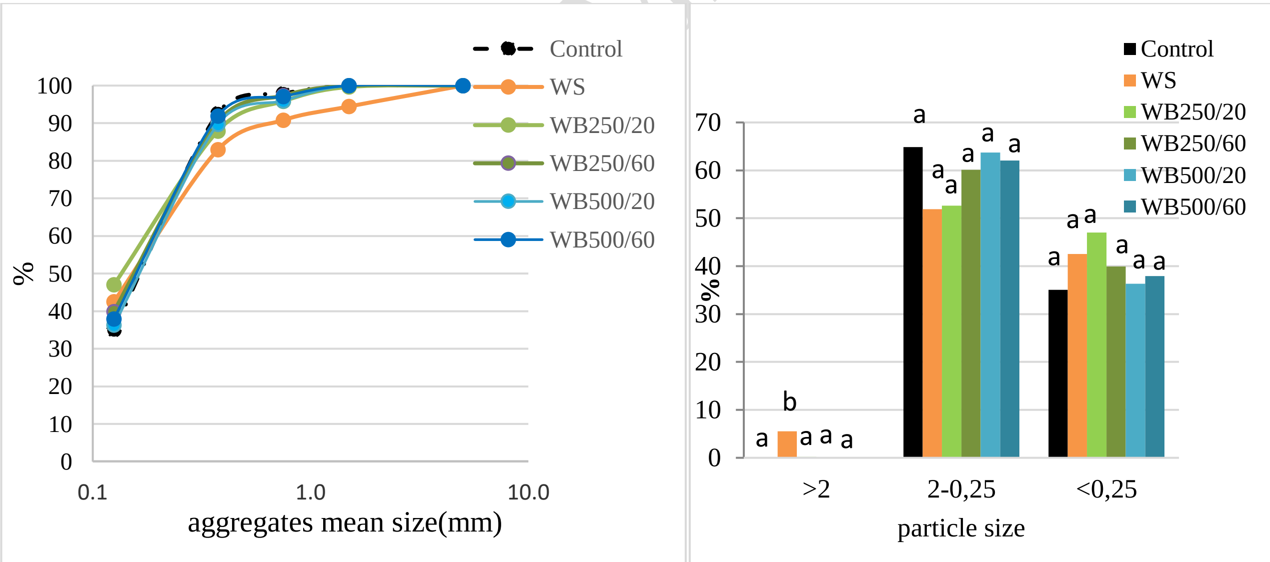


Figure 2b. Cumulative Particle Size Distribution and percentage change of the large (8-2mm) and small (2-1, 1-0.5 and 0.5-0.25mm) macro-aggregates and of the micro-aggregates (<0.25mm) of the sandy soil under various treatments.

3.3.2 Water aggregate stability

In general, all the treatments improved the WAS of the soils compared to the respective control (Table 4) As it was expected, the highest increase was observed with the addition of wheat straw in both soils as increases in SOC after the incorporation of organic residues enhance aggregate stability (Six et al., 2004).

In the loam soil the increase was significant only for the two biochar with the longer pyrolysis time. Pyrolysis temperature also affected WAS as WB250 was more prominent than WB500 in the improvement of WAS of this soil, but differences were not significant. On the contrary, in the sandy soil all biochar treatments significantly increased WAS. For this soil also, biochar with longer pyrolysis time resulted in higher aggregate stability values. Islam et al. (2021), in a meta-analysis report that biochar addition improved aggregate stability regardless of biochar/experimental/soil

Table 4. Water aggregate stability and clay dispersion of fresh wheat straw (WS) and the produced 4 types of wheat straw biochar (WB)

	loamy soil		**sandy soil**	
	T%	**WAS %**	**T%**	**WAS %**
WS	25.3b	75.37d	59.3d	68.77d
WB250/20	19.4a	42.86ab	33.45a	37.43b
WB250/60	18.5a	61.20c	39.35b	42.07b
WB500/20	27.55b	37.11a	49.45c	38.46b
WB500/60	28.45c	51.26bc	58.12d	48.63
Control	17.2a	35.71a	34.15	25.56a

conditions. According to Blanco-Canqui, (2017), the positive effect of biochar application on WAS can vary with soil texture and biochar type. Significant increases in WSA after biochar addition in relation to the control were found by Hammam et al. (2022) for a clayey loam soil and a sandy soil and were attributed to the fact that biochar provides an organic binding agent. According to our results, biochar with longer pyrolysis time had higher C content (Table 3). Burrell et al.

(2016) consider that biochar, due to its high EC results in increased electrolyte concentration that promotes flocculation and make more efficient other aggregation mechanisms as organic matter that sustain WAS. This was observed and in our research as biochar with longer pyrolysis time had higher EC (Table 2) and was more effective in stabilizing the 2-1 mm macro-aggregates structure of both soils.

3.2.3 Clay dispersion

WS and WB500 addition resulted in a significant decrease of clay dispersion in both soils. High temperature pyrolysis biochar with longer pyrolysis time resulted in reduced clay dispersion. On the contrary, biochar produced at lower temperature had no effect on clay dispersion of the loamy soil while only WB250/60 decreased clay dispersibility of the sandy soil (Table 4). High temperature biochar has a high specific surface with negative charges, which enable cation bridges with clay particles (Usman 2015), increase interparticle bonding and form aggregates which are highly resistant to slaking (Ajayi and Horn, 2016). Another possible mechanism is that reported by Hu et al. (2021) that biochar addition reduces net repulsive forces between soil particles.

4. CONCLUSIONS

Pyrolysis temperature affected the decomposition rate of the wheat biochar as lower temperatures resulted in higher decomposition in both soils, due to incomplete carbonization. Pyrolysis duration affected negatively only low temperature biochar decomposition. Decomposition of the low-temperature biochar was significantly higher in the sandy soil in comparison to the loamy one. Decomposition of the high pyrolysis temperature biochar was not affected by soil texture or by the duration of pyrolysis. Biochar addition reduced the cohesiveness of the loamy soil, decreased the percentage of large macro-aggregates and turned ASD to values more favorable for plant growth. Biochar produced in higher pyrolysis temperature enhanced the formation of smaller aggregates while pyrolysis time had no effect. On the contrary, none of the four types of biochar altered the ASD of the no cohesive sandy soil. Biochar with longer pyrolysis time resulted in higher aggregate stability values for both soils because of its higher C contents and EC that promote flocculation and other aggregating mechanisms. Higher pyrolysis temperature promoted WAS only for the sandy soil. High pyrolysis temperature and duration biochar resulted in reduced clay dispersion in both soils while biochar produced at lower temperature had no effect on clay dispersibility. Biochar produced at higher temperature (500◦C) was more efficient in mitigating greenhouse gas emission into the environment as it mineralized slower than biochar pyrolyzed at lower temperature (250◦C) and simultaneously, most of the times it affected in a positive way the structural quality of the two different textured soils.

Figure captions

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