DOCTORAL DISSERTATION THESES

Gyöngyi Barna
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MAGYAR AGRÁR- ÉS
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Hungarian University of Agriculture and Life Sciences

EFFECTS OF SURFACTANT AND BIOCHAR ON SOIL PHYSICAL PROPERTIES

Gyöngyi Barna
Keszthely
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The name of the doctoral school: Festetics György Doctoral School

Field of study:	Environmental sciences
Head:	Dr. Angéla Anda university professor, DSc. Hungarian University of Agriculture and Life Sciences
Supervisors:	Dr. Gábor Csitári associate professor, PhD Department of Animal Nutrition and Nutritional Physiology, Hungarian University of Agriculture and Life Sciences
	Dr. András Makó scientific advisor, university professor, DSc. HUN-REN Centre for Agricultural Research, Institute for Soil Sciences

1. Background and objectives of the work

In recent decades, there has been growing interest in the possibilities and limitations of adding various industrial by-products and potential ameliorants to soil in order to exploit its ability to filter, retain, buffer, store, degrade, or otherwise mitigate the hazards of pollutants. Soils have a significant but limited capacity to render pollutants harmless. Soil self-cleaning processes involve physical transport phenomena and complex chemical and microbiological interactions, which mainly take place in the upper layer of the soil (MAKÓ et al., 2017).

Numerous mathematical models have been developed to estimate the leakage of petroleum derivatives into the soil and their migration with groundwater, which pollute the environment (e.g., PARKER et al., 1987; WEAVER et al., 1994; FAGERLUND, 2006). An essential input parameter for all contamination spread models is the hydraulic conductivity of the soil layer under investigation. Since it is difficult to measure the oil conductivity of soils in practice, oil contamination spread models generally use hydraulic conductivity to estimate the oil conductivity characteristic of the soil layer, which, along with oil retention capacity, determines the spread of the infiltrated oil. In many cases, due to a lack of measurement data, models determine the value of hydraulic conductivity by estimating it from soil properties that are easier to measure. According to recent research, air permeability data can also be used effectively to estimate the oil-conducting capacity of soils instead of hydraulic conductivity (DUNAI et al., 2007).

Water flow, and thus oil flow, is determined by the combined properties of the soil and the permeable fluid (HEAD, 1984; OOSTROM et al., 2003). Important soil properties include porosity, particle size distribution, particle shape and surface, mineral composition, and structural condition. Important parameters for fluids include density, viscosity, dielectric constant, and temperature.

Surfactants or tensides are dual-character substances: they consist of a hydrophilic head and a hydrophobic chain, the latter usually being a long alkyl chain (10-20 carbon atoms) (PATZKÓ, 1998). The hydrophilic part may contain cations or anions, has an electric charge and can form hydrogen bonds. Surfactants are most often released into the environment and thus into the soil through wastewater, but many pesticides also contain surfactants (adjuvants, wetting agents that promote their adhesion).

By binding to the soil surface (adsorption), surfactants can alter many physical, chemical, and microbiological characteristics of soils, depending on their type (DOBOZY et al., 1970; ARORA et al., 2024). For example, they can influence infiltration, hygroscopicity, porosity, water retention capacity, oil retention capacity, aggregate stability, capillary water rise, hydraulic conductivity, and plasticity limits. They affect pH, redox potential, ion exchange capacity, microorganism activity, population composition, and plant development and cell function. Surfactants are also used in the remediation of oil-contaminated areas (JI et al., 2021). When introduced into the soil, they reduce the surface tension of the non-aqueous phase liquids (NAPL) phase, increase its solubility, etc., making it easier to remove (FENG et al., 2025); at the same time, they can also promote the binding of insoluble organic pollutants (PARIA, 2008). Meanwhile, surfactants themselves become co-pollutants.

In recent decades, there has been considerable scientific interest in the development of new soil improvers that promote plant growth and yield by providing more favorable soil conditions for plants. Biochar is a stable material produced by the oxygen-deficient or completely oxygen-free pyrolysis of organic materials (mainly plant residues), which can be used for soil improvement and nutrient replenishment (KOCSIS & BIRÓ, 2015). Based on the literature, it also appears to be suitable for removing carbon from the carbon cycle for longer periods (even centuries), offsetting greenhouse gas emissions (DONG et al., 2020). It can also be successfully used to remove various pollutants (HU et al., 2020).

Biochar added to soil changes its chemical (MASLOUSKI et al., 2025), microbiology (ANDERSON et al., 2011), and physical-hydrophysical properties (TOKOVÁ et al., 2023), and these changes can ultimately affect soil fertility and crop yield (GASCÓ et al., 2016). The addition of biochar affects soil and plant health and must therefore be carefully examined before agricultural use.

In my thesis, we sought to answer the following questions

I. Which soil properties influence the adsoprtion of a cationic surfactant, and how do certain physical properties of the soil change under the influence of a cationic surfactant? We hypothesised that changes in the pore system would alter the structural and hydrophysical properties of the soil.

II. how the 1) water management and 2) physical properties of soils change during the development of a crop plant when biochar is added. We hypothesize that soil properties may also change over time depending on the amount of biochar: the addition of increasing amounts of organic matter will improve soil structure and water and nutrient management.

2. Materials and Methods

2.1. Surfactant experiments

The following soils, sediments, and mineral samples are involved in our investigations. Their basic properties are listed in Table 1.

1) Karcag, meadow solonetz, B horizon, 5-30 cm;
2) Keszthely, brown forest soil (according to Ramann), A horizon, 0-30 cm;
3) Keszthely, brown forest soil (according to Ramann), B horizon, 30-50 cm;
4) Várvölgy, brown forest soil with clay illuviation, A horizon, 0-20 cm;
5) Várvölgy, brown forest soil with clay illuviation, B horizon, 20-50 cm;
6) Salföld, pannonian quartz sand;
7) Magyarszombatfa, pseudogley brown forest soil, B horizon, 20-50 cm;
8) Paks, loess;
9) Kápolnásnyék, Calcareous chernozem, A horizon, 0-30 cm;
10) Mád, Bentonite;
11) Zettlitz, Kaolin (Czech Republic);
12) Kisújszállás, meadow soil, A horizon, 0-30 cm

Table 1. *Physical and chemical properties of the samples*

Sample code	$K_{A\,\#}$	hy_1	Clay + Fe *	Silt	Sand	Soil Organic Matter	$CaCO_3$	pH (H_2O)	CEC-value	Specific surface area
			%						meq· 100 g^{-1}	$m^2 \cdot g^{-1}$
1	90	3,90	51,09	45,90	0,88	2,00	0,13	6,92	40,85	43,0
2	30	1,24	20,99	33,13	44,28	1,55	0,05	7,04	11,84	11,0
3	36	1,49	22,89	33,87	42,29	0,94	0,00	6,83	12,38	19,0
4	29	1,07	15,27	29,35	54,05	1,33	0,00	6,59	10,36	10,0
5	38	1,58	22,25	26,56	50,49	0,70	0,00	6,64	12,78	20,0
6	29	0,07	0,98	0,40	98,60	0,00	0,02	7,44	0,70	1,0
7	59	2,22	38,96	25,93	34,61	0,49	0,00	5,74	16,78	30,0
8	38	1,02	16,08	46,00	9,25	0,63	28,04	8,17	19,74	12,0
9	46	2,25	27,60	51,68	7,50	3,70	9,52	7,83	30,25	14,0
10	143	4,50	64,72	29,44	4,94	0,00	0,90	9,63	36,35	48,5
11	127	0,84	49,83	48,98	0,09	0,00	1,10	8,69	14,54	17,5
12	74	4,49	55,01	41,19	1,05	2,76	1,10	7,51	35,69	47,0

**: Clay and Fe-minerals together #: Upper limit of liquid limit according to Arany*

The cationic surfactant we use, hexadecylpyridinium chloride monohydrate, or cetylpyridinium chloride (CPC) (molecular formula: $C_{21}H_{38}ClN * H_2O$) is mainly used in the pharmaceutical and cosmetics industries due to its good bactericid and fungicid properties (HRENOVIC et al., 2008).

The treatment of soil samples with surfactants was based on the results of static equilibrium experiments (FÖLDÉNYI et al., 2013). We added a quantity of surfactant to the samples that we assumed would form a monomolecular surfactant layer on the surface of the soil particles, thereby making them completely hydrophobic.

During the static equilibrium experiments, I observed structural degradation. Therefore, I also performed the experiment with distilled water only, without adding any surfactant. Thus, I continued working with the control, distilled water, and surfactant samples.

I determined the the samples:

- hygroscopic water content according to Sík (hy_1);
- microaggregate stability based on the Vageler structure factor. To do this, we determined the clay content of the samples using the pipette method in accordance with the Hungarian standard, with and without a dispersing agent, and took the ratio of the clay content obtained in two ways.

$$MiAS = \frac{c_d - c_{nd}}{c_d} \times 100 \quad [\%]$$

where c_d is the clay fraction obtained with dispersant, c_{nd} is the clay fraction obtained without dispersant

- macroaggregate stability (MaAS) was determined using an Eijkelkamp wet sieving apparatus with a 0.25 mm mesh sieve, in three parallel repetitions, from fractions between 0.5 and 1 mm.

- For saturated hydraulic conductivity measurements (K_w), I prepared artificial soil columns in 100 cm^3 cylinders (5 cm high and 5 cm in diameter) in at least five parallel repetitions, with the same bulk densitye. The measurements were performed with tap water in an Eijkelkamp open system permeameter.

- For saturated oil conductivity measurements (K_o), I also prepared artificial soil columns with the same bulk density, in at least five parallel repetitions. For the oil measurements, I used a non-aqeouos liquid free of aromatic components, known as Dunasol 180/220 (MOL NYRT, Százhalombatta). The measurements were performed in a closed-system Eijkelkamp permeameter.

- I determined the air permeability of the samples in the laboratory using a UGT (Umwelt Geräte Technik GmbH, Müncheberg) PL-300 device. For the tests, I prepared artificial soil columns of ~800 cm^3 (in PVC pipes with a diameter of 10 cm and a height of 10 cm) with the same bulk density as in the liquid conductivity measurements, in three parallel repetitions.

We used SPSS and Excel software packages for statistical processing of the results. We also conducted correlation analyses to determine the relationships between the parameters studied. The specific tensile adsorption of the soil samples was compared using variance analysis (SPSS 13.1/One-way ANOVA). Before applying the statistical tests, we tested the variance distribution of the groups to be compared (Levene's test).

2.2. Biochar experiments

The soil sample examined is brown forest soil with clay illuviation, with loam texture, which comes from the top 28 cm layer of a long-standing vineyard (Balatoncsicsó). The biochar is commercially available (Sonnenerde, Austria). It was produced in a Pyreg reactor from paper pulp and grain husks at a temperature of nearly 600 °C. Their properties are listed in Table 2.

Table 2: Properties of the control soil sample and the biochar

	Particle size distribution			pH-H_2O	organic C (%)	Total N (%)	$CaCO_3$ (%)
	< 6,6 µm (%)	6,6 – 52,5 µm (%)	52,5 – 2000 µm (%)				
biochar	1,57	13,90	84,52	10,33	27,89	1,01	-
soil	24,13	50,03	25,84	7,94	0,93	0,14	10,4

For the air-dry soil samples sieved through a 2 mm sieve, we mixed biochar in three different ratios, 0.5, 2.5, and 5% (m/m) (hereinafter referred to as BC0.5, BC2.5, and BC5). We placed 2 kg of these mixtures in pots, in 7 parallel replicates. We planted sweet pepper (*Capsicum annuum L.)* seedlings with 2–4 leaves in the pots.

After planting, the pots were disassembled at three different times: week 6: end of the exponential plant growth; week 10 represents fruit development of mature plants; and week12 when fruit harvesting was performed. (Figure 1.) (hereinafter referred to as W6, W10, and W12).

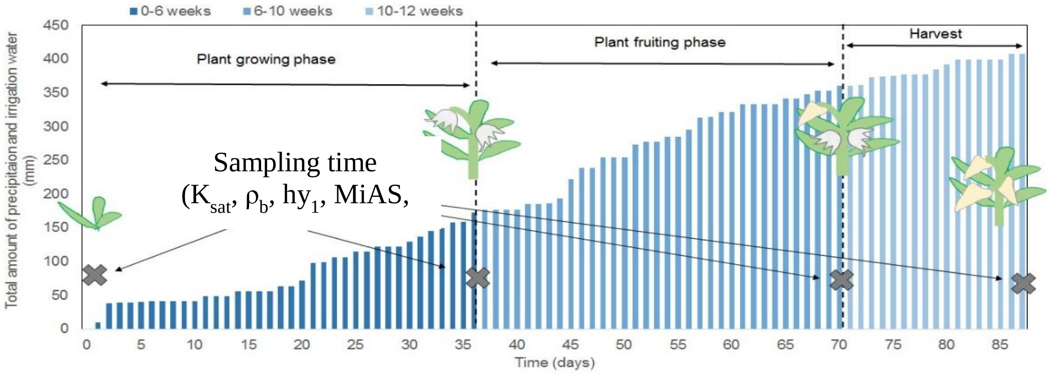

Figure 1: Sampling time, and total amount of precipitation

After the pots were disassembled I determined:

- hygroscopic water content according to Sík (hy_1);
- The stability of microaggregates was calculated in the same way as the Vageler structure factor. We determined the percentage clay content of the samples using distilled water and a dispersing agent, and took the ratio of the clay content obtained in two ways. However, due to the low density of biochar, traditional sedimentation methods could not be used here. The full particle size distribution curve and thus the clay contents were determined using the laser diffraction method (LDM) with a Malvern Mastersizer 2000 device in a HydroG dispersing unit, in three parallel repetitions. During the measurement with distilled water only, there was no chemical or ultrasonic dispersion.
- Based on the dispersed and non-dispersed particle size distribution curves, we also calculated the geometric mean diameter (GMD) of the particles and, based on their ratio, an aggregate stability index (SI_{GMD}).
- The macroaggregate stability was determined in a similar way to the surfactant samples, with the difference that the measurement was performed on the fraction between 1 and 2 mm.
- The aggregate size distribution (ASD) was determined by dry sieving using sieves with the following mesh sizes: 0.25 mm; 0.5 mm, and 1 mm (Kemper & Rosenau, 1986). I shook 100 g of soil sample at the maximum setting of the sieve shaker (level 10) for five minutes, repeating the process three times in parallel.
- To quantify the degree of classification of structured soils, I defined the U uniformity coefficient (U_{ASD}) as the ratio of diameters corresponding to 60 and 10 percent by weight (d60 and d10) of the cumulative aggregate size distribution curve.

- For saturated hydraulic conductivity measurements (K_{sat}), I prepared artificial soil columns in 100 cm^3 cylinders (5 cm high and 5 cm in diameter) in at least five parallel repetitions, with the same bulk density. The measurements were performed with tap water in an Eijkelkamp closed system permeameter.
- to determine the specific surface area, the water vapor adsorption/desorption isotherms were obtained using the gravimetric method in accordance with the Polish standard PN-Z-19010-1. Soil and biochar mixture samples weighing 4 g were placed in glass vessels and placed above a sulfuric acid solution, which was gradually increased (adsorption step) and then decreased (desorption step) in concentration. We also determined it by nitrogen gas adsorption using a Mircomeritics Flowsorb 2300 II instrument.

Statistical analyses were performed using SPSS 13.0 software. We used an independent samples t-test, one-way analysis of variance, and Duncan's or Tamhane's test based on the homogeneity of the variables, which was determined using Levene's test. The effect of biochar treatment and changes occurring during plant development stages (hereinafter referred to as “time”) on individual soil properties was evaluated using boxplots. The combined effect of treatment and time was also analyzed using variance analysis (ANOVA, general linear model). The relationships between different soil properties were examined using linear regression.

3. Results

3.1. Results of surfactant experiment

By analyzing the surfactant adsorption values, I found that the surfactant amounts required for monomolecular layer coverage of each sample generally differed significantly from sample to sample (Figure 2). The specific CPC quantity was found to be highest in the smectite samples with high clay content (1, 10, and 12) and lowest in the Salföld sand sample.

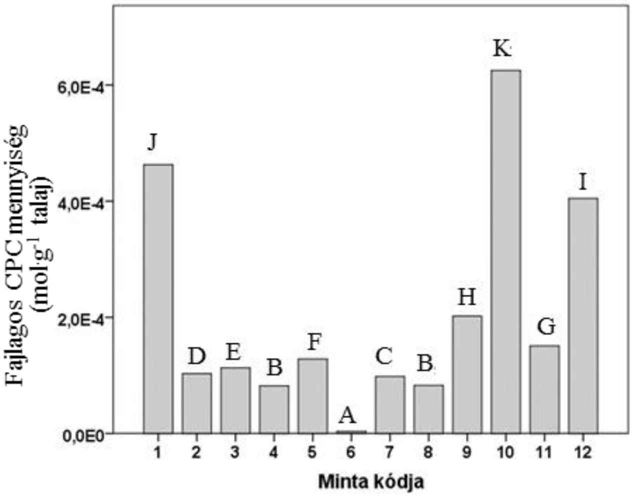

Figure 2: Comparison of specific CPC quantities required to form monomolecuar layer (Different letters indicate significantly different values)
Sample codes: 1) Karcag, meadow solonetz, B horizon;2)Keszthely, brown forest soil (according to Ramann), A horizon; 3)Keszthely, brown forest soil (according to Ramann), B horizon; 4)Várvölgy, brown forest soil with clay illuviation, A horizon; 5)Várvölgy, brown forest soil with clay illuviation, B horizon; 6)Salföld, sand; 7)Magyarszombatfa, pseudogley brown forest soil, B horizon; 8) Paks, loess; 9)Kápolnásnyék, Calcareous chernozem, A horizon; 10)Mád, Bentonite; 11)Zettlitz, Kaolin;12) Kisújszállás, meadow soil, A horizon

Strong stochastic relationships were detected with the cation exchange capacity (CEC) and with the adsorbed water vapour (hy$_1$), which can also be considered as monomolecular. A weaker but significant correlation was found with the soil pH(H_2O) (Table 3).

Table 3. Correlation matrix for the relationship between adsorbed surfactant quantities and soil parameters.

	specific. CPC, (mol$^{\cdot}$g soil^{-1})	Clay + Fe, (%) $^{\#}$	pH (H_2O)	SOM (%)	$CaCO_3$, (%)	SSA (m$^{2\cdot}$g^{-1})	CEC (meq· 100g^{-1})	hy$_1$
specific. CPC, (mol$^{\cdot}$g soil^{-1})	1							
Clay + Fe, % $^{\#}$	0,856**	1						
pH(H_2O)	0,498**	0,413*	1					
Soil organic matter (%)	0,194	0,089	-0,178	1				
$CaCO_3$ (%)	-0,17	-0,239	0,299	0,078	1			
spec. surface area, (m$^{2\cdot}$g^{-1})	0,899**	0,902**	0,206	0,155	-0,239	1		
CEC (meq· 100g^{-1})	0,888**	0,791**	0,347*	0,503**	0,096	0,841**	1	
hy$_1$	0,929**	0,834**	0,233	0,376*	-0,177	0,957**	0,917**	1

Notes: * and ** correlation is significant at the 0,05 and 0,01 level..
Clay and Fe-minerals together

Both treatments (distilled water and surfactant) resulted in a decrease in hygroscopicity (hy1) compared to the control samples (Figure 3). This may be due to structural degradation and the fact that the samples became more hydrophobic under the influence of the surfactant.

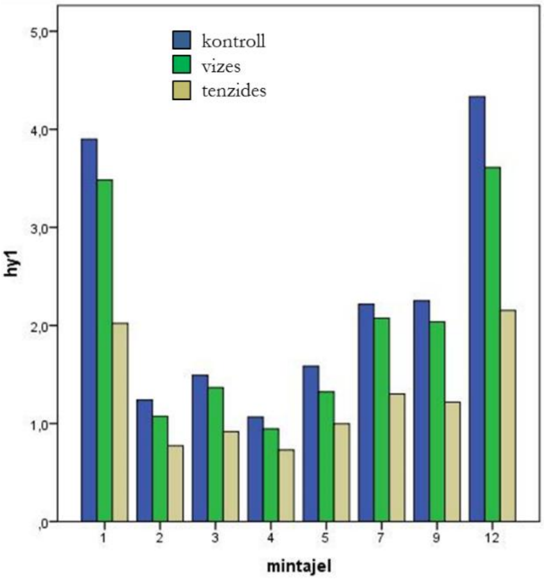

Fig. 3. Hygroscopic water content of the treated samples
Sample codes: 1) Karcag, meadow solonetz, B horizon;2)Keszthely, brown forest soil (according to Ramann), A horizon; 3)Keszthely, brown forest soil (according to Ramann), B horizon; 4)Várvölgy, brown forest soil with clay illuviation, A horizon; 5)Várvölgy, brown forest soil with clay illuviation, B horizon; 7)Magyarszombatfa, pseudogley brown forest soil, B horizon; 9)Kápolnásnyék, Calcareous chernozem, A horizon; Kisújszállás, meadow soil, A horizon

Lower microaggregate stability values occurred in samples with lower cation exchange capacity and in the Karcag solonetz soil, which may indicate that it was already somewhat dispersed. The microaggregate stability of the other samples increased as a result of the hydrophobic effect of CPC. There was no significant difference between the control and distilled water MiAS values. Comparing the water and surfactant results, the role of hydrophobicity in increasing macroaggregate stability is clearly evident in all cases (KUHNT, 1993). The greatest increase was observed in the brown forest soil (according to Ramann) B horizon (sample 3).

Increasing sand content (which has a stronger effect) and increasing organic matter content resulted in an increasing difference (decrease) in the saturated hydraulic conductivity values of the control and surfactant treated soils. This may be related to changes in the bulk density of the soils (e.g., Keszthely_A: control: 1.55; dest. water: 1.60; surfactant: 1.62 g/cm^3), the rearrangement of the pore system (the proportion of gravitational pores increased), and the waterrepellent effect of the surfactant. The oil permeability values were higher than the water permeability values in all cases, except for the quartz sand from Salföld, where there was no significant difference between the two permeability values. Oil permeability (K_o) was estimated using the frequently used Kozeny–Carman equation, based on water permeability (K_w) and the viscosity (μ) and density (ρ) of the fluids. This estimation gave relatively accurate results for sandy samples (e.g., Salföld), but calculated differences of magnitude for those with high clay content (e.g., Karcag). Treatment with surfactant reduced oil conductivity not only compared to samples treated with distilled water, but also compared to untreated soils (Figure 4). The greatest reduction was observed in brown forest soil (according to Ramann) B horizon, which has the highest clay content and the lowest sand content. The organic liquid conductivity of the samples is demonstrably influenced by both the quality of the soil sample (clay content, structure, etc.) and the pretreatment applied (distilled water or surfactant).

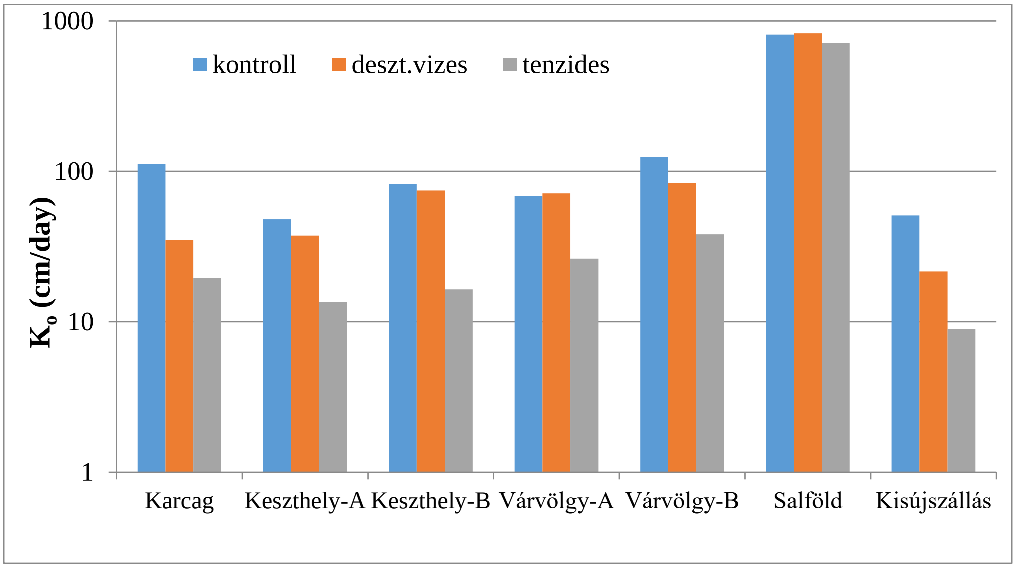

Figure 4: Saturated oil conductivity of the samples

We also performed linear regression analysis, selecting the predictor variables based on backward elimination (Table 4). Air permeability was included among the variables for both fluids and both treatments, including the surfactant treatments.

Table 4: The dependence of fluid conduction on soil properties (backward elimination)

Treatment	Hydraulic conductivity	R^2	Oil conductivity	R^2
controll	clay content bulk density log_K_air	0.953	clay content log_K_air	0.935
dist.water	log_K_air	0.883	clay content bulk density log_K_air	0.529
surfactant	clay content sand content bulk density log_K_air	0.960	clay content bulk density log_K_air	0.528

3.2. Results of biochar experiment

In general, we found that the amount of time elapsed and the concentration of biochar together determine the extent of changes in various soil properties. When examining the distribution of aggregates, the amount of particles smaller than 0.25 mm decreased in all samples (both control and treated) by week 12. At the same time, the highest proportion of aggregates between 1 and 2 mm was present in the control sample at week 12; as a result of the biochar treatment, their proportion increased in all treatments by the end of the experiment. In our samples, both microaggregate stability (MiaAS) and macroaggregate stability values increased with the addition of biochar compared to the control (Figure 5). However, due to environmental factors such as regular irrigation, we also observed a decrease in MaAS over time by the end of the experiment. The stability index was calculated as the ratio of the average geometric diameters based on the dispersed and non-dispersed particle size distribution curves. Its values were similar to those for microaggregate stability. The highest value was obtained with 5% biochar treatment in all cases studied. We assume that biochar promotes the permanent adhesion of aggregates (at both the micro- and macro-aggregate levels), not only through carbon bonds, but also as a result of increased root development and microbiological activity, and possibly even mycorrhization (ALBURQUERQUE al., 2013).

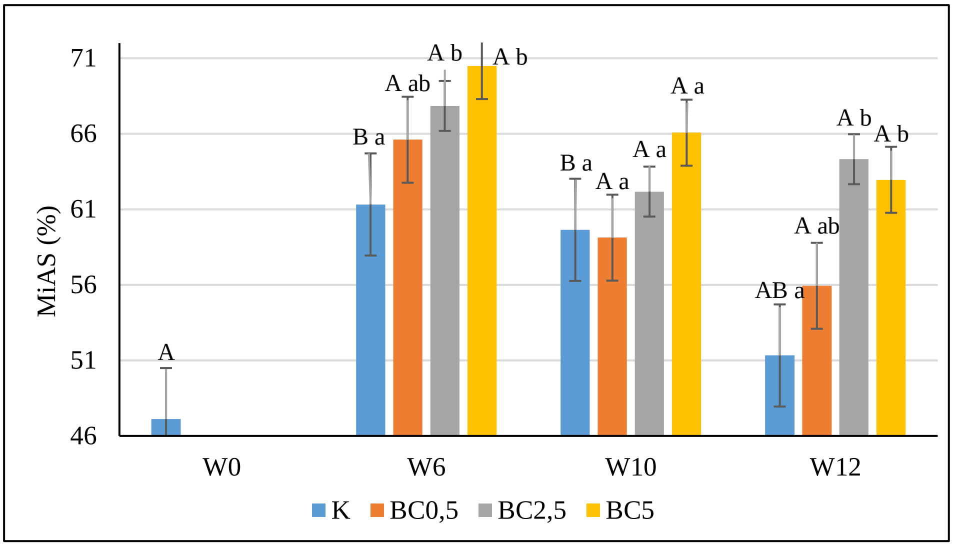

Figure 5: Changes in microaggregate stability (vertical axis) by treatment at different time points (horizontal axis). C: control; BC0.5, BC2.5, and BC5: treated with 0.5, 2.5, and 5% biochar; W6, W10, and W12: sampling at 6, 10, and 12 weeks. Letters of the same type do not differ significantly ($p < 0.05$); lowercase letters were used for comparisons between different biochar treatments, while uppercase letters were used for comparisons over time.

The biochar treatment significantly increased the size of the external and internal surfaces, as illustrated by the Sík hygroscopicity results, although there was no significant difference at the largest dose over the 12 weeks.

Due to the low density of biochar, the bulk density gradually decreased with the addition of increasing amounts of biochar, but the slight compacting effect of precipitation and irrigation cannot be completely ruled out. Saturated hydraulic conductivity values increased, except during the initial period (until the plants reached full height) (Figure 5). The higher Ksat values may have been due to the increased porosity resulting from the biochar treatment. The U gradation values calculated from the aggregate distribution correlated well with both bulk density and saturated hydraulic conductivity.

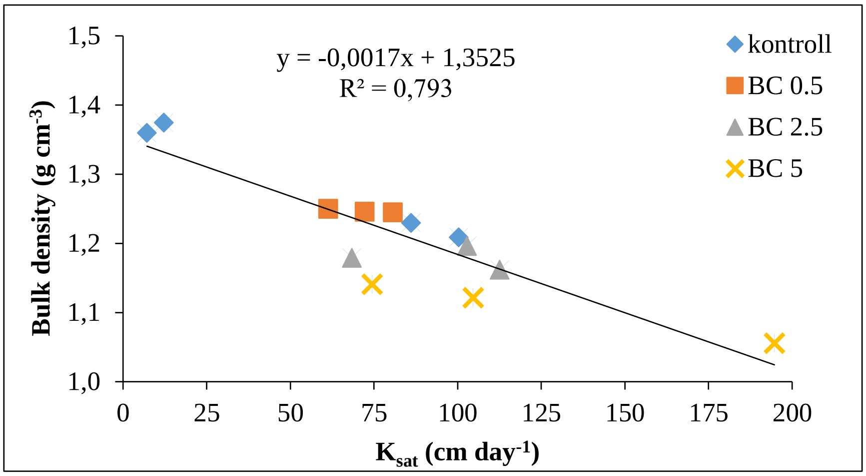

Figure 6: Relationship between saturated hydraulic conductivity (horizontal axis) and bulk density (vertical axis).
K: control; BC0.5, BC2.5, and BC5: treated with 0.5%, 2.5%, and 5% biochar, respectively.

We used ANOVA to examine the effect of biochar treatment, time, and the combined effect of these two factors on the measured soil properties (Table 5). The two factors (treatment and time) had a mostly significant effect on the soil properties examined. Since MaAS showed varying values during the treatment of the culture vessels due to the wetting and drying associated with irrigation, we did not find a significant effect of the Time factor on this parameter. The hy1 value showed a tendency to increase due to the prolonged effect of irrigation. In the case of saturated hydraulic conductivity, bulk density, and degree of gradation, we observed only a combined effect of the two factors (Treatment × Time).

Table 5: Effect of biochar treatment, time, and the combination of the two on the soil properties examined. Overall results of the ANOVA test

Factors	Soil property examined						
	MaAS	MiAS	SI_{GMD}	K_{sat}	ρ_b	hy_1	U_{ASD}
	p						
Treatment	<0,001**	0,002**	<0,001**	<0,001**	<0,001**	0,148	0,002*
Time	0,111	0,012*	<0,001**	<0,001**	<0,001**	<0,001**	<0,001**
Treatment × Time	0,057	0,736	0,117	<0,001**	<0,001**	0,096	0,001*

* significant difference $p < 0.05$ and ** $p < 0.01$.

Significant changes in specific surface area (both SSAwv measured by water vapor adsorption and SSA_N2 measured by nitrogen) were observed over time in the biochar-treated samples compared to the control soil. These observed changes can be attributed to the oxidation of the biochar surface during the experiment, which leads to the formation of polar functional groups (mainly hydroxyl, phenol, and carboxyl groups). In most treatments, an increase in water vapor adsorption capacity was observed at the end of the experiment compared to the initial soil data (W0), with the highest values obtained for BC5.0 in all phenological phases studied. This was also confirmed by specific surface area tests using nitrogen gas, although the differences were not statistically significant.

4. Conclusions and recommendations

4.1 Effects of surfactant treatment on the physical properties of soil

We found that the amounts of surfactant required to cover each sample with a monomolecular layer generally differed significantly between samples. This CPC amount was found to be highest in samples with high clay content and smectite, and lowest in quartz sand samples. The amount of surfactant was closely related to the hygroscopicity (hy_1), clay content, specific surface area (BET surface area), and cation exchange capacity (CEC value) of the soil—soil properties that generally influence adsorption processes (KUHNT, 1993; PATZKÓ & DÉKÁNY, 1996). According to the regression equations describing CPC adsorption, five soil parameters determine the specific amount of surfactant: clay content, organic matter content, lime content, chemical effect, and specific surface area.

During the treatment of the samples with surfactant, I observed structural degradation, so I performed the treatment with distilled water only, without adding surfactant. Thus, I worked with a control sample, a sample treated with distilled water, and a sample treated with surfactant.

The surfactant caused changes in the physical parameters of the soil samples. Most of the changes were presumably caused by the fact that the surface of the soil samples became more hydrophobic due to the surfactant. This was also confirmed by the contact angle measurement results of CSATÁRI al. (2013) on the soil samples examined in their paper: after surfactant surface modification, the wettability of the soils decreased. The hygroscopicity of the soil samples decreased in both treatments (distilled water and surfactant). This may be due to structural degradation, the possibility that part of the colloidal fraction was washed out during the treatment, and the fact that the samples became more hydrophobic due to the surfactant. The greatest change occurred in the case of the high-clay-content meadow solonetz and meadow samples. The cationic surfactant bound to the surface of clay minerals and humic substances or other negatively charged surfaces occupied some of the binding sites suitable for water molecule binding. Macroaggregate stability was shown to increase under the influence of the surfactant as a result of the aforementioned increase in hydrophobicity.

The saturated oil conductivity of the control samples was higher than their saturated water conductivity. After some modifications, we adapted the Eijkelkamp permeameter to determine the saturated oil conductivity of soils. The use of a closed-system permeameter is a more environmentally friendly and cost-effective solution, especially in the case of surfactant treatments. The surfactant reduced both hydraulic and oil permeability, which is beneficial in remediation cases where the goal is to prevent the spread of oil pollution due to reduced mobility (RASHID et al., 2004). We estimated oil conductivity using the commonly used Kozeny–Carman equation (based on known hydraulic conductivity and the density and viscosity of water and the liquid I used in my model (DUNASOL 180/220)), but we found significant differences between the measured and estimated values for several soils. In contrast, the air permeability of the samples is well suited for estimating oil permeability (IVERSEN et al., 2003; MAKÓ et al., 2009).

4.2 Effect of biochar treatment on certain physical properties of soil

In general, we found that the amount of time elapsed and the concentration of biochar together determine the extent of changes in various soil properties.
Biochar increased not only the formation of microaggregates, but also their stability, even at low doses (0.5%). Traditional sedimentation MiAS tests are not suitable for soils with a specific weight lower than water, and the laser diffraction method (LDM) provided the methodological possibility for this (HOREL et al., 2019). By the end of the experiment, in week 12, we observed an increase in the macroaggregate stability of the soils, not only in the treated samples but also in the control samples. In the control samples, root growth and the glomalin produced may have contributed to the improvement in structure. However, increasing doses of biochar did not result in proportionally greater growth.

The biochar treatment resulted in a significant increase in the size of the external and internal surfaces, as illustrated by the Sík hygroscopicity results. Compared to the control, the greatest increase was observed at the 5% dose. The most noticeable change over time occurred with the 0.5% treatment, although we also observed a slight increase in surface area in the control samples over time. The larger surface area may have resulted in greater water and nutrient retention, which may also have contributed to the higher yield of peppers (POKOVAI et al., 2020). With the decrease in bulk density, the saturated water conductivity increased, indicating more favorable air and water management. We found a close correlation between the two parameters studied. It was also confirmed that only water conductivity, bulk density, and degree of gradation were significantly affected by treatment, time, and the combination of the two. The two factors (treatment and time) had a mostly significant effect on the soil properties examined. In the case of macroaggregate stability, the time factor is not significant due to the wetting and drying caused by irrigation. Water vapor adsorption tests showed that the amount of bound water increased with increasing biochar dosage. Nitrogen adsorption tests also showed an increasing specific surface area with increasing biochar dosage.

The role of biochar is multifaceted, and the studies presented here have only shed light on a small part of it (related to soil physics). All of this suggests that biochar is a versatile additive that promotes soil and plant health by improving the water management properties of the soil. Due to these and other positive effects, research in this area continues to be the focus of interest.

New scientific results

1) We investigated the adsorption of hexadecylpyridinium chloride (CPC), a cationic surfactant, on various soils, sediments, and mineral powders. I found that the specific amounts of surfactant required for monomolecular layer coverage of each sample generally differed significantly from sample to sample. The specific amount of CPC was found to be highest in the case of the smectite sample with a high clay content and lowest in the case of the quartz sand sample. The specific surfactant quantity was closely correlated with the hygroscopicity (hy1), clay content, specific surface area (BET specific surface area), and cation exchange capacity (T value) of the samples. Statistical analyses also confirmed the effect of organic matter content, lime, and pH—which influence the formation of external and internal soil surfaces—on monomolecular surfactant adsorption.

2) The surfactant caused changes in the soil physical parameters. Most of the changes were related to the fact that the surfactant made the samples more hydrophobic. The hygroscopicity of the soil samples decreased in both treatments (distilled water and surfactant). Macroaggregate stability was shown to increase under the influence of the surfactant, as a result of the aforementioned increase in hydrophobicity. The saturated oil conductivity of the control samples was higher than their saturated water conductivity. Under the influence of the surfactant, both water and oil conductivity decreased, which may facilitate a remediation process. Air permeability can also be used to estimate the oil permeability of soils in the case of samples treated with surfactant.

3) In general, we found that the elapsed time and the concentration of biochar together determine the extent of changes in various soil properties. On the one hand, biochar promotes the permanent cohesion of aggregates (at both the micro- and macro-aggregate levels), not only through carbon bonds, but also as a result of increased root development and microbiological activity, and even through mycorrhization, thus contributing to structural stabilization. Biochar increased the formation and stability of microaggregates, even at low doses (0.5%).

4) The biochar treatment significantly increased the size of the external and internal surfaces, which was confirmed by water vapor adsorption and nitrogen

gas specific surface area tests. The larger surface area results in greater water and nutrient retention.

5) It was proven that only the "treatment," "time," and the combination of the two had a significant effect on water conductivity, bulk density, and degree of gradation. The "treatment" and "time" had a mostly significant effect on the other soil properties.

6) During the experiments, I successfully applied several methodological innovations:

a) After modification, I was the first to use a closed-system permeameter after modifications to measure the water and oil conductivity of soils treated with surfactants. This solution made it possible to conduct the experiments in a material-efficient and environmentally friendly manner.

b) I was the first to measure the air permeability of soil treated with surfactants using a PL300 instrument under laboratory conditions in order to estimate the oil permeability of the same soils (using a faster and more environmentally friendly method) and possibly replace oil permeability measurements.

c) I first used the laser diffraction measurement method to determine the microaggregate stability of soils treated with biochar, replacing sedimentation methods.

Major publications related to the thesis

Scientific articles in foreign language in peer-reviewed journals with impact factor

1. Horel, Á., **Barna, Gy**., Makó, A. 2019. Soil physical properties affected by biochar addition at different plant phenological phases I. International Agrophysics. 33:2. 255-262. (Q2)
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Scientific articles in Hungarian language in peer-reviewed journals and book chapters

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