Original Paper

Temporal Changes in Surface Properties of Sandy Haplic Podzol and Aging Biochars During Growing Season in North-Western Region of Russia

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The objectives of the study were to evaluate the temporal changes in: (1): the content of film water during adsorption-desorption processes on the surfaces of aging biochars and samples from topsoil of a sandy Haplic Podzol; (2) the distribution of areas of adsorption bands for oxygen-containing functional groups (OFGs) such as hydroxyl, carboxyl and phenolic on the surfaces of aging biochars. Samples of the soil and the biochar were collected from 0–10 cm layer in May, June and September of 2022, six years after the initial biochar application into the 0–10 cm soil layer (20 t·ha^{-1}) in 2016. A WP4n dewpoint potentiometer was used to measure the relationships between potentials of the adsorbed film water and its content in the soil and biochar samples. An IR Fourier FSM 2202 spectrometer was applied to determine the areas of adsorption bands of OFGs on the biochar surfaces. The results showed that there were non-significant differences in the mean content of adsorbed film water between the soil with and without biochars. The mean content of adsorbed film water was significantly higher (p <0.01) in the initial biochar than in the aged biochars. The aged biochars did not demonstrate any significant temporal differences in the mean contents of the adsorbed film water. The spectroscopic results showed that the initial biochar was characterized with the highest areas of adsorption bands of OFGs. The aged biochars showed a decrease in the areas of adsorption bands of OFGs compared to them of the initial biochar.

Keywords: soil, biochar, aging, water vapor desorption, oxygen-containing functional groups

1 Introduction

Biochar is a product of slow or fast pyrolysis of different forest and agricultural wastes under limited oxygen concentrations and temperatures of 300–950 oC (Ngernyen et al., 2007; Skic et al., 2024). After the pyrolysis, biochar is characterised by a high content (>80%) of highly aromatic and recalcitrant carbon, which is weakly sensitive to biotic and abiotic effects (Keiluweit et al., 2010). Therefore, biochar is mainly recommended as a management tool to increase carbon sequestration in soils (Tsolis, Barouchas, 2023).

Biochar has also shown its more or less pronounced potential for improving soil quality due to: changes in water-holding capacity (Sun et al., 2015), soil pH (Zhang et al., 2021), cation exchange capacity (Thapa et al., 2024), microbial activity (Lehmann et al., 2011), water-stable aggregation (Šimanský et al., 2024), soil bulk density (Sun et al., 2015), thermal properties (Khaledi et al., 2023), autotrophic nitrification and denitrification (Zhang et al., 2022), N_2O emission from soils (Balashov et al., 2021; Horák et al., 2022).

Nevertheless, Brtnicky et al. (2021) in the recent review reported about the adverse biochar effects on soil properties due to a decrease in content of plant available water, imbalance between the liquid and gaseous phases of the soil (relative field capacity lower than critical limit), immobilisation of available nitrogen forms, incorporation of toxical substances (hydrocarbons), negative changes in bacterial community structure.

Studies of biochar effects on the soil water-holding capacity are mainly focused on the relationships between the soil moisture content and matric water potentials higher than –1.5 MPa (Marshall et al., 2019). For instance, incorporation of biochar (produced from walnut shell) at rates of 10 t·ha^{-1} and 20 t·ha^{-1} into sandy soil increased its film water retention at matric potential of -1.5 MPa (Wang

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et al., 2019). The results of these studies are important for understanding the biochar effects on the content of plant available water.

The relationships between the adsorbed film water content and water potentials lower than -1.5 MPa are usually presented as water vapor sorption isotherms. Such isotherms can be used for analysis of the temporal changes in the surface chemistry and porous structure of soils and biochars or to study the mechanisms of water vapor adsorption and desorption on soil and biochar surfaces (Balashov et al., 2022; Ngernyen et al., 2007).

More prolonged presence of biochar in soils leads to "biochar aging". The aging of biochar can result in its surface oxidation and changes in its porous structure (Tsolis, Barouchas, 2023). During biochar aging in soils an increase in the density of OFGs on its surface can occur (Cao et al., 2017). The OFGs are located at the edges of the basal planes of the graphite layers (Do, Do, 2000). The OFGs can contribute to increasing the cation exchange capacity of the biochar (Tsolis, Barouchas, 2023) and water vapor adsorption on its surfaces (Balashov et al., 2022). The OFGs include carboxyl, carbonyl, phenolic, and hydroxyl groups. The magnitude of carboxyl groups interaction with water vapor is two orders stronger than that of carbonyl or hydroxyl groups (Nguyen et al., 2014).

Ngernyen et al. (2007) reported that oxidation (with HNO_3) of biochar produced from eucalyptus wood chip at 600 °C and 900 °C had resulted in a decrease of amounts of phenolic OFGs because of a decrease in volumes of micropores of biochar. Hardy et al. (2017) also informed that a long-term presence of biochar in cultivated soils had resulted in a decrease in areas of carboxyl OFGs on its surface. Microbial mineralisation of organic structural compounds associated with OFGs can be a reason of their decrease on the surface of aged biochar.

According to the known cluster model of Do and Do (2000), adsorption of water vapor on the surfaces of adsorbents, including biochars, begins with strong chemisorption of water molecules at the OFGs. The process of accumulation of water molecules results in the formation of a growing water cluster. When the growing water cluster exceeds its critical size, it has sufficient energy for its transport into micropores until the micropore volume is filled with water. The increase in water cluster size in the micropores and then in mesopores continues until the capillary condensation pressure is reached in the latter at the relative pressure of water vapor of 0.9. The desorption of the water clusters from adsorbents occurs in the reverse order and can demonstrate hysteresis of water vapor desorption isotherm.

The density of OFGs on the surface of biochar may increase and decrease during its aging in soils. Temporal changes in the degree of affinity of OFGs to retaining film water may be different. Therefore, it is necessary to analyze the consequences of biochar aging in soils for better understanding of its impacts on soil surface properties.

The objectives of the study were to evaluate the temporal changes in:

1. the content of adsorbed film water during adsorption-desorption processes on the surfaces of aged biochar and topsoil samples of sandy Haplic Podzol;
2. the distribution of areas of adsorption bands of OFGs (hydroxyl, carboxyl and phenolic groups) on the surfaces of aged biochars.

2 Material and Methods

The experimental plots were located at the experimental station of the Agrophysical Research Institute in the St. Petersburg region of Russia (59° 34′ N, 30° 8′ E). The field experiment was established in 2016 on a sandy Haplic Podzol with 91.7% sand, 5.2% silt, and 3.1% clay particles. The experiment included 3 plots (16 m^2) without and 3 plots (16 m^2) with biochar rate of 20 $t \cdot ha^{-1}$. The applied biochar consisted mainly of birch wood pyrolyzed at 600 °C through fast pyrolysis. Properties of the incorporated initial biochar were: total carbon content – 825.5 g $C \cdot kg^{-1}$, total N content – 5.7 g $N \cdot kg^{-1}$, C/N ratio – 145, pH_{H_2O} – 7.0, moisture content – 1.92% and ash content – 0.23%. Chemical and physical analyses were conducted using standard and traditional methods from Russian soil science laboratories (Rastvorova et al., 1995; Vadjunina, Korchagina, 1986).

Disturbed soil samples were collected from the 0–10 cm layer on the plots under spring wheat (*Triticum aestivum* L.) in May, June and September of 2022. The soil samples were air-dried and sieved. Soil particles of 2–3 mm in size were used for measurements of water vapor desorption isotherms.

Particles of the initial and aged biochar were crushed, sieved through 5 mm and 2 mm mesh sieves to obtain the 2–5 mm size fraction of biochar for the measurements of water vapor desorption isotherms.

A dewpoint potentiometer (WP4-T, Decagon Devices, Inc., Pullman, WA, USA) was used to measure the water potential of the biochar and the soil samples. The weight of biochar and soil samples was equal to 0.5 g and 3 g, respectively. One water vapor adsorption-desorption cycle was carried out for each sample of the biochar and soil. Prior to the measurements, air-dried samples of soil and biochar were subjected to 24-hour water vapor saturation in hermetically closed plastic vessels (100 cm^3) filled with distilled water. During the process of sample desorption (drying) regular measurements of water potential and sample weight were recorded. More detailed information about the measurements is provided in Balashov et al. (2022).

An infrared Fourier spectrometer FSM 2201/2202 (Infraspek, Russia) was used to measure the FTIR spectra and densities of OFGs on the biochar surfaces in a mid-infrared range of wavenumbers of 4000–400 cm^{-1}. The mid-infrared range of wavenumbers corresponds to the adsorption bands areas of carboxyl, phenolic, and hydroxyl groups (Brennan et al., 2001). Particles of biochar were crushed, sieved through sieves with mesh size of 0.25 mm.

Statistical assessment of the results included the calculation of means and standard deviations. Means of the parameters were calculated for the content of the film water in all the studied soil and biochar samples in each cycle of water vapor desorption. One-way analysis of variance (ANOVA) was applied to evaluate the significance of differences ($p \leq 0.05$) between the means of the experimental data.

3 Results and Discussion

3.1 Water Vapor Desorption Isotherms of Soil and Biochar

The results of the studies showed that in the soil without biochar, the maximum content of adsorbed film water (after 24-hour saturation by water vapor) reached 3.92%, 3.79% and 3.98% (by mass) in May, June and September, respectively (Figure 1A). There were no significant differences in the maximum content of adsorbed film water in the soil between the different sample collection dates, likely because the studied sandy soil was not subjected to treatments with substances having high affinity to water vapor.

In the biochar-treated soil, the maximum content of adsorbed film water in the soil samples reached 4.31%, 3.91% and 4.01% (by mass) in May, June and September, respectively (Figure 1B). There were only negligible differences in the maximum content of adsorbed film water between the soil with and without biochar. The obtained results were somewhat ambiguous but agreed with the results reported by Cybulac et al. (2016). Huang et al. (2021) also showed that the effect of biochar produced at higher pyrolysis temperature (600 °C versus 300 °C) on water vapor adsorption in soil (granite eluvium) was not significant, despite the enhancement in specific surface area and porosity at the higher pyrolysis temperature. This was possibly due to the dissolution of organic matter and OFGs present in the biochar at 600 °C that might not be favourable for water vapor adsorption.

The water vapor desorption isotherms for the soil both with or without biochar did not indicate clear differences in the soil film water content between the different dates

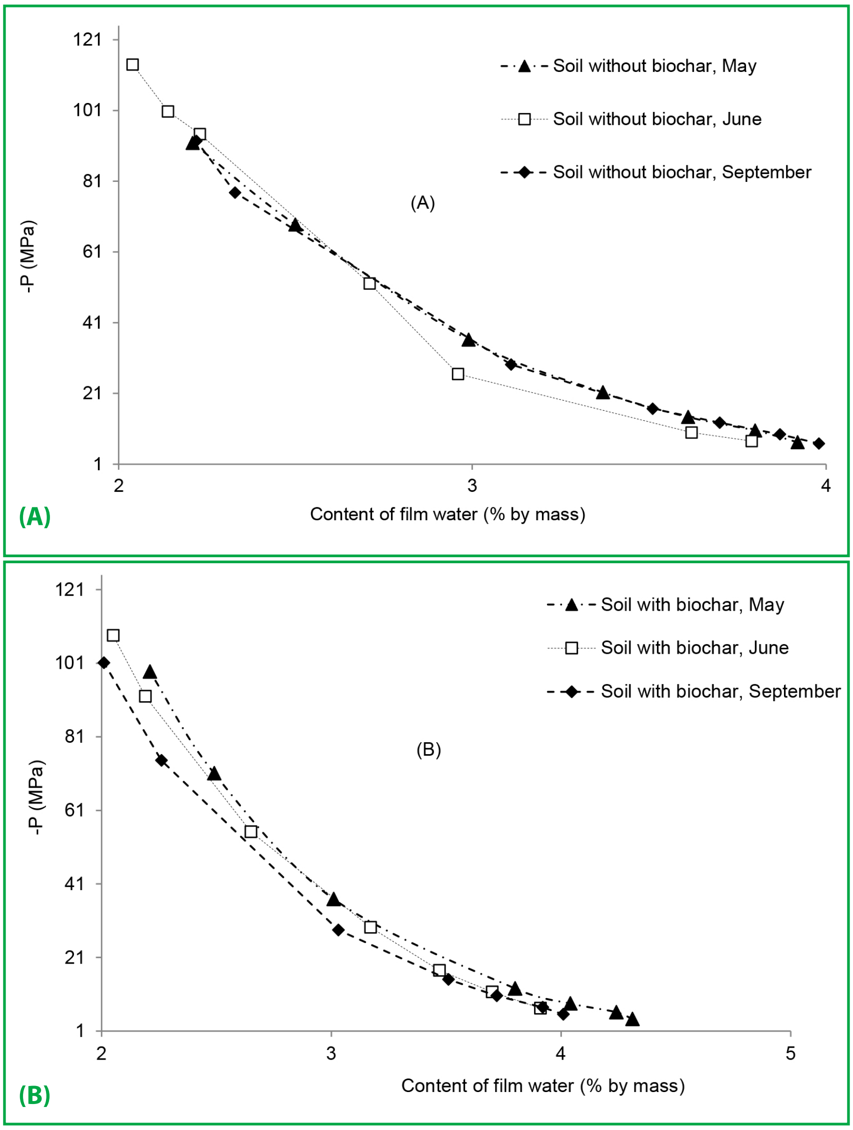

Figure 1 Water vapor desorption isotherms of a sandy Haplic Podzol without (A) and with (B) biochar in May, June and September of 2022

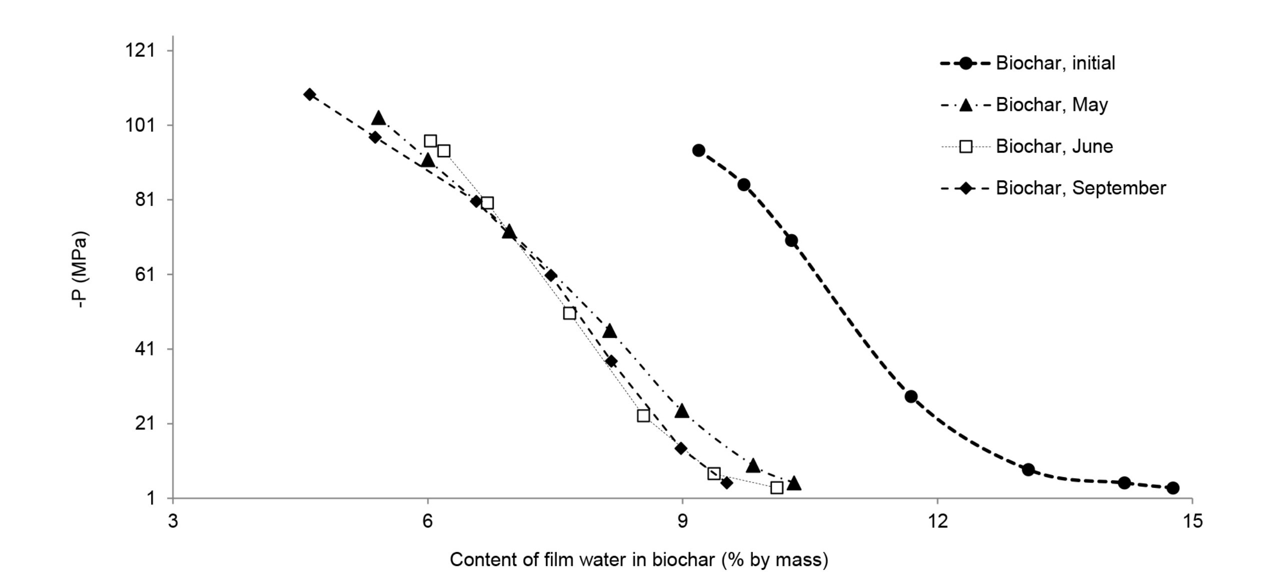

Figure 2 Water vapor desorption isotherms of initial biochar and aging biochar from a sandy Haplic Podzol in May, June and September of 2022

of the sample collection. Furthermore, the presence of aged biochar in the studied soil did not result in distinct changes in the soil film water content compared to the soil without biochar in the studied range of water potentials (Figure 1A and 1B). However, some other results, such as Qian et al. (2020), indicated that biochar application at a rate of 45 t·ha^{-1} to a Ferrosol (with 36.03% sand, 28.2% silt, and 35.72% clay) resulted in an increase in the hygroscopic coefficient after 7-day saturation by water vapor at air relative humidity of 98%.

Conversely, the initial biochar had a significantly (p <0.01) higher film water retention capacity than the aged biochar in May, June and September of 2022 (Figure 2).

After 24-hour saturation, there were only little differences in the maximum content of adsorbed film water in biochar particles collected in May (10.31% by mass), June (10.11% by mass) and September (9.52% by mass). The maximum content of adsorbed film water in the biochar particles was the lowest in September, likely due to infilling by fine-textured mineral solid phase, organic matter or due to physical disturbance (Cao et al., 2017; Tsolis, Barouchas, 2023). Such changes can lead to a decrease in the volume and size of pores in biochar particles.

The water vapor desorption isotherms of aged biochars did not show significant temporal differences in the content of adsorbed film water. However, in May, its content (8.14–9.83% by mass) was still higher than in June (7.67–8.98% by mass) and September (5.14–7.45% by mass) at the beginning of the water vapor desorption cycle. This was likely a result of differences in the volume and size of pores of aged biochar paricles. Therefore, the mean content of adsorbed film water was significantly higher (p <0.01) in the initial biochar (11.85 ±2.22% by mass) than in the aged biochar in May (7.95 ±1.89% by mass), June (7.80 ±1.60% by mass) and September (7.24 ±1.82% by mass) of 2022.

3.2 Density of Oxygen-containing Functional Groups on Surface of Aging Biochar

The FTIR spectroscopy is considered a good tool for a better understanding of temporal changes in surface properties of aging biochars in soils (Cao et al., 2017).

Table 1 Areas of adsorption bands for OFGs on the surfaces of the initial and the aged biochars in May, June and September of 2022

Treatments	Carboxyl	Hydroxyl	Phenolic groups
Areas of adsorption bands (%)			
Initial biochar	30	37	47
Aged biochar, May	23	27	45
Aged biochar, June	29	29	40
Aged biochar, September	22	25	42

The analysis of OFGs behaviour allows evaluating their contribution to processes of water vapor adsorption-desorption on surfaces of aging biochars. According to the results of the FTIR analysis of biochar, the highest areas of adsorption bands for major groups as hydroxyl, carboxyl and phenolic correspond to the wavenumbers of 3,000, 1,700 and 1,500 cm^{-1}, respectively. The interaction of water with carboxyl groups is two orders of magnitude stronger than that of carbonyl or hydroxyl groups (Nguyen et al., 2014). Distributions of the areas of adsorption bands for OFGs on the surfaces of the initial and aged biochars are presented in Table 1.

The highest areas of adsorption bands of OFGs were measured on the surface of the initial biochar. The initial biochar also demonstrated the highest hydrophilic surface after measurements of water vapor desorption isotherms (Figure 2). The aged biochar showed a decrease in the areas of adsorption bands of OFGs probably as a results of decreasing content of hydrophilic organic matter associated with OFGs (Huang et al., 2021) or an incorporation of clay particles into pores of biochar particles (Chen et al., 2024). However, results of other studies showed that aging (chemical oxidation) of biochar had led to an increase of density of OFGs groups, especially hydroxyl groups (Fan et al., 2018), which have the strong affinity to adsorption of water vapors. Quan et al. (2020) also reported than aging of biochars led to an increase in density of OFGs on their surfaces. Ivanova et al. (2023) have shown that application of a mineral fertilizer to the soil with aging biochar for six years resulted in a decreased wettability of the biochar lateral surfaces due to a decrease in the polar component of surface energy and the crusting of the surface with fine soil material, which blocked the pore space of the biochar. Longer studies of temporal changes in these properties of the biochar can contribute to the better understanding of the reasons of biochar aging in soils.

4 Conclusions

The results have shown that there were non-significant temporal differences in the mean content of adsorbed film water in soil with and without biochar within one growing season. The initial biochar demonstrated the highest hydrophilic surface after the measurements of the water vapor desorption isotherms. Therefore, the mean content of adsorbed film water was significantly higher (p <0.01) in the initial biochar than in the aged biochars collected in May, June and September of 2022 – six years after the biochar application to the soil. The aged biochars did not demonstrate significant temporal differences in the mean content of adsorbed film water during the period of studies. Results of IR Fourier spectroscopy showed that the highest areas of adsorption bands of OFGs were measured on the surface of the initial biochar. The aging biochars showed a slight temporal decrease in the areas of adsorption bands of the OFGs.

Conflict of Interest

The authors declare that there is no conflict of interest.

Author contributions

Eugene Balashov: original draft, writing – review and editing, analysis of hydrophysical results, Dmitry Fetisov: spectroscopic measurements, Anna Burova: hydrophysical measurements, Yury Khomyakov: analysis of spectroscopic results.

AI and AI-assisted technologies use declaration

No generative AI tools/AI-assisted technologies were used during the preparation of the manuscript.

References

Balashov, E. et al. (2021). Effects of slow and fast pyrolysis biochar on NO emissions and water availability of two soils with high water-filled pore space. *Journal of Hydrology and Hydromechanics*, 69(4), 467–474. https://sciendo.com/article/10.2478/johh-2021-0024

Balashov, E. et al. (2022). Content of adsorbed film water and density of oxygen-containing functional groups on surface of ageing biochar in sandy spodosol. *Acta Horticulturae et Regiotecturae*, 25(2), 115–120. https://doi.org/10.2478/ahr-2022-0015

Brennan, J. K. et al. (2001). Water in porous carbons. *Colloids and surfaces A: Physicochemical and engineering aspects,* 187, 539–568. https://doi.org/10.1016/S0927-7757(01)00644-6

Brtnicky, M., et al. (2021). A critical review of the possible adverse effects of biochar in the soil environment. *Science of the Total Environment*, 796, 148756. https://doi.org/10.1016/j.scitotenv.2021.148756

Cao, T. et al. (2017). Surface characterization of aged biochar incubated in different types of soil. *BioResources*, 12(3), 6366–6377. https://doi.org/10.15376/biores.12.3.6366-6377

Chen, Z. et al. (2024). Influence of biochar on the water permeability of compacted clay subjected to freezing–thawing cycles. *Acta Geophysica*, 72(3), 2071–2081. https://doi.org/10.1007/s11600-023-01141-1

Cybulak, M. et al. (2016). Hygroscopic moisture content of podzolic soil with biochar. *Acta Agrophysica*, 23(4), 533–543.

Do, D. D., & Do, H. D. (2000). A model for water adsorption in activated carbon. *Carbon*, 38(5), 767–773. https://doi.org/10.1016/S0008-6223(99)00159-1

Fan, Q. et al. (2018). Effects of chemical oxidation on surface oxygen-containing functional groups and adsorption behavior of biochar. *Chemosphere*, 207, 33–40. https://doi.org/10.1016/j.chemosphere.2018.05.044

Hardy, B. et al. (2017). Long term change in chemical properties of preindustrial charcoal particles aged in forest and agricultural temperate soil. *Organic Geochemistry*, 107, 33–45. https://doi.org/10.1016/j.orggeochem.2017.02.008

Horák, J. et al. (2022). Mitigation of greenhouse gas emissions with biochar application in compacted and uncompacted soil. *Agronomy*, 12(3), 546. https://doi.org/10.3390/agronomy12030546

Huang, H. et al. (2021). Effects of pyrolysis temperature, feedstock type and compaction on water retention of biochar amended soil. *Scientific Reports*, 11(1), 7419. https://doi.org/10.1038/s41598-021-86701-5

Ivanova, N. et al. (2023). Effect of biochar aging in agricultural soil on its wetting properties and surface structure. *Biochar*, 5(1), 75. https://doi.org/10.1007/s42773-023-00272-4

Keiluweit, M. et al. (2010). Dynamic molecular structure of plant biomass-derived black carbon (biochar). *Environmental science & technology*, 44(4),1247–1253. http://pubs.acs.org/doi/abs/10.1021/es9031419

Khaledi, S. et al. (2023). Effects of biochar particle size, biochar application rate, and moisture content on thermal properties of an unsaturated sandy loam soil. *Soil and Tillage Research*, 226, 105579. https://doi.org/10.1016/j.still.2022.105579

Lehmann, J. et al. (2011). Biochar effects on soil biota – a review. *Soil Biology and Biochemistry*, 43(9), 1812–1836. https://doi.org/10.1016/j.soilbio.2011.04.022

Marshall, J. et al. (2019). Pyrolysis temperature effects on biochar-water interactions and application for improved water holding capacity in vineyard soils. *Soil Systems*, 3(2), 27. https://doi.org/10.3390/soilsystems3020027

Ngernyen, Y. et al. (2007). Effect of surface functional groups on water vapor adsorption of Eucalyptus wood-based activated carbon. *Suranaree Journal of Science and Technology*, 14(1), 9–23. https://www.researchgate.net/publication/237511299

Nguyen, V.T. et al. (2014). Water as a potential molecular probe for functional groups on carbon surfaces. *Carbon*, 67, 72–78. https://doi.org/10.1016/j.carbon.2013.09.057

Quan, G. et al. (2020). Effects of laboratory biotic aging on the characteristics of biochar and its water-soluble organic products. *Journal of hazardous materials*, 382, 121071. https://doi.org/10.1016/j.jhazmat.2019.121071

Rastvorova, O. G. et al. (1995). *Chemical analysis of soils.* St. Petersburg University Publishing, Russian Federation (in Russian).

Šimanský, V., & Juriga, M. (2024). Soil organic carbon sequestration in size-fractions of water-stable aggregates in Haplic Luvisol after organic amendment. *Acta fytotechnica et zootechnica*, 27(2), 1336–9245. https://orcid.org/0000-0003-3271-6858

Skic, K. et al. (2024). Surface areas and adsorption energies of biochars estimated from nitrogen and water vapour adsorption isotherms. *Scientific Reports*, 14(1), 1–14. https://doi.org/10.1038/s41598-024-81030-9

Sun, Z. et al. (2015). Pore structure characteristics after 2 years of biochar application to a sandy loam field. *Soil Science*, 180(2), 41–46. https://www.researchgate.net/publication/281669888

Thapa, R. B. et al. (2024). Enhancing corn yield and soil quality in irrigated semiarid region with coal char and biochar amendments. *Soil Systems*, 8(3), 82. https://doi.org/10.3390/soilsystems8030082

Tsolis, V., & Barouchas, P. (2023). Biochar as soil amendment: The effect of biochar on soil properties using VIS-NIR diffuse reflectance spectroscopy, biochar aging and soil microbiology – A review. *Land,* 12(8),1580. https://doi.org/10.3390/land12081580

Vadjunina A. F., & Korchagina Z. A. (1986). *Methods of studies of soil physical properties*. Agropromizdat, Moscow, Russian Federation (in Russian).

Wang, D. et al. (2019). Impact of biochar on water retention of two agricultural soils – A multi-scale analysis. *Geoderma*, 340, 185–191. https://doi.org/10.1016/j.geoderma.2019.01.012

Zhang, X. et al. (2022). N_2O and NO production and functional microbes responding to biochar aging process in an intensified vegetable soil. *Environmental Pollution*, 307, 119491. https://doi.org/10.1016/j.envpol.2022.119491

Zhang, Y. et al. (2021). The effects of biochar addition on soil physicochemical properties: A review. *Catena*, 202, 105284. https://doi.org/10.1016/j.catena.2021.105284