Physico-chemical, Agrochemical and Eco-chemical Characteristics of Biochar-treated Fluvisol

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Abstract. Recently there has been considerable interest in the use of biochar to improve soil quality and mitigate climate change. The aim of this study was to investigate the effect of two types of biochar on physico-chemical, agro-chemical and eco-chemical characteristics of a Fluvisol. The study site is the experimental field of Tsalapitsa village (Plovdiv). Wheat was cultivated with maize in crop rotation. The following treatments were included in the study: control with no biochar addition, biochar applied in 2 t.ha⁻¹ in 2016, produced by pyrolysis of rice straw; biochar applied in 3 t.ha⁻¹ in 2017, obtained by pyrolysis of oak barks at 500 °C. Biochar effect on the pH, EC, CEC and OM was negligible. The concentrations of the studied anions in water and $0.01M$ $CaCl_2$ extracts do not exceed the maximum permissible levels (MPCL) for drinking water except for nitrates in biochar (2017) in both extracts, where biochar from oak barks was applied. Dissolved organic carbon (DOC) content in water and $0.01M$ $CaCl_2$ decreased in variants with BC addition compared to the controls, most likely due to the ability of biochar to sorb DOC. Manganese and zinc in the studied soils are represented by free aqua-ions (M^{2+}), especially high is the percentage of free manganese ions (96.3%), while for aluminium and iron, fulvic complexes are the predominant species, but no biochar effect on metal speciation was observed.

Key words: biochar, physico-chemical properties; soil solution composition, geochemical modeling, DOC.

Introduction

Intensification of agricultural production and anthropogenic impact are the cause for significant deterioration of soil fertility. The need to implement effective measures to improve soil quality and mitigate climate change requires the use of soil ameliorants (LAL, 2004). Recently there has been considerable interest in the use of biochar (MIKOVA, 2014; LEHMANN & JOSEPH 2009; OLIVEIRA *et al.*, 2017). Studies of (ATKINSON *et al.*, 2010; SUKARTONO *et al.*, 2011; LIU *et al.* 2012; OUYANG *et al.*, 2013; KHAN *et al.*, 2017, WU *et al.*, 2018) have shown that biochar increases water retention in soils, improves their physical properties, reduces leaching and export of nutrients, increases cation exchange capacity, carbon sequestration, immobilises soil pollutants, increases yields, reduces gas emissions in agriculture, etc.

Depending on the feedstock materials and the pyrolysis conditions, biochar acquires different physical and chemical characteristics that can modify the physical and chemical properties of soil. The large surface area of biochar increases ion exchange capacity and nutrient sorption (LEHMANN & JOSEPH, 2009). Application of

biochar modifies the composition of dissolved organic matter in soil (SMEBYE *et al.,* 2016) which directly or indirectly controls the mobility of metal ions and their bioaccumulation (LI *et al.,* 2018). All that makes biochar an efficient, cost-effective and environmentally friendly material for application and management of agroecosystems in the future (VERHEIJEN *et al.,* 2010).

There is insufficient information on the chemical processes which control the effect of biochar and its adsorption potential to retain and immobilize nutrients in soil solution, as well as the mechanisms of interaction with solution components, therefore development of research in this direction is necessary.

The aim of this study was to investigate the effect of two types of biochar on physico- chemical, agro-chemical and eco-chemical characteristics of a Fluvisol upon treatment with biochar.

Materials and Methods

The study site is the experimental field of Tsalapitsa Village, Plovdiv District, ($24^0$35'E; $42^0$14'N), located 4 km off the left bank of the Maritsa River at an altitude of 160 m. The topography is flat, with a slight slope to the river (1 - 2 °). The soil type is Alluvial-meadow soil (Fluvisol). The surface A^Ip Horizon (0 – 20 cm) is brown (10YR5/3/) with sandy loam texture.

The soil samples from a field experiment with wheat "Sadovo 1" cultivar were analyzed. The N_{100} P_{120} K_{100} fertilization was applied: N in the form of urea -100 kg.ha^{-1}, P as triple superphosphate -120 kg.ha^{-1} and K as potassium sulphate -100 kg.ha^{-1}. The P and K fertilizers were introduced prior to the main soil tillage in autumn and N fertilizer before the pre-sowing treatment in spring (March). The biochar was applied before sowing of the crop. The following treatments were included in the study: 1) Control, with no biochar addition; 2) Biochar applied in 2 t.ha^{-1} in 2016, produced by pyrolysis of rice straw at 500 °C; 3) Biochar applied in 3 t.ha^{-1} in 2017, obtained by pyrolysis of oak bark at 500 °C (pH = 7.9, CEC = 10.9 cmol.kg^{-1}, C 29.8%). Pooled soil samples were taken to a depth at 0 - 10 cm and 10 - 20 cm, using a grid Δ 2 m, ~ 40 m^2 with a 3 cm wide and 25 cm long soil sampler. Soil samples were taken in three replications in spring. Lack of water repellency was noticed (water drop penetration time, WDPT was 1 - 5 s) according to the scale of DE BANO (1981).

Cation exchange capacity (CEC) was assessed as sum of titratable acidity (pH 8.2) and extractable Ca, by saturation with K malate at pH 8.2 (GANEV & ARSOVA, 1980). Electrical conductivity was determined in soil: water (1: 5), ISO 11265 : 2002. Soil pH/Eh were measured in a soil: water slurry of 1: 2.5. Total organic carbon (TOC) was determined by oxidation with $K_2Cr_2O_7$/ H_2SO_4 and fractionated TOC into humic organic carbon (HOC) and fulvic organic carbon (FOC) upon treatment with 0.1M $Na_4P_2O_7$ and 0.1M NaOH by the methods of KONONOVA (1966). Mineral nitrogen was assessed by the method of Kjeldahl (after PAGE *et al.,* 1982) and available P and K by the method of IVANOV (1984).

Soluble heavy metals in soils were determined by the following methods: 0.01M CaCl$_2$ extractable forms in soil: sollution ratio (1: 5) and shaking for 2 hours (VAN RANST *et al.,* 1999); water soluble forms in soil:water ratio 1: 5, by shaking for 1 hour, centrifuging and filtering (0.45 μm acetate cellulose filter), after KATOH *et al.,* (2012). Anions in the soil solution (Cl$^-$, NO$_3^-$, SO$_4^{2-}$, phosphates, including dissolved organic carbon (DOC) were analysed with Spectroquant tests, Merck Millipore (PHARO 100). The ions speciation in soil solution was performed by Visual Minteq V. 3.1.

Statistical processing of the data was performed using One-way Anova from the statistical program Statgraphics Centurion 18.

Results and Discussion
Physicochemical characteristics
According to the physico-chemical analysis of the Fluvisol in the Tsalapitsa

experimental field, it can be classified as slightly acidic (pH 5.8 - 6.1), Table 1. The pH values of the control soils are very similar to those of the variants with biochar addition. The soil acidity in the biochar treated variants increased significantly ($p \leq 0.05$) by 0.2 - 0.4 units in both layers. Similar results for increasing soil pH with biochar applied, produced by rice husks and mixed wood residues have been observed (LAIRD *et al.,* 2010). The decrease of pH in the top layer of the soil compared to the deeper soil layer is also significant in all the variants and reaches 0.2 - 0.5 pH units, which is related to the long-term nitrogen fertilization. There is a low decrease of the electrical conductivity, ranging from 0.04 - 0.01 ms.cm^{-1} in the upper soil layer of biochar treated soil compared to the control. In a field experiment, JONES *et al,* (2012) indicate that the electrical conductivity of the soil (46 to 43 µS.cm^{-1}) was not affected significantly after a 3-year addition of biochar.The level of the colloidal activity based on the cation-exchange capacity (CEC 15.4 cmol.kg-1) in the control variants is defined as weak. There is a slight decrease of exchange capacity in the variants with biochar addition. Total acidity (full hydrolytic acidity at pH 8.2) is in the range of 4.0 - 4.7 cmol.kg-1 in the control variants while in the variants with biochar addition slightly but significantly decreases (exch.H 3.2 - 3.6).The total carbon content in the studied soil ranges between 0.89 - 0.92% in controls without biochar (Table 2). It is characterized by low humus content (1.5%) of the humic type (Cx/Cf 2.80) according to the classification of Orlov and Grishina (ORLOV, 1985). The humic acids are 100% bound to Ca and Mg ions. Treating the soil with biochar does not significantly change the total carbon content. There is a slight decrease in organic carbon in biochar addition in depth. The humic type of humus has not changed (Ch/Cf > 2.0) in

biochar addition variants. At the same time in all variants the humic acids are bound with alkaline ions, which is a precondition for the more favorable hydro-physical properties of the soil.

The agrochemical analysis showed that the mineral nitrogen content in the control soils in both layers ranges between 10.9 - 21.9 mg.kg^{-1} (Fig. 1). In the soil samples taken after soil treatment with biochar, mineral nitrogen content in the upper layer is higher than the control. Especially in variant BC_{2017} in the layer 0-10 cm a significant amount of mineral nitrogen is formed. In the soil treated with BC_{2016}, low nitrogen level is observed, indicating that the effect of the applied biochar is reduced over time. The data obtained for mobile phosphorus did not show large changes compared to the control variant. It can be seen (Fig. 1) that the applied biochar has an effect on the available K, increasing its soil storage by variants.

Anions contents in the soil solution

CHENG *et al,.* (2008); MAO *et al.,*(2012); CUI *et al.,* (2016); Li *et al.,* (2017) found that, depending on the source materials used and the pyrolysis conditions of plant biomass, biochars with different surface chemical and functional groups are obtained, which specifically interact with ions in the soil solution. The content of Cl$^-$ anions in the soil solution varies within a narrow range of 7.5 - 24 mg.l^{-1} (Fig. 2). It was found that in the variants treated with biochar the chloride concentration was lower than in the controls. It is known that chloride ions maintain nearly constant concentration in the arable soils which varies in narrow range. Chlorides are weakly adsorbed by the soil adsorption complex and have a transitional behavior in soil, which is assessed by the higher levels noted at the lower depths (Fig. 2). In a study conducted by NOVAIS *et al.* (2018) with contaminated wastewater, biochar was significantly less successful in adsorbing chloride and nitrate anions.

Table 1. Physico-chemical characteristics of the soil from the study site.

Variants depth, cm	pH/H₂O	EC ms.cm⁻¹	CEC	exch.H₈,₂	exch.Ca	exch.Mg	V %
				cmol.kg⁻¹			
Control 0-10	5.8±0.1	0.09±0.02	15.4±0.2	4.7±0.2	9.0±0.1	1.8±0	69.7±1.0
Control 10-20	6.1±0.2	0.06±0.02	15.1±0.1	4.0±0.1	9.2±0.2	1.9±0.1	73.5±0.6
BC₂₀₁₆ 0-10	6.2±0.1	0.05±0.01	14.9±0.6	3.2±0.1	9.2±0.1	1.9±0.1	78.3±0.4
BC₂₀₁₆ 10-20	6.4±0	0.04±0.01	14.8±0.1	3.1±0.1	9.4±0.1	1.9±0	79.3±0.4
BC₂₀₁₇ 0-10	6.0±0	0.08±0.01	14.9±0.1	3.6±0.1	9.0±0.1	1.9±0.1	76.3±0.4
BC₂₀₁₇ 10-20	6.3±0.6	0.06±0.01	15.0±0.1	3.6±0.1	9.3±0.1	1.9±0.1	75.8±0
LSD p≤0.05	0.2	0.02	0.2	0.2	0.2	0.1	1.0

Table 2. Content and composition of soil organic matter in the control and biochar-treated soil. *Designation:* a - % of soil sample, b - % of total C, humic to fulvic acids ratio (Ch/Cf).

| Soil sample, depth, cm	Total C %	SOM %	Organic C % Extacted with $0.1M\ Na_4P_2O_7 + 0.1M\ NaOH$			Ch/Cf
			Total	Humic acid	Fulvic acid	
Control 0-10	0.89	1.53	0.19[a] / 21.35[b]	0.14 / 15.73	0.05 / 5.62	2.80
Control 10-20	0.92	1.58	0.20 / 21.74	0.16 / 17.39	0.04 / 4.35	4.00
BC₂₀₁₆ 0-10	1.10	1.89	0.21 / 19.09	0.16 / 0.21	0.05 / 4.55	3.20
BC₂₀₁₆ 10-20	0.82	1.41	0.19 / 23.17	0.19 / 23.17	0.00	-
BC₂₀₁₇ 0-10	0.99	1.70	0.21 / 21.21	0.18 / 18.18	0.03 / 3.03	6.00
BC₂₀₁₇ 10-20	0.89	1.53	0.18 / 20.22	0.14 / 15.73	0.04 / 4.49	3.50
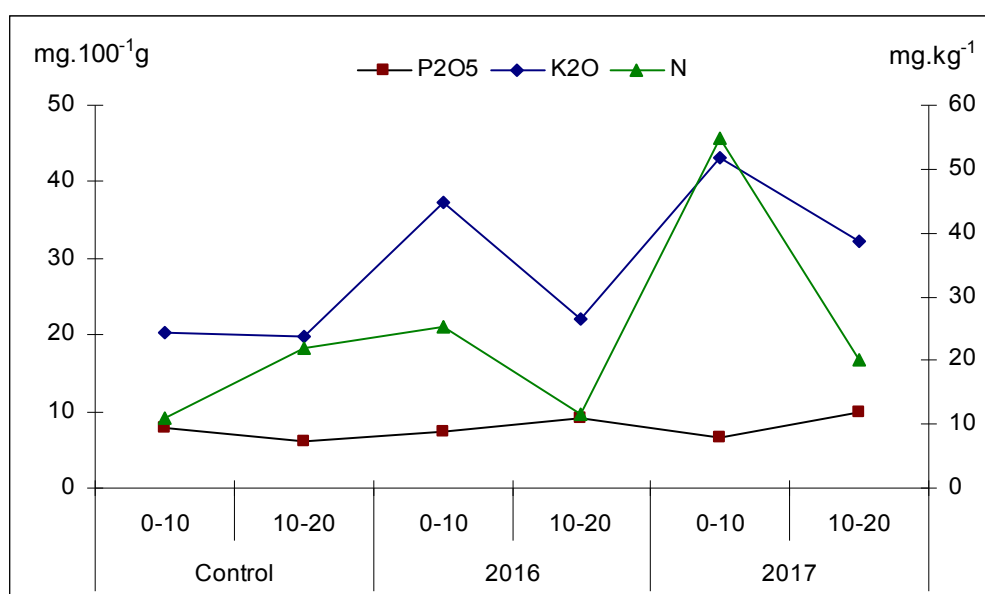
Fig. 1. Content of mineral nitrogen (mg.kg⁻¹),
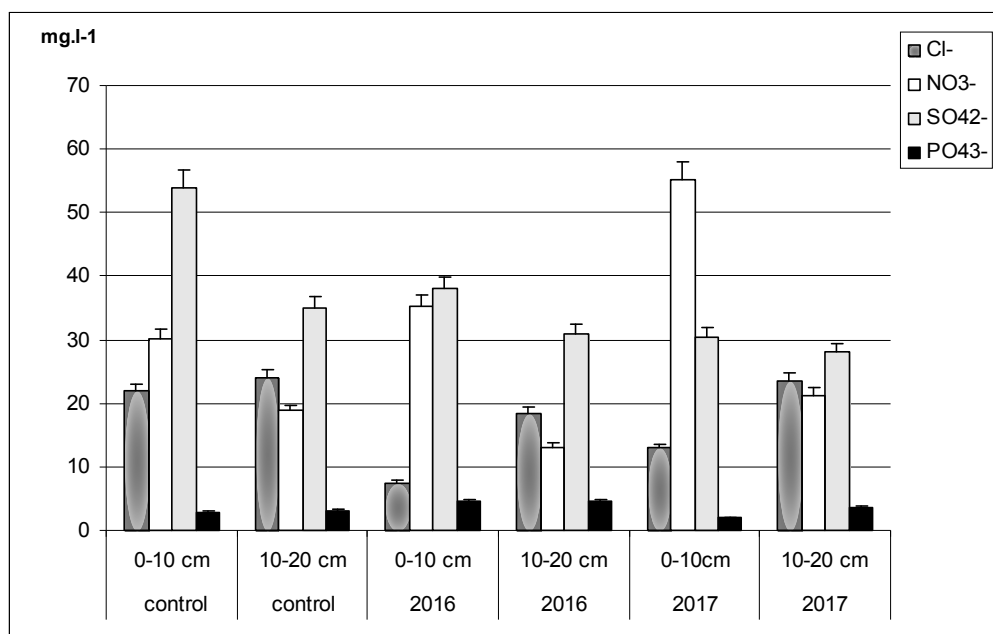available phosphorus and potassium (mg.100⁻¹g) in the Fluvisol.

Fig. 2. Content of chlorides, nitrates, sulphates and phosphates (mg.l^{-1})
in biochar-treated Fluvisol.

The loss of nitrates through the soil profile and their reaching groundwater level, as well as eutrophication of surface waters is a major concern of anthropogenic soils and agricultural production. The application of significant amount of nitrogen and other biogenic elements is the reason for accumulation of residual mineral nitrogen in the soil profile after cultivation of crops, which is a potential source of deterioration of the quality of solid and liquid phase of soil (Stoicheva *et al.,* 2003; Bordoloi *et al.,* 2013; Wang *et al.,* 2013; Simeonova *et al.,* 2017). The most vulnerable to nitrate loadings are territories where there is a combination of soils with light texture (such as the Alluvial-meadow soils, Fluvisols) and low water holding capacity, shallow aquifers and intensive farming (often vegetable production), leading to high levels of nitrates in the liquid phase, exceeding MPCL 50 mg.l^{-1} as a the standard for drinking water. Many studies (Laird *et al.,* 2010; Knowles *et al.,* 2011; Libutti *et al.,*

2016; Borchard *et al.,* 2019) show that addition of biochar to arable soils can reduce nitrate and phosphate leaching. This could be explained with an increase in the anion exchange capacity of biochar, although the mechanisms are not yet well studied. Addition of biochar in soils also improves the biological fixation of nitrogen from nitrogen-fixing bacteria (Rondon *et al.,* 2007). In other studies (Yao *et al.,* 2012; Hollister *et al.,* 2013; Borchard *et al.,* 2019) limited or no ability of biochar to retain nitrates from the soil solution was found.

In our study, the nitrate content in the soil solution ranges from 11.8 to 55.2 mg.l^{-1} (Fig.2). The data indicate that the concentration of nitrates in solution in the variants with biochar is higher for the 0 - 10 cm layer compared to the controls, while in the lower soil layers (10 - 20 cm) they decrease. The nitrate values do not exceed the MPCL (50 mg.l^{-1}) in the standard for drinking water with one exception for the 0 - 10 cm layer of 55.2 mg.l^{-1} in 2017 biochar-treated soil.

The increase of solution nitrates in the BC_{2016} and BC_{2017} variants coincides with the higher levels of mineral nitrogen (Fig. 1) and might be due to the fertilizer applied.

It is known that phosphates can be prevented from leaching by chemisorption, as a result of which difficult or poorly soluble compounds are formed, in contrast to soluble nitrates. The phosphate content of the soil solution is low and the variation is slight from 2.05 to 4.7 mg.l^{-1} (Fig. 2). LEHMANN & JOSEPH (2009) reported that soil treatment with biochar leads to higher capacity to sorb phosphorus compared to soil where only manure has been applied. According to a number of authors (CHINTALA *et al.*, 2014; XU *et al.*, 2014; TAKAYA *et al.*, 2016; BORNØ *et al.*, 2018) the sorption efficiency of biochar is determined by different mechanisms which control the phosphorus sorption capacity in soil, and hence the availability of P. As they themselves noticed, depending on the soil type and pH, the calcium and magnesium concentrations in the soil solution, the used plant material and other factors, sorption varies. In our study in the variants with BC_{2016} addition the phosphate content in solution is slightly higher compared to BC_{2017} variants in which lower than control concentrations were analyzed in the surface layers (Fig. 2).

For the sulphates, the trends are the following: the concentration in the solution ranges from 28.0 to 54.0 mg.l^{-1} and higher concentration in the control variants are observed (Fig. 2). A decrease of sulphate content in both layers in the variants with biochar is found, confirming a sorption effect for the biochar.

Anion contents in the 0.01M CaCl$_2$ soil extracts

The nitrate content in the 0.01M CaCl$_2$ solution varies significantly (Fig. 3) in biochar variants (from 3.4 to 87.9 mg.l^{-1}). In the control variants the variation is in narrower limits (17.7 - 26.8 mg.l^{-1}). In all the variants a decrease in NO$_3^-$ concentrations in the lower depth was found. In BC_{2017} treated soil similarly to the H$_2$O extracts, the concentration of nitrates is also higher in the 0 - 10 cm layer, exceeding the maximum permissible contaminant level of 50 mg.l^{-1} for drinking water. As mentioned above, the introduction of nitrogen fertilizers in spring months possibly coincide with a period of drought, resulting in higher nitrogen content in the surface soil layer. For the sulfates smaller variation in the range of 41 - 52 mg.l^{-1}, was observed and the concentration differences between the controls and the biochar variants are insignificant (Fig. 3). The data shows slightly higher sulphate content of the biochar variants which may be related with the effect of the chloride ion on displacing sulphate.

For the phosphates, lower values for the CaCl$_2$ extracts, than the H$_2$O extracts were obtained, which might be due to the immobilizing effect of Ca ions on phosphate desorbed. In respect to the phosphate anions in the solution of 0.01M CaCl$_2$, the highest content is found in the control for 0 - 10 cm soil layer – 6.5 mg.l^{-1} and about four times lower content in the biochar variants (1.5 - 1.6 mg.l^{-1}), which proves the effectiveness of biochar towards phosphate adsorption displayed in this extractant. Significant differences in the CEC and pH between the biochar-treated and the control variants were not observed, however studies of (KUZYAKOV *et al.,* 2009; MAO *et al.,* 2012) have shown that although the biochar is relatively stable, it can be partially mineralized by biological and chemical reactions in the soil, resulting in change of its surface characteristics and functional groups, making it more difficult to study the effects of adding it.

Dissolved organic carbon in water and 0.01M CaCl$_2$ extracts

The data show (Fig. 4) that in the control variants the concentrations of dissolved organic carbon (DOC) in water

and 0.01M CaCl$_2$ extracts (13.5 mg.l^{-1} and 15.6 mg.l^{-1}) are higher than those of biochar treated soil (5.2 - 12 mg.l^{-1}). With respect to both extracts, the DOC concentration of the biochar variants is higher in CaCl$_2$ extraction, which can be attributed to the capacity of chloride to desorb specifically adsorbed organic ligands.

Studies of DUME *et al.,* (2015) show that biochar produced by different raw materials at low or high temperatures leads to an increase in the dissolved organic matter in soil. When biochar is mixed in soil, it causes changes in soil properties (pH and EC) that affect the potential release of DOC, for instance the natural content of DOC from biochar will directly increase the total stock of organic matter in the soil. SMEBYE *et al.,* (2016) found higher DOC values in soil mixtures (containing 10% biochar) than the sum of the dissolved organic carbon values in the soil and biochar. In our experiment the addition of biochar leads to a decrease in DOC in the soil solution. This is consistent with the study of (MUKHERJEE *et al.,* 2011), which established a decreasing in DOC in a similar experiment using biochar, suggesting that this was due to the ability of biochar to sorb DOC. Our results are also similar with studies of the (JONES *et al,.* 2012), which added 0.25 and 50 t.ha^{-1} biochar in three long field experiments and cultivated corn (in the first year) and grass (in the second and third). They found that biochar had no effect on the dissolved organic matter. On the other hand, biochar changes the composition of soil dissolved organic matter by adsorbing into its porous structures (KASOZI *et al.,* 2010).

Metal speciation and geochemical modeling in 0.01 MCaCl$_2$

Geochemical modelling *Visual Minteq* (Tables 3 and 4) was carried out on the speciation interactions in the soil solution of biochar-treated Fluvisol and the control soil without biochar addition.

In the surface layer (0 - 10 cm) of the control soil the following trends in the solution of 0.01M CaCl$_2$ were established. Aluminum cations are presented ~10% as aqua non-complexed free ions and other charged hydroxy-complexes, but the largest share (~76%) belonged to organic fulvic - aluminum complexes and hydroxy-fulvic complexes at pH~ 6. Manganese and zinc are represented mainly by free uncomplexed ions (M^{2+}), especially high is the percentage of free manganese ions (96.3%).

The following trends in variants with BC$_{2016}$ addition are observed. The free and hydroxy complexes of Al are ~ 12.5%, 84% are fulvic complexes, for Mn - 98% are free aqua complexes, and for Zn 91% are free ions. In the BC$_{2017}$ treated soil the share of free and hydroxy complexes of aluminium is increased, ~ 25%, ~70% are aluminium and hydroxy-complexes of aluminium. Manganese (98%) and zinc (93%) are represented as free ions.

Chemical speciation of aluminium in sub-surface layer indicated that 33.5% are free and hydroxy-complexes. For Zn and Mn, over 90% of the species in solutions are represented by the free aqua complexes which are most reactive and bioavailable.

Metal speciation (geochemical modeling) in H$_2$O

Geochemical modeling of the ionic forms in the soil solution (water) was also performed. The obtained specific interactions are presented in the example in Table 4. When evaluating the speciation in water and 0.01M CaCl$_2$, changes in the ratios between different ionic forms were outlined. Dissolved iron was found in water solution at concentrations of 0.125 - 1.085 mg/L and the Fe^{3+} ionic forms are mainly represented by soluble fulvic complexes - 99% of the total forms. The percentage of Mn^{+2} is slightly lower than in 0.01M CaCl$_2$ and a certain share (3.5%) has complexes in the gel phase of the organic matter.
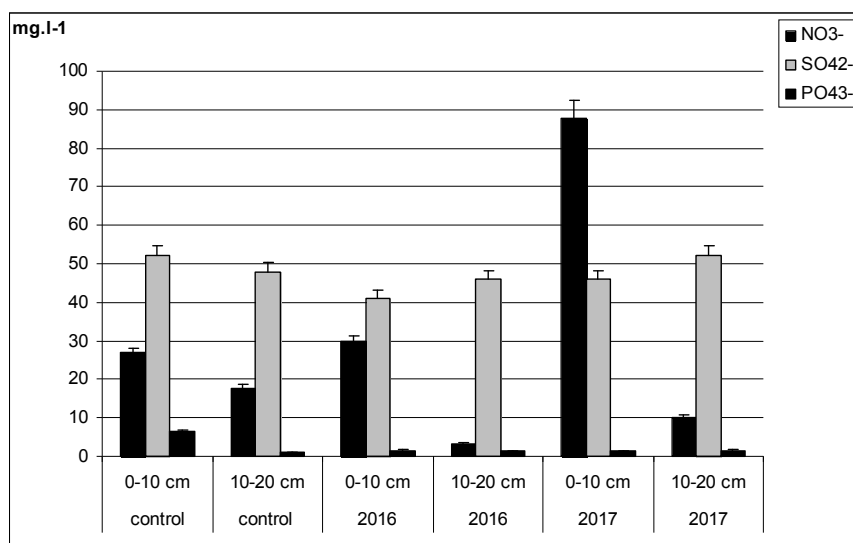
Fig. 3. Concentration of nitrates, sulphates and phosphates (mg.l^{-1}) in 0.01M CaCl$_2$ of biochar-treated Fluvisol.
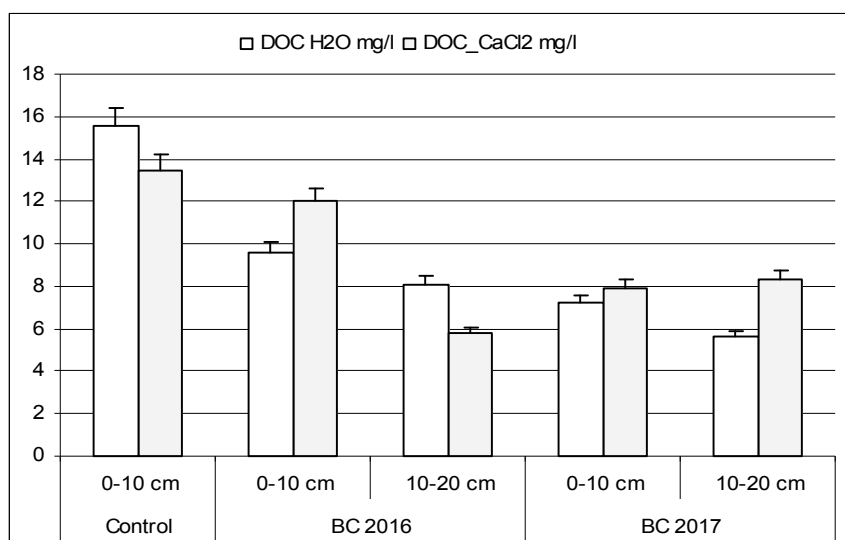

Fig. 4. Dissolved organic carbon (mg.l^{-1}) in water and 0.01M CaCl$_2$ extracts in controls and BC-treated soil by variants.

Table 3. Metal ions speciation in the surface layer (0-10 cm) of the studied soil in 0.01M CaCl$_2$.

Compo-nent	Control 0-10 cm		BC$_{2016}$ 0-10 cm		BC$_{2017}$ 0-10 cm	
	% of total concen-tration	Ion/complex/ form	% of total concen-tration	Ion/complex/ form	% of total concen-tration	Ion/complex/ form
Al^{+3}	0.256	Al^{+3}	0.429	Al^{+3}	0.831	Al^{+3}
	1.534	AlOH^{+2}	2.02	AlOH^{+2}	3.89	AlOH^{+2}
	5.676	Al(OH)$_2^+$	6.458	Al(OH)$_2^+$	12.392	Al(OH)$_2^+$
	2.046	Al(OH)$_3$ (aq)	2.21	Al(OH)$_3$ (aq)	4.235	Al(OH)$_3$ (aq)
	1.116	Al(OH)$_4^-$	1.27	Al(OH)$_4^-$	2.437	Al(OH)$_4^-$

	%	Ion/complex/form	%	Ion/complex/form	%	Ion/complex/form
	13.22	$AlHPO_4^+$	3.639	$AlHPO_4^+$	6.386	$AlHPO_4^+$
	57.401	/FA2AlOH(aq)	63.11	/FA2AlOH(aq)	52.261	/FA2AlOH(aq)
	18.533	/FA2Al+(aq)	20.705	/FA2Al+(aq)	17.189	/FA2Al$^+$(aq)
Mn^{+2}	96.31	Mn^{+2}	97.575	Mn^{+2}	97.522	Mn^{+2}
	0.627	$MnCl^+$	0.524	$MnCl^+$	0.521	$MnCl^+$
	2.073	MnSO4 (aq)	1.321	$MnSO_4$ (aq)	1.474	$MnSO_4$ (aq)
Zn^{+2}	88.481	Zn^{+2}	90.566	Zn^{+2}	92.761	Zn^{+2}
	1.661	$ZnCl^+$	1.403	$ZnCl^+$	1.431	$ZnCl^+$
	2.344	$ZnSO_4$ (aq)	0.059	$ZnNO_3^+$	1.725	$ZnSO_4$ (aq)
	0.33	$ZnHPO_4$ (aq)	6.134	/FAZn$^+$(aq)	0.063	$ZnHPO_4$ (aq)
	6.83	/FAZn$^+$(aq)	0.103	/FA2Zn(aq)	3.671	/FAZn$^+$(aq)
Ca^{+2}	95.183	Ca^{+2}	96.541	Ca^{+2}	96.346	Ca^{+2}
	1.556	$CaCl^{l+}$	1.303	$CaCl^+$	1.294	$CaCl^+$
	2.64	$CaSO_4$ (aq)	1.684	$CaSO_4$ (aq)	1.876	$CaSO_4$ (aq)

Table 4. Metal ions speciation in the surface soil layer (0-10 cm) in water (BC_{2016}).

BC_{2016} 0-10 cm					
Component	% of total concentration	Ion /complex/ form	Component	% of total concentration	Ion /complex/ form
Fe^{+3}	0.424	$Fe(OH)^{2+}$	Zn^{+2}	70.891	Zn^{+2}
	99.401	/FA2FeOH(aq)		0.986	/FA-Zn+2G(aq)
Mn^{+2}	92.389	Mn^{+2}		3.449	$ZnSO_4$ (aq)
	3.653	$MnSO_4$ (aq)		24.05	/FAZn$^+$(aq)
	1.285	/FA-Mn+2G(aq)		0.231	/FA2Zn(aq)
	2.228	/FAMn$^+$(aq)	Ca^{2+}	92.004	Ca^{2+}
Al^{+3}	0.061	Al^{+3}		4.687	$CaSO_4$ (aq)
	0.452	$AlOH^{+2}$		1.279	/FA-Ca+2G(aq)
	1.908	$Al(OH)^{2+}$		1.763	/FACa$^+$(aq)
	0.72	$Al(OH)_3$ (aq)			
	0.375	$Al(OH)^{4-}$			
	62.275	/FA2AlOH(aq)			
	31.007	/FA2Al$^+$(aq)			

With manganese and zinc there was a decrease in the proportion of aqua complexes and an increase in the fulvic complexes due to the fact that the higher ionic strength of the $CaCl_2$ solution caused some complexation with chlorides (Table 3). On the other hand, the competitive interactions of Mn and Zn with Ca for free ligands, lead to an increase in the proportion of free ions in solution with higher ionic strength of $CaCl_2$.

No noticeable differences between control samples and biochar-treated soils in metal speciation in 0.01M $CaCl_2$ and water were found.

Conclusions

The study shows that biochar effect on general soil properties pH, EC, CEC and OM was negligible, however effect of low doses of biochar on soil solution composition was observed. The chloride anions reduce their content in the soil solution at the variants with biochar compared to the control. The concentrations of nitrate anions in the soil solution are higher in the surface layer of the variants treated with biochar compared to the control and decreased in depth in all the studied variants. A significant nitrate variation in $CaCl_2$ extracts was established. The

concentrations of the studied anions in the water extract and in the 0.01M $CaCl_2$ do not exceed the maximum permissible levels MPCL for drinking water except for nitrates in BC_{2017} in both extracts, where biochar from oak barks was applied. Sulfates have lower values in the variants with biochar compared to the controls, while for the phosphate anions there was no significant difference in their concentration in the solution compared to the controls. Dissolved organic carbon in water and 0.01M $CaCl_2$ decreased in variants with biochar compared to the controls, most likely due to the ability of biochar to sorb DOC. Manganese and zinc in the studied soils are represented by free aqua ions (M^{2+}), especially high is the percentage of free manganese ions, while for aluminium and iron, fulvic complexes are the predominant species.

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