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Effect of Humic Amendment on Selected Hydrophysical Properties of Sandy and Clayey Soils

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Abstract: In recent years, products containing humic acids have been increasingly used in agriculture to improve soil parameters. Quantifying their impact on soil quality is, therefore, of key importance. This study seeks to evaluate the impact of the commercial humic acid product (HA) on the hydrophysical parameters of sandy and clayey soils sampled from different sites in Slovakia. Specifically, the study hypothesizes that humic amendment will enhance particle density (ρ_s), dry bulk density (ρ_d), porosity (Φ), saturated hydraulic conductivity (K_s), soil water repellency (SWR), and water retention capacity in sandy and clayey soils. The results of the laboratory measurements were analyzed using NCSS statistical software at a statistical significance of $p < 0.05$. In sandy soil, there was a statistically significant decrease in ρ_d and K_s and an increase in Φ and a contact angle (CA) after the application of 1 g/100 cm^3 HA. At a dose of 6 g/100 cm^3 HA, the values of ρ_s, ρ_d, and K_s decreased, and the Φ and CA values increased. In clayey soil, the K_s value significantly decreased by −35.5% only after the application of 6 g/100 cm^3 HA. The addition of HA increased the full water capacity (FWC) and available water capacity (AWC) of clayey and sandy soils. The positive influence of HA on the studied soil parameters was experimentally confirmed, which can be beneficial, especially for their use in agricultural production.

Keywords: soil properties enhancement; particle density and dry bulk density; soil hydraulic conductivity; pF curves; leonardite

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1. Introduction

Climate change has caused a rise in droughts over the last few decades, and experts predict that the risk of global droughts will increase even more in the 21st century [1]. Drought is a complicated phenomenon that cannot be measured using a single physical quantity or definition. Compared to the usual climate average of the area, a lack of precipitation is the leading cause of drought. Droughts are intensified when there is an increase in evapotranspiration, often due to higher air temperatures, lower humidity, fewer clouds, more intense sunlight, or faster airflow. When there is a shortage of water for animals and plants, it is called a physiological or agricultural drought (AD). AD predominantly hinges on available water capacity, a characteristic intricately connected to soil properties, particularly organic carbon content and aggregation [2–5]. Strategies to mitigate water scarcity in agricultural production often involve increasing soil organic matter (SOM) [6].

In recent decades, significant attention has been paid to the addition of organic materials to the soil to improve its properties and retain the water in the soil for longer periods of time, especially during days without precipitation. Organic materials (biochar, compost, peat, manure, etc.) appear to be an effective tool in preventing the formation of AD because they allow longer availability of soil water and nutrients to the plants and thus higher crop production. The hydrophysical properties of soil, such as porosity, saturated hydraulic conductivity, soil water repellency, and water retention capacity, are the most important factors that affect the soil environment. Some authors found that the soil water retention capacity and porosity increased in sandy soil after biochar amendment [7–9] decreased saturated hydraulic conductivity and bulk density [10,11] and had no effect on soil water repellency [12] or altered it [13,14]. The impact of biochar on clayey soil is studied to a lesser extent, and the results are different. Andrenelli et al. [15] found higher porosity and lower bulk density, but Lim et al. [16] observed an increase in saturated hydraulic conductivity, and Major et al. [17] discovered no effect on biochar. An increase in soil retention capacity was observed by Sun et al. [18] and Nguyen et al. [19]. Contrary, a decrease or no effect, was found by Kameyama et al. [20]. Humic substances also belong to organic materials, but there are only a few studies describing their effect on soil hydrophysical properties. Thus, we decided to explore this topic in more detail.

Humic substances, traditionally fractionated into humic acids (insoluble in acidic media), fulvic acids (soluble both in alkali and acidic media), and humin (insoluble in water at all pH values), represent a significant proportion of the total organic carbon in the global carbon cycle, constituting the major organic fraction in soils [21]. They are involved in many processes in soils and differently affect soil physical–chemical properties (e.g., stability of aggregates of soil particles, water-holding capacity, hydraulic conductivity). Humic acids are a mixture of molecules rich in carboxyl groups (–COOH), hydroxyl groups (–OH), amino groups (–NH_2), quinonyl groups (–$C_6H_3O_2$), and others, which results in versatile properties and a multitude of environmental functions [22].

Polyfunctional groups of humic acids can absorb water and increase the water-holding capacity [23–25]. Humic acids are rich in organic matter, which can significantly improve the soil structure and increase the content of SOM. In various studies, these substances have been used to affect the soil hydrophysical characteristics [26,27]. For instance, Xu et al. [28] and Ma et al. [29] discovered that the application of humic acids increased the soil's water retention capacity by enhancing macroaggregation. Likewise, Wu et al. [30] conducted a soil column experiment and reported that the incorporation of humic acids promoted soil infiltration. From the plant production perspective, the humic amendment of the soil caused growth stimulation and higher crop productivity in the form of biomass, seeds, and grain yield. The total soil water storage, plant water use efficiency, and nutrient availability from mineral fertilizers increased [31–34].

Humic acids are mainly extracted from peats and low-rank coals and commercialized for industrial and agricultural purposes [35]. Humic acids are ecofriendly natural organic amendments that improve soil properties [13]. Commercially available humic acid products, generated from Leonardite (a brown coal precursor) as sodium or potassium salts, have been recognized for altering soil solids' surface chemistry and improving soil fertility [36]. Humic compounds offer a range of benefits, including enhanced biological activity, nutrient availability, cation exchange capacity, pH buffering, carbon sequestration, and soil-water relations [37–40]. Their capacity to promote plant stress tolerance by influencing hormonelike effects and micro-organism activity has also been noted [41–43].

Humic acids are complex organic molecules that contain both hydrophobic and hydrophilic domains, which are stabilized by noncovalent interactions [44]. One of the most significant characteristics of soil humic substances is their hydrophobicity, which is believed to result from the complex organo-mineral interactions between the lipid and humic fractions [21]. The molecular composition of these fractions and the association patterns of these components can significantly influence soil water repellency [45]. Predominantly hydrophobic humic acid amendments can possibly induce water repellency of the soil organo–mineral matrix. However, even in highly repellent (contact angle > 90°) soils, hydrophilic functional groups may still be present, and soil type-dependent factors may affect the relationship between different organic compounds and the contact angle [46]. The specific effects of humic acid additives on soil contact angle and water repellency may vary depending on factors such as soil type, organic matter content, application rate, and environmental conditions. Research has indeed been conducted on the effects of humic acid additives on soil contact angle and water repellency, although it may not be as extensive as studies on other soil parameters.

The investigated product comes from a unique deposit of leonardite in Central Europe. There are different deposits of leonardite in the world, characterized by different chemical compositions and humic acid contents. Several studies [47,48] focused on the potential use and analysis of leonardite products for improving soil properties and increasing plant production. The application of leonardite products confirmed the improvement of organic matter, humic acids, and the contents of some plant nutrients in the soil. Sugier et al. [49] found that, independently of the dose, after applying leonardite to the soil, there was a positive effect on the activity of enzymes catalyzing the transformation of the most important processes of soil organic matter. Other authors' studies aimed to quantify the impact of leonardite application through the growth and yields of different crops. The results point to the importance of leonardite-based humic amendment of soils for maintaining the biogeochemical stability of soils, maintaining their healthy microbial community structure, and increasing crop agronomic productivity [50–52].

Considering these factors, the potential effects of humic acid products warrant further investigation. Regarding leonardite, various studies confirm its ability to improve the content and quality of organic matter and the soil's nutrient content and increase plant production. Many studies [23–26,28–30] examined the effect of humic acids on soil hydrophysical properties, but only a few dealt with leonardite as a source of humic acids. The purpose of this study was to assess how a commercial humic acid product affects the hydrophysical properties of sandy and clayey soils. We hypothesized that applying the tested humic material would increase the soil contact angle due to its moderate hydrophobicity. Our second hypothesis was that the humic amendment would alter the particle density, bulk density, porosity, saturated hydraulic conductivity, and water retention capacity in both types of soils.

2. Materials and Methods

2.1. Humic Material

In this study, the commercial product HUMAC® Agro (Humic Acid Material—HA) from HUMAC Ltd., Košice, Slovakia with a high content of humic acids was used (Figure 1).

The humic acids in the product come from one of the purest deposits of Leonardite in central Europe. They are of 100% organic origin, without any chemical treatment or chemical additives. The basic hydrophysical properties of the powder form of HA were measured in laboratory conditions (Table 1). The texture was analyzed by the laser diffraction method using the dry unit (Scirocco 2000) on the Mastersizer 2000 (Figure 2).

Table 1. Summary table of measured physical properties of HA.

Parameter	Dimension	Value (Measured)	Value (Published Data)
Particle density	g/cm^3	1.88	-
Dry bulk density	g/cm^3	1.45	1.4 [4]–1.6 [1]
Wet bulk density	g/cm^3	1.72	-
Porosity	%	22.84	7.4 [2]
Gravimetric moisture	wt. %	20.01	48.7 [3]; 11.8 [4]; 8.12 [5]
Volumetric moisture	vol. %	29.08	-
Contact angle		103.71	-

[1] [51], [2] [47], [3] [52], [4] [50], [5] [48].

The analysis shows that 10% of the particles are smaller than 12.0 µm, 50% smaller than 14.4 µm, and 95% smaller than 37.5 µm. The largest volume (8%) consists of particles with a size of 30.0 µm.

The particle density was determined pycnometrically [53]. Dry bulk density (weight of a unit volume of HA dried at 105 °C) and wet bulk density (weight of a unit volume of

HA with actual water content) were determined in soil cylinders with a defined volume of 100 cm^3.

The contact angle measured in HA was 103.71°, obtained with the OCA 11 optical goniometer, indicating a moderate degree of water repellency.

Figure 1. Powder form of the product. HUMAC® Agro (Humic Acid Material (HA)).

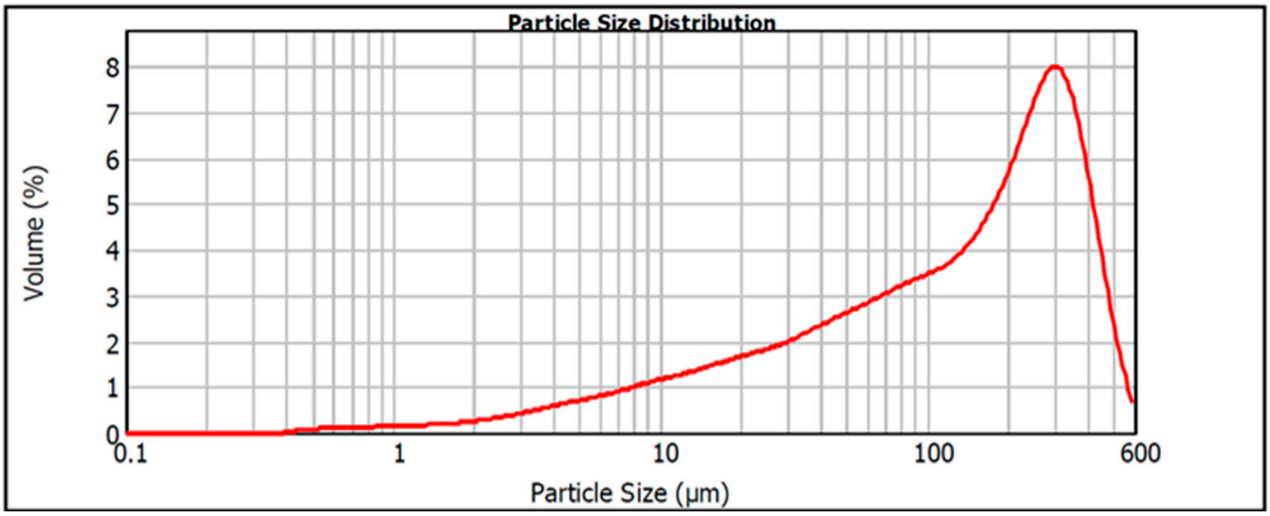

Figure 2. HA particle size distribution measured by laser diffraction.

2.2. Soils Identification and Sampling

In order to conduct a study on the impact of HA on soil quality, we chose two different soil types to represent contrasting environments. The first soil type selected is characterized as clayey soil, which is classified as hydromorphic soil. The second soil type is sandy soil. These particular soil types were intentionally chosen as they embody the two extremes of hydrophysical perspective. Clayey soils are also recognized for their distinct volume changes in response to moisture. These changes often result in the formation of cracks and vertical movements in natural conditions [54,55].

The collection of disturbed soil samples was carried out at two sites. A sample containing clayey soil, classified as Gleysol [56], with a high clay fraction content, was taken from the Senné site (48°39.900′ N; 22°02.859′ E) in the East Slovakian Lowland, Slovakia. A sample of sandy soil, classified as Arenosol [56], was taken from the Plavecký Štvrtok site (48°21.972′ N; 16°59.821′ E) in the Záhorská Lowland, Slovakia. Disturbed soil samples were extracted from the top layer of uniform soil profiles at both sites using a spade and shovel and gathered into plastic bags. Samples were taken from three points, each approximately 1 m apart, and finally mixed together. The soil texture was determined using Casagrande's hydrometer method. The amounts of sand, silt, and clay were approximately 20, 40, and 40% for clayey soil and 91, 7, and 2% clay for sandy soil, respectively.

2.3. Preparation of Soil Samples

The soil samples were air-dried at a temperature of 20 °C. Subsequently, the samples were milled and sieved through a sieve with a hole diameter of 2 mm to separate coarse fragments. The sieved soil was used to prepare samples for laboratory measurements. Fifteen soil samples were prepared for each soil type (30 samples in total). The samples were divided into three groups of five samples each. The first group contained soil without the addition of HA and was used as a control group. In the second group, 0.98 g $\approx$ 1 g of HA was added to each sample, which corresponds to a dosage of 5 kg/10 m^2 (the manufacturer's recommended dosage as a substitute for farmyard manure). In the third group, 6 g of HA was added to the samples, corresponding to a dose of 30 kg/10 m^2 (the maximum dose for soil revitalization given by the manufacturer). The samples with HA additions were mixed thoroughly to create a homogeneous mixture. Subsequently, all samples were poured into soil cylinders with a volume of 100 cm^3 and saturated with water. The soil samples in the cylinders were compacted by applying a pressure of 32 kPa (a force of 63 N acting on the surface area of the cylinder of 19.63 cm^2). During the compaction process, the change in height (decrease) of the sample was monitored. The samples were considered compacted when no subsidence was visible. After this compaction, the soil samples reached approximately the bulk density corresponding to the values in natural conditions (1.5–1.75 g/cm^3 for clayey soil and 1.59–1.66 g/cm^3 for sandy soil). Finally, the soil cylinders were adjusted to an exact volume of 100 cm^3.

2.4. Determination of Hydrophysical Properties of Soil Samples

Particle density (ρ_s) expresses the weight of the volume of the solid phase of the soil without pores, i.e., without water and air. It was determined pycnometrically [53] and expressed according to Equation (1):

$$\rho_s = \frac{m_z}{V_{ds}} \tag{1}$$

where ρ_s (g/cm^3) is the particle density, m_z (g) is the mass of absolutely dry soil, and V_{ds} (cm^3) is the volume of absolutely dry soil.

Dry bulk density (ρ_d) is the weight of an undisturbed unit volume of the examined soil dried at a temperature of 105 °C [57]. It is calculated according to Equation (2):

$$\rho_d = \frac{m_z}{V_s} \tag{2}$$

where ρ_d (g/cm^3) is dry bulk density, m_z (g) is the mass of absolutely dried soil, and V_s (cm^3) is the volume of an undisturbed dry sample.

Porosity (Φ) is the total pore volume, expressed as a percentage of the total volume of the soil sample in its natural state. It is expressed according to Equation (3):

$$\Phi = (1 - \frac{\rho_d}{\rho_s}) \times 100 \tag{3}$$

where Φ (%) is the total porosity.

The determination of K_s was conducted using a soil permeameter (Eijkelkamp laboratory permeameter) by the method with a constant head [58]. The K_s values of the soil samples were calculated according to Relation 4:

$$K_s = \frac{V \times L}{A \times t \times h} \tag{4}$$

where K_s (cm/d) is the saturated hydraulic conductivity, V (cm^3) is the volume of water flowing through the sample, L (cm) is the length of the soil sample, A (cm^2) is the cross-section surface of the sample, t (d) is the time used for flow through the water volume V, and h (cm) is the water level difference during the measurement. The hydraulic conductivity of the soil is determined by the viscosity of the soil solution, which is dependent on temperature. The water temperature in the laboratory is usually between 18 and 22 °C, compared to the average groundwater temperature of 10 °C. Therefore, K_s values were corrected according to the viscosity of the soil solution according to Equation (5):

$$K_s = K_T \times h_T / h_{10} \tag{5}$$

where K_s (cm/d) is the corrected value at 10 °C, K_T (cm/d) is the conductivity at the laboratory temperature, h_T (Pa $\times$ s) is the dynamic viscosity of water at the laboratory temperature, and h_{10} (Pa $\times$ s) is the dynamic viscosity of water at 10 °C.

Water retention curves (WRC) were determined using the pressure plate extractor method (TLAKON SK, Ltd., Žilina, Slovakia). The WRC expresses the retention properties of the porous medium (i.e., soil). It is expressed by the dependence of the moisture potential (h_w) on the volumetric moisture (θ_v) of the porous environment: $h_w = f(\theta_v)$. During the measurement, the loss of water from the soil samples due to the defined pressure is monitored. The measurements were carried out following the ISO standard [59]. The dewatering process was carried out by applying pressures defined by the rules of the international laboratory ring test (1st FSCC soil physical ring test) [60] (Table 2).

Table 2. Values of moisture potential (h_w) [60].

cm	0	10	51	102	337	1020	2549	15296	10^7 *
kPa	0	1	5	10	33	100	250	1500	10^6 *
pF	0.0	1.0	1.7	2.0	2.5	3.0	3.4	4.2	7.0 *

* The value of the moisture potential h_w after drying the samples at 105 °C.

When determining h_w, to increase accuracy, one pressure point with a value of 700 kPa was added to the pressures according to the FSSC. In the case of clayey soils, volume changes must be considered when determining their θ_v [61]. It is, therefore, necessary to monitor the shrinkage process during drainage. Each time the samples are weighed, the height and diameter of the soil samples are measured using a digital caliper, and the volume of the soil samples is calculated. At the end of the measurement, the samples were dried in an oven at a temperature of 105 °C to obtain residual moisture (Figure 3).

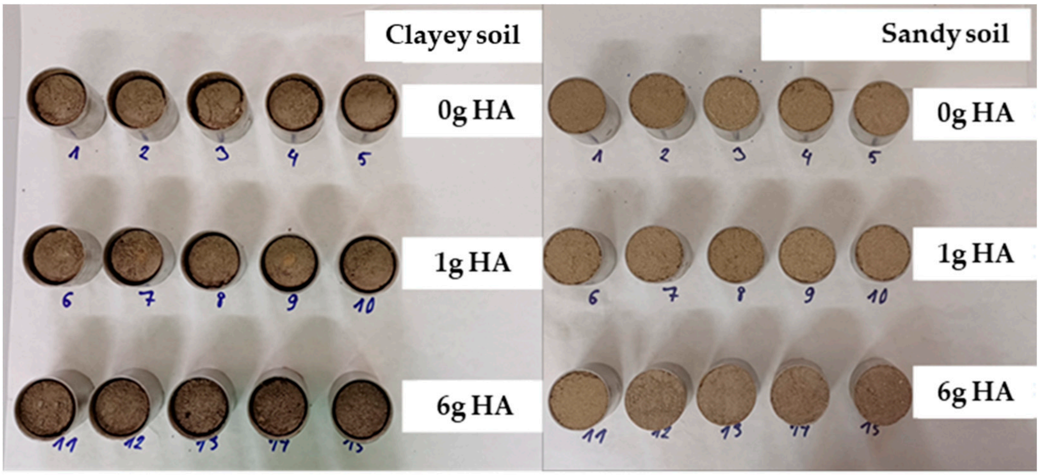

Figure 3. Samples at the end of the measurement of WRC after drying at 105 °C.

Average values were expressed from the measured points of the WRC for each group of samples with the same HA content. Based on these values, the parameters of the analytical expression of pF were determined using the RETC program in version 6.02 [62].

Soil hydrolimits were identified on the measured soil WRC. Hydrolimits are soil moisture values that characterize soil water availability for plants [63]. By convention, the following hydrolimits have been established for most field crops: full (saturated) water capacity (FWC), field capacity (FC) [64,65], threshold point (TP), and permanent wilting point (PWP) [66,67]. The interval in which water is available to plants is defined as available water capacity (AWC). It is expressed as follows [68]:

$$AWC = FC - PWP \tag{6}$$

The severity of soil water repellency (SWR) can be measured by the contact angle (CA). To estimate the CA, a sessile drop method is used, which involves placing a water droplet on the surface of the soil sample. The static contact angle, CA, is then analyzed by examining the image recordings captured using an optical goniometer OCA 11 (DataPhysics Instruments GmbH, Filderstadt, Germany). As per Bachmann et al. [69], the samples are prepared by covering a glass slide with double-sided adhesive tape and pressing soil particles onto it for a few seconds. The slide is then shaken carefully to remove any unglued soil particles, and a 5-µL drop of deionized water is placed on the sample surface using a 0.91 mm syringe needle. After 1 s, when mechanical disruption of the surface is complete after drop placement, CA is evaluated by analyzing the shape of the drop (ellipsoid approximation) and fitting tangents on both sides of the drop using dpiMAX version 1.51.90.75 software (DataPhysics Instruments GmbH, Filderstadt, Germany), according to Goebel et al. [70]. The arithmetic mean of the CA values on the left and right sides determines the CA of each drop. Each sample's CA is estimated with five replicates. The severity of SWR can be categorized into the following classes: nonwater-repellent (wettable) soil (CA < 40°), slightly (40° ≤ CA < 90°), moderately (90° ≤ CA < 110°), strongly and very strongly (110° ≤ CA < 130°), and extremely (CA ≥ 130°) water repellent soil [71].

2.5. Statistical Data Processing

The results of the measurements were processed using mathematical and statistical methods. In order to refine the results, the method of robust estimation was used [72,73], which allows excluding maximum and minimum values in the case of a small number of data sets. This made it possible to exclude outliers and increase the accuracy of the results.

The data was subjected to an omnibus normality test, which combines skewness and kurtosis tests. If the data passed the test, differences between parameters were evaluated using ANOVA with Tukey's Honest Significant Difference (HSD) post-hoc test. However, if the data did not follow a normal distribution, we employed the Kruskal–Wallis test with multiple comparisons and Kruskal–Wallis Z test. This approach does not require the normality assumption and is designed to test the pairs of medians after conducting the Kruskal–Wallis test. We defined the statistical significance of the analysis at $p < 0.05$. We conducted all statistical analyses using the statistical software NCSS 12, version 12.0.18 (NCSS 12 Statistical Software, 2023).

3. Results and Discussion

The assumed effect of the HA application in soils, as an organic source, was the physical improvement of the condition of the soils. The expected influence of humic acids should be manifested by improving the stability of aggregates and reducing the compactness of soils. These processes should lead to a decrease in bulk density and an increase in porosity in the soils [74].

3.1. Basic Physical Properties

The ρ_s and ρ_d values of the analyzed clayey and sandy soils according to the HA content are shown in Figure 4. The ρ_s average value of clayey soil was 2.64 g/cm^3 in the case of samples without HA content. Applying 1 g of HA to the samples resulted in a slight increase in ρ_s by 1.44% (2.68 g/cm^3). After the addition of 6 g of HA, on the contrary, ρ_s decreased by −0.18% (2.63 g/cm^3). The average ρ_s of sandy soil without HA application was 2.64 g/cm^3. Adding 1 g of HA to the samples reduced the value of ρ_s by −0.23% and adding 6 g of HA by −1.82% (2.63 g/cm^3 and 2.59 g/cm^3, respectively). The ρ_s decrease in both evaluated soils after the application of HA was caused by the fact that ρ_s of HA is significantly lower (1.88 g/cm^3) than ρ_s of the investigated soils. However, the rate of induced decrease in ρ_s was statistically significant only after the application of the highest dose of HA to the sandy soil (Figure 4).

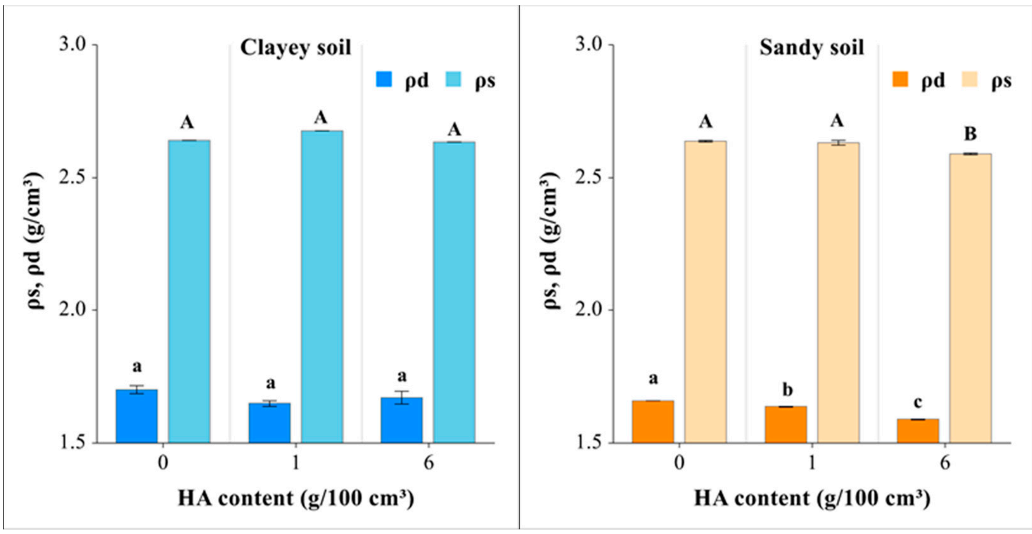

Figure 4. Average particle density, ρ_s (light blue and light orange) and dry bulk density, ρ_d (dark blue and dark orange) of both soil types with different doses of HA. Whiskers represent standard error of the mean. Bar plots with different letters are significantly different at a 0.05 significance level.

The average ρ_d was 1.70 g/cm^3 for clayey soil without HA addition. By adding 1 g of HA, the average value of ρ_d decreased by −3% (1.65 g/cm^3), and after the application of a higher dose (6 g) of HA, there was a decrease in ρ_d by only −1.76% (1.67 g/cm^3) compared to soil without HA. The mean ρ_d of the sandy soil without HA was 1.66 g/cm^3 on average. With the addition of 1 g of HA, ρ_d decreased by −1.33% (1.64 g/cm^3), and with 6 g of HA, the decrease in ρ_d was −4.28% (1.59 g/cm^3) compared to the soil without HA. A statistically significant decrease in ρ_d was confirmed after the application of 1 g

HA, as well as after the application of 6 g HA to the sandy soil samples (Figure 4). A significant difference was also observed between the application rates of 1 g and 6 g of HA to sandy soil.

The reduction in bulk density after the application of humic acids was also documented in other studies. Ahmat et al. [75] analyzed the influence of different doses of humic acids (from 0.01 to 0.15 kg/10 m^2) on the hydrophysical characteristics of soils. They found that higher application rates significantly reduced the bulk density of loamy sand. From the original value of 1.65 g/cm^3, there was a reduction to values from 1.60 (−3%) to 1.40 g/cm^3 (−15%). Our results confirmed a significant decrease in dry bulk density when HA was applied to sandy soil. The reduction in dry bulk density of the mixtures probably results from the lower particle and dry bulk density of HA material compared to soils without admixture. The addition of HA favorably affects soil structure by reducing the particle density of the soil due to the addition of low particle density organic matter to the soil mineral fraction. This positive effect is associated with an increase in porosity through the interaction between organic and inorganic fractions. The organic fraction in the soil has a lower density than the mineral fraction. In this context, an increase in the amount of the organic fraction is manifested by a decrease in the total weight and dry bulk density of the soil [40].

The Φ of clayey soil without the HA addition was, on average, 35.59% (Figure 5). Adding 1 g of HA increased the Φ by 2.82% to an average value of 38.41%. The higher dose of 6 g HA caused an increase in Φ by only 1.00% to a value of 36.59%. The initial average Φ of the sandy soil was 37.07%. After application of 1 g HA, Φ increased by 0.83% to a value of 37.90%. When applying 6 g of HA to the samples, the Φ value reached 38.63% (an increase of 1.56%). The increased measured porosity values due to HA application are directly related to the decrease in dry bulk density, which is confirmed by the fact that a statistically significant increase in porosity was observed only after the application of 6 g of HA to sandy soil. Changes in porosity after application of HA to clayey soil were not statistically significant, similar to changes in dry bulk density. Bulk density is a function of porosity, so any trend in total porosity change corresponds to the opposite trend in bulk density change. Mahmout et al. [33] reported that the application of humic acids to calcareous soil positively influenced bulk density and total porosity. The effects were more pronounced with higher application doses of humic acids to the soil. After the humic acid application of 15 and 30 kg/ha, there was an average increase in porosity to 51.80% and 54.10% compared to the control of 47.80%. The average bulk density decrease was 1.28 g/cm^3 (−5.88%) and 1.22 g/cm^3 (−10.29%) compared to the control of 1.36 g/cm^3. In this case, soil aggregation caused by humic acids was the reason for the decrease in bulk density. Nan et al. [34] observed a porosity increase and a bulk density decrease after the combined dose application of gypsum with lignite humic acids on sandy clay loam soil. At doses of 1.60 and 3.20 g/cm^3 of gypsum with 1.50 g/cm^3 of humic acids, the total porosity increased to 47.70% and 49% compared to the control of 47.10%. Bulk density decreased to 1.39 g/cm^3 (−0.71%) and 1.35 g/cm^3 (−3.57%) against the control 1.40 g/cm^3.

Other authors also noted the increase in soil porosity due to the dose of organic material containing humic acids. Barzegar et al. [76] analyzed the influence of different amounts and types of organic material on soil hydrophysical characteristics. Different doses of added organic material (5, 10 and 15 kg/10 m^2) caused a decrease in bulk density from 1.65 g/cm^3 to 1.51 g/cm^3 (−1.95%), 1.50 (−2.60%) and 1.45 g/cm^3 (−5.84%) and an increase in soil porosity by 0.80%, 1.45% and 2.07%.

The static CA of clayey soil without added HA was 0°, as were the values of CA measured in soil enriched with 1 g and 6 g of HA (Figure 6). Clay minerals have a unique ability to eliminate SWR due to their structure and surface properties. The crystalline lattice structure of clay particles provides numerous sites for water molecules to adhere through hydrogen bonding. Additionally, the negatively charged surfaces of clay particles attract and hold onto water molecules, overcoming the hydrophobic forces that contribute to SWR. The direct addition of clay to the soil successfully eliminates the SWR. Harper and

Gilkes [77] found that SWR was reduced by a 1% increase in clay content and eliminated with a 5% increase. Kaolin clays have been found to be most effective in rendering soil wettable [78,79].

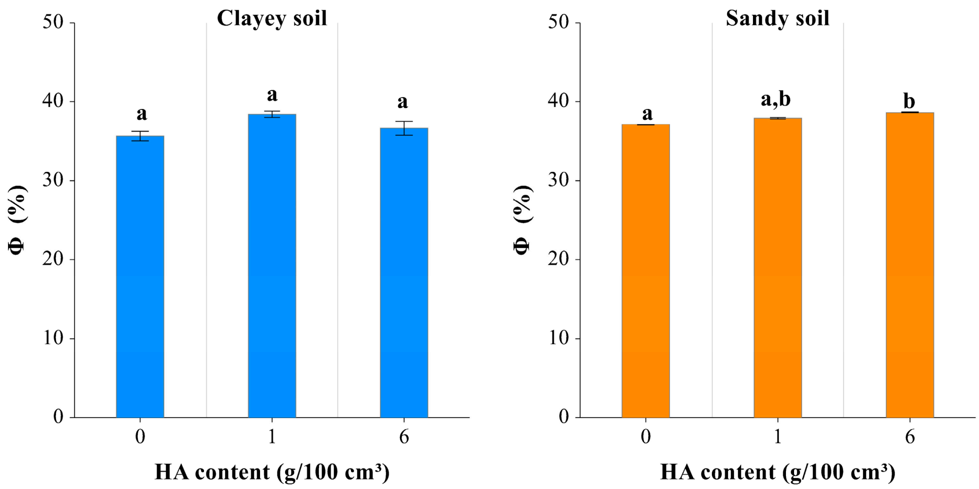

Figure 5. Average porosity (Φ) of both soil types with different doses of HA. Whiskers represent standard error of the mean. Bar plots with different letters are significantly different at a 0.05 significance level.

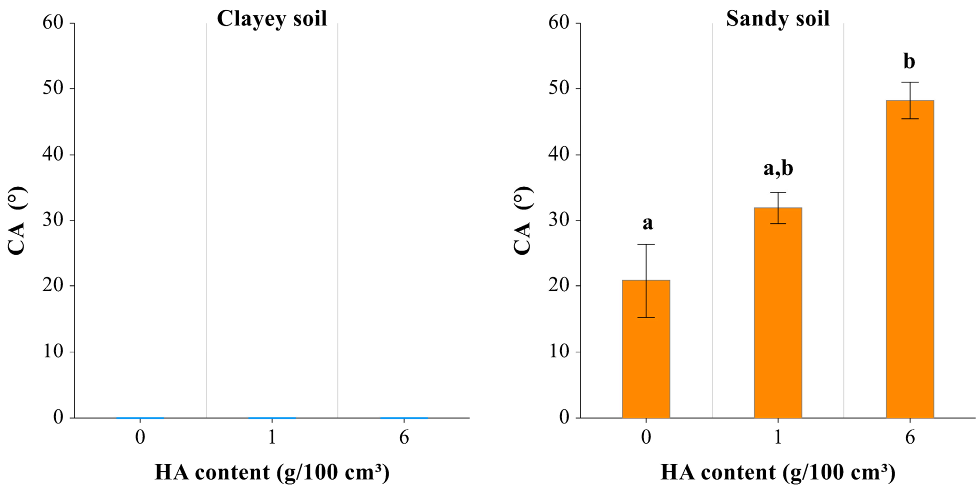

Figure 6. Average static contact angle (CA) values of both soil types with different doses of HA. Whiskers represent standard error of the mean. Bar plots with different letters are significantly different at a 0.05 significance level.

The average value of the contact angle measured in the sandy soil without the addition of HA was 20.9°, indicating a wettable soil. Applying 1 g of moderately water-repellent HA induced an insignificant increase in CA to 31.9°, and a dose of 6 g of HA significantly increased CA to 48.3°, indicating a slightly water-repellent soil (Figure 6). These findings align with Steenhuis et al.'s [80] findings that as little as 5.5% of hydrophobic particles could prevent water entry into the soil.

3.2. Saturated Hydraulic Conductivity

The results of K_s measurements in all samples and their average values with standard deviations are summarized in Table 3. The resulting analysis of the measured K_s values was again based on three samples for each HA concentration (0 g/100 cm^3, 1 g/100 cm^3, and 6 g/100 cm^3) after excluding outliers using the robust estimation method.

Table 3. Measured saturated hydraulic conductivity (K_s) in soil samples.

Soil Type	HA Content in Soil Samples ($g/100\ cm^3$)	Measured K_s (cm/d) Measurement Replications							K_s Average (cm/d)
		1	2	3	4	5	6	7	
Clayey soil	0	1.93	1.71	1.70	1.47	1.72	1.37	1.81	1.69
	0	1.81	1.81	1.67	1.39	1.51	1.21	1.66	
	0	1.91	2.03	1.79	1.91	1.60	1.75	1.74	
	1	1.88	1.93	1.78	1.78	1.62	1.11	1.71	1.60
	1	1.65	1.85	1.60	1.69	1.51	1.74	1.66	
	1	1.56	1.65	1.49	1.44	1.46	1.13	1.45	
	6	1.06	0.93	1.19	1.17	1.19	1.13	0.91	1.09
	6	1.10	1.12	1.17	1.14	1.13	1.18	1.05	
	6	1.12	1.11	1.08	1.10	1.08	1.10	0.89	
Sandy soil	0	1835	1830	1859	1798	1765	1861	1825	2054
	0	2230	2317	2126	2053	2193	2122	2174	
	0	2308	2147	2147	2124	2152	2104	2164	
	1	1671	1581	1669	1654	1508	1657	1623	1819
	1	2061	2018	1838	2006	1893	1916	1955	
	1	1900	1954	1924	1908	1689	1892	1878	
	6	1806	2104	1843	1861	1888	2060	1927	1730
	6	1548	1504	1413	1591	1469	1578	1517	
	6	1746	1626	1788	1838	1724	1759	1747	

The Figure 7 shows the K_s values for individual HA concentrations in clayey and sandy soil samples. Descriptive statistical parameters are presented in Table 4. Figure 7 shows that saturated hydraulic conductivity values decrease with increasing HA content.

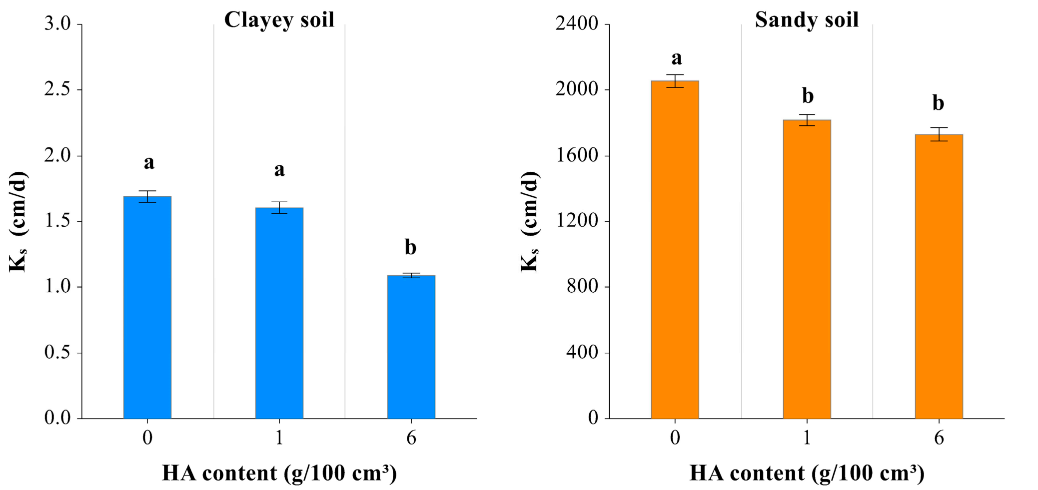

Figure 7. Average K_s values of both soil types measured in samples with different doses of HA. Whiskers represent standard error of the mean. Bar plots with different letters are significantly different at a 0.05 significance level.

For clayey soil samples without HA addition, the average value of K_s was 1.69 cm/d. By adding 1 g of HA to the soil samples, the average value of K_s decreased by −5.30% to a value of 1.60 cm/d. In the case of the maximum concentration of 6 g of HA in the samples, the average value of K_s decreased by −35.50% to a value of 1.09 cm/d. In sandy soil samples, after the addition of 1 g of HA, a decrease in K_s by −11.40% (from 2054 to 1819 cm/d) was measured. In the case of a 6 g HA dose, the decrease in K_s was −15.80% (1730 cm/d). The reduction in saturated hydraulic conductivity was more pronounced after the application of HA to the sandy soil, as a statistically significant decrease was already confirmed at the application rate of 1 g (and also after the 6 g rate); a significant decrease in K_s was observed in the clayey soil only after the application of 6 g of HA.

Table 4. Summary statistics of measured K_s.

Summary Statistics	HA content in Soil Samples (g/100 cm^3)					
	Clayey Soil			Sandy Soil		
	0	1	6	0	1	6
Count	21	21	21	21	21	21
Average	1.69	1.60	1.09	2054.00	1818.81	1730.33
Median	1.72	1.65	1.11	2124.00	1892.00	1747.00
Standard deviation	0.20	0.21	0.09	177.41	162.17	189.23
Minimum	1.21	1.11	0.89	1765.00	1508.00	1413.00
Maximum	2.03	1.93	1.19	2317.00	2061.00	2104.00
Range	0.82	0.82	0.30	552.00	553.00	691.00
Lower quartile	1.60	1.49	1.08	1859.00	1669.00	1578.00
Upper quartile	1.81	1.74	1.14	2164.00	1924.00	1843.00
Interquartile range	0.21	0.25	0.06	305.00	255.00	265.00

In Figure 8, the dependence of the saturated flow rate of water in the soil, according to the HA content, is expressed as a form of linear regression. In the case of clayey soil, a very high degree of dependence was demonstrated (R^2 = 0.999).

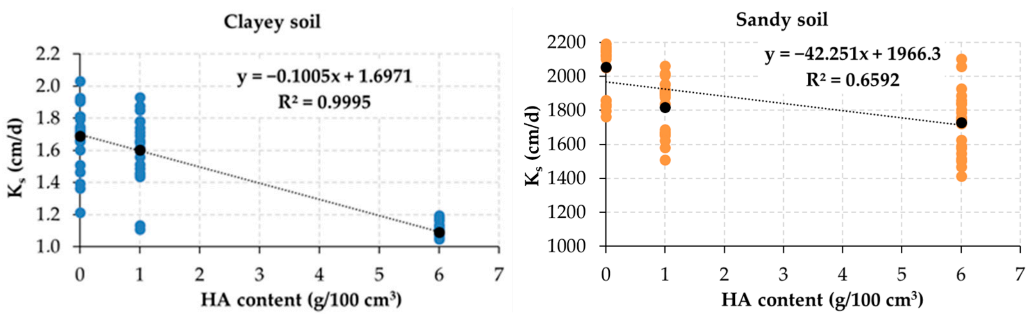

Figure 8. Linear dependence between averaged K_s and HA content.

The linear dependence between K_s values and HA content was slightly lower in the sandy soil. The regression coefficient value R^2 = 0.659 represents a significant degree of tightness. In both cases, the linear dependence is based on three points, each of which represents an average value from seven measurements. The mentioned dependence includes the entire dosage range of HA declared by its manufacturer.

A decrease in water flow rate with increasing HA content was observed in all samples. In field conditions, this means that the infiltrated water remains in the soil for a longer time and can be used by the vegetation. This decrease represents a positive change in sandy soils where K_s values are high. In the soil without HA application, water would infiltrate faster towards the saturated zone of the soil and into groundwater.

The decrease in flow rate is probably the result of an increased proportion of small pores < 0.1 mm (micropores) in samples containing HA. The movement of water in micropores is affected not only by gravity but also by capillary, adhesive, and cohesive forces. In addition, HA has shown significant volume changes, up to 53% compared to the saturated state, which means that HA can bind a significant amount of water into its structure, similar to clay minerals in clayey soils. This not only increases the retention capacity but also affects the hydraulic conductivity of the soil. The decrease in hydraulic conductivity in sandy soil may be related to subcritical soil water repellency by HA, which may affect flow at the pore scale and pore-clogging by finer HA particles. Similar results were obtained with biochar (an organic material with a high carbon content) amendment in sandy soil by Liu et al. [81], who found that hydraulic conductivity decreased after the application of moderately water-repellent biochar particles into sandy soil. The authors found that the decrease in K_s depended not only on the dose of biochar, but also on the fineness of the admixture particles. In the case where the concentration of biochar increased from 0 to 10%, the K_s values decreased by 72% when the fineness of the biochar particles was smaller than the sand particles. With biochar particles coarser than sand particles, K_s decreased by 15%. At biochar particle sizes comparable to sand particles, no effect on K_s was observed. The reason for the decrease in K_s with finer biochar particles was the filling of the spaces between the sand particles, which increased the tortuosity and reduced the pore size of the mixture. The decrease in K_s associated with coarser biochar was due to a bimodal particle size distribution, resulting in a more compact structure and increased tortuosity. The decrease in K_s after the application of different forms of organic matter (walnut sawdust, earthworm manure, and farmyard manure) to sandy soils was also documented in the study by Demir and doğan demir [15]. The authors state that increasing the addition of organic matter (1%, 2%, 4%, and 8%) to the soil leads to a reduction in K_s. The decrease in K_s was in the range of 35–51%. Botková et al. [8] observed a decrease in the saturated hydraulic conductivity in sandy soil by 60–80% after application of the smallest biochar fraction (<125 μm). The measured decrease in saturated hydraulic conductivity in the analyzed soils contrasts with the study results of the other authors [75]. In this study, Ahmat et al. [75] reported that, with higher applied doses of humic acids, an increase in saturated hydraulic conductivity related to an increase in soil organic carbon and aggregate stability was observed. After the application of humic acids to loamy sandy soil in doses of 0.01–0.15 kg/10 m^2, there was an increase in K_s from 60 cm/d (25%)–120 cm/d (150%) compared to the control 48 cm/d.

3.3. Water Retention Curve

The laboratory-measured WRC of pure HA is in Figure 9. For clarity, the figure also shows the WRC of the analyzed soils without HA content. A comparison of the WRC of HA and clayey soil shows that the retention capacity of HA exceeds the retention capacity of clayey soil. Water in HA is energetically more available than in clayey soils. Analysis of laboratory measurements shows that the water retention properties of HA are very high. The FWC is equal to 72%. Such values are practically unattainable in soil. Water in HA, especially at higher moisture levels, is more movable compared to clayey soils and has energetically better conditions for its availability and, thus, usability for plant cover. It is available in a wide range.

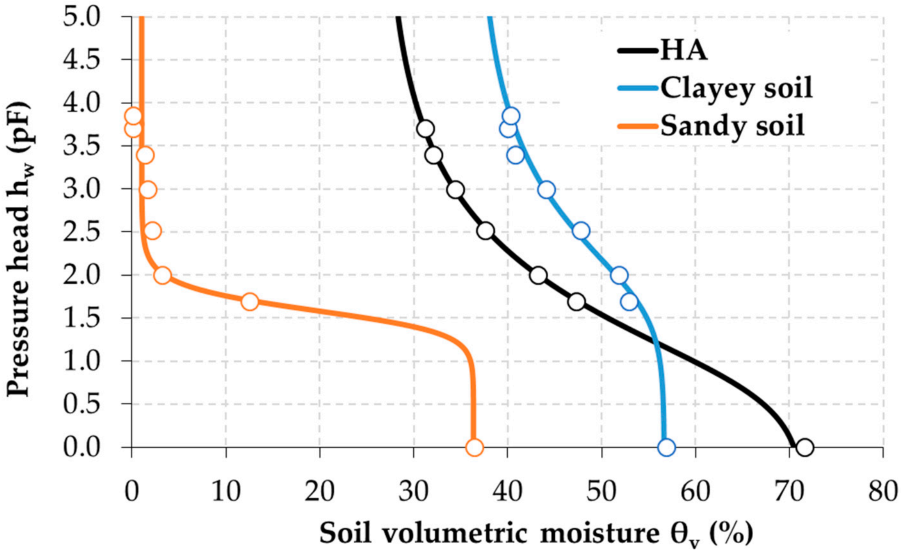

Figure 9. Fitted WRC of HA and analyzed soils with the measured points (circles).

The measured points of the WRC in the examined soils according to the HA content are shown in Table 5.

Table 5. Source data from the WRC measurements.

Soil Type	**HA Content in Soil Samples ($g/100\ cm^3$)**	**Soil Water Potential h_w (Applied Pressures during the Samples Drying)**								
		cm	0	51	102	336	1019	2548	7136	14,271
		kPa	0	5	10	33	100	250	700	1400
		pF	0.0	1.7	2.0	2.5	3.0	3.4	3.9	4.2
		Soil Volumetric Moistures θ_v (%)								
Clayey soil	0		56.79	51.95	50.71	47.76	44.17	40.72	39.88	40.35
	0		56.59	53.25	51.08	47.31	43.94	39.99	39.82	41.14
	0		57.29	52.36	52.50	49.14	45.53	42.99	42.19	41.73
	0		56.99	53.29	52.39	47.93	43.67	41.70	39.96	40.42
	0		56.99	53.59	52.29	46.89	43.11	38.46	38.12	38.05
	1		57.69	52.99	52.46	47.88	43.69	41.27	39.88	42.26
	1		58.39	54.21	54.16	47.88	44.14	39.57	39.47	40.09
	1		58.29	54.48	51.71	47.73	43.41	38.96	39.16	40.04
	1		58.19	52.77	52.25	47.71	44.00	39.21	38.61	39.13
	1		57.69	52.76	52.61	49.04	45.04	41.87	40.15	40.57
	6		56.69	53.29	52.57	47.85	44.48	40.83	39.74	40.21
	6		57.99	53.16	52.79	47.66	43.57	40.56	38.88	38.46
	6		56.89	54.06	52.99	48.07	44.38	41.09	39.45	39.21
	6		57.39	53.89	51.03	48.38	44.14	40.33	39.37	38.96
	6		56.69	52.94	50.52	47.78	43.45	40.51	39.24	38.69
Sandy soil	0		36.86	11.58	3.11	1.83	1.54	1.40	0.15	0.07
	0		36.16	12.46	3.15	2.21	1.73	1.45	0.14	0.06
	0		36.68	11.62	3.04	1.89	1.59	1.42	0.16	0.07
	0		36.11	13.65	3.57	2.51	2.02	1.54	0.15	0.06
	0		35.98	12.98	3.21	1.87	1.59	1.42	0.09	0.30
	1		35.31	14.42	3.75	2.69	2.23	1.79	0.16	0.06
	1		37.66	13.52	3.52	2.30	1.99	1.75	0.17	0.07
	1		37.25	12.25	3.47	2.58	2.29	1.78	0.34	0.16
	1		36.81	14.49	3.89	2.87	2.21	1.80	0.20	0.08
	1		37.83	14.80	3.77	2.64	2.25	1.84	0.15	0.06
	6		37.89	17.26	5.55	3.89	3.45	3.08	0.49	0.23
	6		39.70	15.39	5.30	3.82	3.44	3.01	0.80	0.43
	6		38.90	15.75	5.53	4.00	3.50	3.10	0.85	0.46
	6		39.20	15.74	5.52	4.34	3.93	3.26	1.10	0.64
	6		39.00	15.07	5.42	3.84	3.45	3.14	0.93	0.53

The resulting analytical expression of the WRC [62] is shown in Figure 10. Table 6 shows the parameter values of the analytical expression using the RETC program. The analytical parameters in Table 6 were expressed from the measured point average values listed in Table 5.

The advantage of the analytical expression is the possibility of extrapolating the dependence $h_w = f(\theta_v)$ to high pressures and low moisture. The h_w values expressed in cm of water column pressure height are in logarithmic scale (pF), where $pF = \log|h_w|$. The figure also shows the hydrolimit values of FC, TP, and PWP.

The sample's θ_v in the saturated state, depending on the HA content, for the clayey soil was as follows: 0 g (56.93%), 1 g (58.05%), and 6 g (57.13%). The θ_v near the AWC after HA application increased as follows: 0 g (7.76%), 1 g (8.21%), and 6 g (9%). In the case of sandy soil, the θ_v was in a saturated state at 0 g (36.36%), 1 g (36.97%), and 6 g (38.94%). The θ_v near the AWC after HA application also increased for the 0 g (0.12%), 1 g (0.13%), and 6 g (0.30%) variants. Water thus becomes more available for the plants, especially in clayey soils.

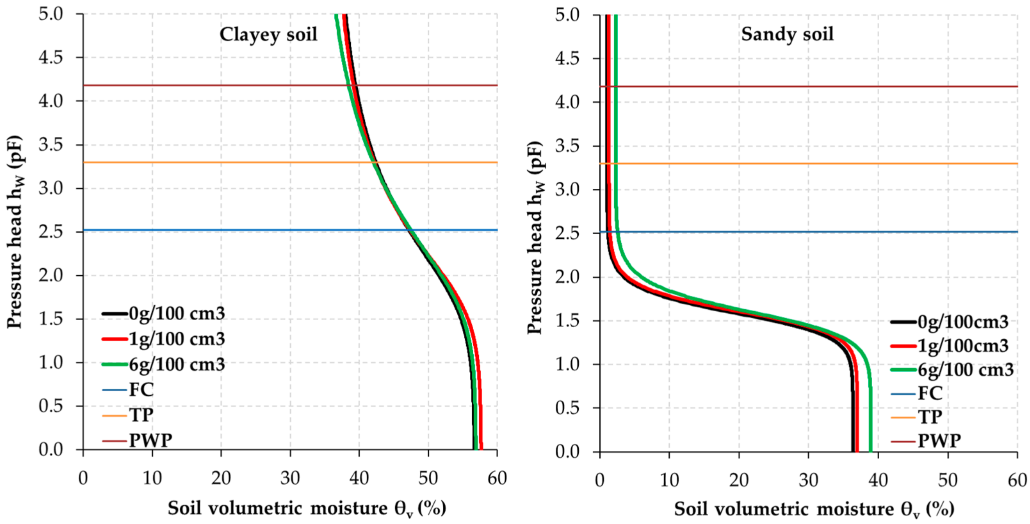

Figure 10. WRC of soil samples according to HA content.

Table 6. The mean parameter values of the RETC analytical expression. Means with different letters are significantly different at a 0.05 significance level.

Soil Type	HA Content in Soil Samples (g/100 cm^3)	Parameters [62]			
		θ_r	θ_s	α	n
Clayey soil	0	0.366 ^{a}	0.567 ^{a}	0.018 ^{a}	1.350 ^{a}
	1	0.366 ^{a}	0.577 ^{b}	0.016 ^{a}	1.382 ^{a}
	6	0.342 ^{a}	0.569 ^{a}	0.017 ^{a}	1.303 ^{a}
Sandy soil	0	0.010 ^{a}	0.364 ^{a}	0.029 ^{a}	3.510 ^{a}
	1	0.013 ^{a,b}	0.370 ^{a}	0.027 ^{a}	3.559 ^{a}
	6	0.023 ^{b}	0.390 ^{b}	0.029 ^{a}	3.139 ^{b}
HA	-	0.267	0.716	0.189	1.339

By comparing the WRC, it can be concluded that the HA improved the retention properties of both soils. There was an increase in FWC and a widening of the AWC interval in both clayey and sandy soil samples containing HA. At lower h_w values (between FWC and FC), the addition of HA in clayey soil was manifested by a shift of WRC to the right. The FWC values, depending on the HA dose, increased from 0.35% to 1.97% compared to the control. Conversely, in the area of higher h_w values (between FC and PWP), there was a leftward shift of WRC. There was an increase in AWC from 5.80% to 15.98% compared to the control variant. This is a positive effect because water in the clayey soil became more available at higher h_w values. In natural conditions, this can mean better water availability for plants during dry periods. The shift of the pf curve to the right at lower h_w values means an increase in the retention capacity of the soil. In sandy soil, only a rightward shift of the pF curve occurred after the application of HA, while a greater effect of the application dose was observed. The addition of HA to sandy soil had a positive effect by increasing the retention capacity. Depending on the dose of HA, an increase in FWC from 1.68% to 7.10% was observed. At the same time, there was an increase in AWC from 8.30% to 150% compared to the soil without the addition of HA. Piccolo et al. [38] reached a similar conclusion. They reported that, when evaluating the effect of humic acids on the soil's physical properties, an increase in the soil's ability to retain more water was observed. The authors report an increase in AWC in different soils from 9.90% to 29.50% in the case of the highest dose of humic acids (1 g/1 kg of soil). The increase in soil retention capacity under the influence of humic acids also follows from the results of the study by other authors [82]. Humic acids are mainly composed of carbon. By adding carbon to the soil, the stability of the soil aggregates is improved, which leads to an improvement in the microand macropores of the soil. Soil macropores also increase aeration and root penetration into the soil, while micropores increase soil retention capacity and water content [34].

4. Conclusions

In this study, a commercial product with a high proportion of humic acids obtained by technological processing of the organic rock Leonardite was investigated. The results showed that the doses of HA declared by its manufacturer as a substitute for manure or revitalization doses improved the hydrophysical properties of soils. There was a decrease in ρ_s, ρ_d, K_s, and an increase in Φ and CA in the studied clayey and sandy soils. Adding HA increased the AWC and FWC, making water more available for plants in clayey soils and increasing the retention capacity of sandy and clayey soils. Overall, the study shows that HA has the potential to improve the water regime of soils. The benefit of this study is new knowledge about the positive properties of organic material obtained from leonardite on the hydrophysical properties of soils. The investigated material has a high potential for use in sectors of the economy focused on plant production (agricultural production, gardening, etc.), hydromelioration, modification of the water regime of soils, or when designing adaptation measures to mitigate the impacts of hydrological extremes. The obtained data can be also beneficial for companies involved in the processing of leonardite.

The presented research is the first phase of investigating HA's influence on soil properties. In the next phases, the authors plan to deal with the impact of HA on other soil types and extend the research to more soil characteristics. In the case of clayey soils, it is planned to investigate the effect of HA on the shrinkage characteristics.

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Data Availability Statement: Data are available from the authors by request.

Conflicts of Interest: The authors declare that they have no conflicts of interest.

Abbreviations

A	cross-section surface of the sample, cm^2;
AD	agricultural drought;
AWC	available water capacity;
CA	contact angle, °;
D	grain diameter, m;
FC	field capacity;
FWC	full water capacity;
h	water level difference during the measurement, cm;
HA	HUMAC® Agro (Humic Acid Material);
HSD	honest significant difference;
h_t	dynamic viscosity of water at the laboratory temperature, Pa × s;
h_w	moisture potential;
h_{10}	dynamic viscosity of water at 10 °C, Pa × s;
K_s	saturated hydraulic conductivity, cm/d;
K_T	conductivity at the laboratory temperature, cm/d;
L	length of the soil sample, cm;
m_v	mass of water displaced by the soil, g;
m_z	mass of absolutely dry soil, g;

SOM	soil organic matter;
SWR	soil water repellency;
t	time used for flow through of water volume V, d;
TP	threshold point;
V_s	volume of undisturbed dry sample, cm^3;
V_{ds}	volume of absolutely dry soil, cm^3;
V_s	volume of undisturbed dry sample, cm^3;
PWP	permanent wilting point;
WRC	water retention curve;
θ_v	volumetric moisture, %;
ρ_d	dry bulk density, g/cm^3;
ρ_s	particle density, g/cm^3;
Φ	porosity, %;
–COOH	carboxyl groups;
$–C_6H_3O_2$	quinonyl groups;
$–NH_2$	amino groups;
–OH	hydroxyl groups;

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