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Biochar Substrates and their Combination with Fertilization as a Factor Affecting the Changes in pH and Surface Charge of Soil Particles in Soils with Different Texture

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ABSTRACT

In 2017 the field experiments were established at two localities of the South-west Slovakia (1 Dolná Streda: sandy Arenosol and 2 Veľké Úľany: loamy Chernozem). The experiments involved biochar substrates (1 BS1 mix biochar, sheep manure and 2 BS2 mix biochar, sheep manure and digestate) in two application doses (10 and 20 t ha^{-1}), which were applied independently compared with the unfertilized control (Co-NF) and combined with additional fertilization versus the fertilized control (Co-F), in order to verify their impacts on the changes of soil properties. In the spring and autumn of 2018–2020, within these experiments the soil samples were taken to determine the range of effect of the tested biochar substrates (BS) and also their combination with fertilization (F) on the changes of soil pH and surface charge of soil particles in the soils different in texture. The results pointed out the fact that a more significant effect of tested BS on soil pH was detected in sandy soil than loamy soil. In sandy soil, only the application of BS2 in doses 10 and 20 t ha^{-1} statistically significantly increased the soil pH in H_2O in comparison with Co-NF. The application BS1 + F in dose 10 t ha^{-1} and BS2+F in dose 20 t ha^{-1} statistically significantly increased pH in KCl compared with Co-F. The fertilization to BS eliminated the considerable decrease of the soil pH in H_2O both soils. In sandy soil, pH was substantially regulated by the content of alkali cations themselves in BS; however, in loamy soil, it occurred as a result of the increase of the content of soil organic carbon after the application of BS (R^2 = 0.339), but also BS + F (R^2 = 0.468). In sandy soil, the application of BS itself, owing to the change of the surface charge, influenced predominantly the sorption of anions. Conversely, the additional fertilization to BS treatments had an impact on the sorption of cations. In loamy soil, the application of BS and BS + F as a result of the change of surface charge did not have any significant effect on the total soil sorption.

Keywords: soil pH, zero charge, *effeco*, arenosol, chernozem.

INTRODUCTION

The important indicator of soil fertility is the value pH which has a direct impact on all processes and reactions in the soil. It affects the adsorption and desorption of cations, the solubility of compounds of biogenic and trace elements, compounds and ions having the toxic impact on plants, the intensity and composition of microorganisms, mineralization of organic substances, decomposition of minerals, coagulation and peptization of colloids, soil structure and other factors. Therefore, the value soil pH belongs to the most general and frequent determined parameters of soil fertility (Šimanský et al., 2018). On the other hand, the parameters of charge characteristics represent a specific part of the soil chemistry which studies the chemical and physico-chemical processes and reactions in soil, in close relation with the natural and anthropogenic factors (Hanes, 1999).

Recently, the scientific community has focused its special attention on the biochar, the effects of which on the changes of soil pH have been documented under the different soil-climatic conditions (Hailegwan et al., 2019; Šimanský et al., 2022). After the biochar is applied into the soil, the increase of soil pH occurs, mainly in acidic soils (Horák, 2015; Heikkinen et al., 2019; Juriga and Šimanský, 2019). The mechanism of this effect is known under the designation the ash alkalinity (Yan et al., 1996). The impact of biochar on pH in soils depends predominantly on its properties that are completely different depending on the feedstock used for its production (Ippolito et al., 2015), or depending on the temperature of pyrolysis (Enders et al., 2012; Heikkinen, 2019). During the production of biochar, the ash materials originate on the surface of biochar, carbonates are precipitated there, and after the application into the soil, they can react with H^+ and in this way, pH is decreased, mainly in acidic soils (Novák et al., 2009). After the application of biochar, these mechanisms of soil pH change can also be interfered with by other external factors, which can also cause further changes in the soil reaction. These factors involve the mixture of biochar with other organic materials of the different physico-chemical character and composition, but also their possible combination with other additional manures or mineral fertilization. The scientific literature reports that the different types of mineral fertilizers, but also manures behave differently under different soil-climatic conditions.

There is not enough information about the behaviour of biochar substrates (mixture of biochar with other organic additives), as well as their different combinations on the change of soil pH and surface charge of particles that has a considerable impact on the sorption in soils, mainly in alkali soils of the different soil texture. Therefore, within this study, the effect of two different biochar substrates was analysed, as well as their combination with the additional fertilization on the change of soil pH and surface charge of soil particles in the texture of the different soils. It was assumed that the different mixture of biochar substrates, their higher application dose and additional fertilization will be reflected also in the changes of the monitored parameters. The biochar substrates will significantly differently affect the range of changes of the observed parameters in sandy and loamy soil, but also in the soil of lower more than higher pH, which will influence considerably the surface charge of the soil particles.

MATERIAL AND METHODS

The experiments were established in the South-west part of Slovakia at the localities Dolná Streda and Veľké Uľany. In Dolná Streda, the field experiment was based on the plot that is used for the cultivation of the common cash crops (sandy Arenosol). In the period of the trial establishment, the soil contained 81.9% sand, 10.5% silt, 7.64% clay, 0.97% (low content) of the total organic carbon (C_{org}), 1,300 mg kg^{-1} N (low content), 175 mg kg^{-1} P (high content), 165 mg kg^{-1} K (appropriate content) and pH was slightly alkaline (pH_{H2O} = 7.60). In Veľké Uľany, the experiment was settled on the plot that was used for the intensive growing of vegetables. The soil was classified as Chernozem with the content of sand 38.5%, silt 47.8% and clay 13.7%. Before the trial establishment, the soil had the medium content C_{org} (1.56%), low content N (966 mg kg^{-1}), high content P (129 mg kg^{-1}), appropriate content K (255 mg kg^{-1}) and pH was slightly alkaline (pH_{H2O} = 7.78). The average annual temperature in both localities is 9–10 ^{o}C and the average annual precipitation varies from 520 to 600 mm.

The experiment in Dolná Streda began in the autumn of 2017. The area of one small field was 90 m^2. The trial was established by using the long parts method. Before trial establishment, the preceding crop was durum wheat. In the autumn of 2017, the biochar substrates were applied into soil to the depth 0.15 m by disk tillage. During the whole period of experiment, the minimizing system of soil cultivation was utilized, i.e. disk tillage, or loosening into the depth 0.15–0.18 m. In the spring of 2018, before the sowing of sunflower and during its growing period, the biochar substrates (BS) were applied along with urea in the dose of 2×100 kg ha^{-1} with the particular treatments. In the spring of 2019, before the sowing of durum wheat, the biochar substrates were applied along with 100 kg Amofos with the individual treatments and in spring before sowing of grain maize 200 kg of urea.

The experiment in Veľké Uľany was established in the spring of 2018. The territory of one small field was 25 m^2 and the buffer strip was left between the small fields. The trial was based by the method of random arrangement in double repetition. The preceding crop was carrot. Before sowing of pepper (crop from 2018), the biochar substrates were applied into soil (to depth 0.10–0.12 m), and also the granular manure Italpollina (in 2018) and NPK (in 2020) were added to the selected treatments. The soil was cultivated in the conventional way, i.e. in autumn it was ploughed into the depth of 0.20 m and in spring the soil was prepared subsequently by the rotary tiller; depending on the cultivated vegetables, also the mechanical hoe was used in combination with the chemical weed killing. The rotation of crops was as follows: in 2018 vegetable pepper, in 2019 red beet and in 2020 again vegetable pepper. In 2018 and 2020, during the growing period of pepper, the drop irrigation was utilized for a total of three times (application dose = soil saturation by water to 80% of field water capacity) and the soil surface was covered by top foil. In the case of the severe weather conditions, the pepper plants were covered by a textile fabric. In 2019, the classical irrigation was used (by spraying) – totally twice during the growing season (1^{st} June; 2^{nd} July; the total dose 50 mm). The established treatments at both research localities are summarized in the Table 1.

The biochar substrates being tested – labelled under the commercial name *effeco 50/50* (BS1) and *effeco 30/30/30* (BS2) – was obtained from the company Zdroje Zeme, Plc., which developes these substrates. *Effeco 30/30/30* is a biochar substrate that originated by the mixture of biochar produced by the slow pyrolysis of hard wood (500°C) with the dried sheep manure and separate from the biogas station (original raw material cow manure) in the proportion 1:1:1. It contains: 45.4% total organic carbon, 1.3% total N, 0.79% P and 15.5% K, and its pH is slightly alkaline. The biochar substrate *effeco 50/50* is the mixture of biochar produced by pyrolysis of hard wood and dried sheep manure in the proportion 1:1. Its pH is 8.18 and contains: 43% total organic carbon, 1.2% total N, 0.49% P and 24.6% K. The content of hazardous elements in both products does not exceed the limit values, which are specified by the regulation 577/2005. In the treatments with organic fertilization, Italpollina was used that is produced from the poultry manure and contains: 4% N, 4% P_2O_5, 4% K_2O and its pH is neutral. The following mineral fertilizers were utilized: urea (N content 46%), AMOFOS NP 12-52 (N content 12%, and 52% P_2O_5) and finally NPK 14-10-20 (N content 14%, 10% P_2O_5 and 20% K_2O).

The soil samples were taken from both experiments twice a year (spring and autumn) during the period of 2018–2020.

Each sampling was taken from the depth 0–0.20 m with the triple repetition of each treatment. Consequently, the samples were carried to the laboratory, where they were homogenized, dried at the laboratory temperature, pulverized, and sifted through the sieve with the diameter less than 0.25 mm. The content of total organic carbon (C_{org}) was determined oxidometrically (Dzadowiec and Gonet, 1999), soil pH in H_2O (pH in H_2O; proportion 1 g of soil to 2.5 ml distilled water) and in KCl (pH in KCl; 1 g of soil to 2.5 ml 1 mol.dm^{-3} KCl), both soil pH potentiometrically (Hrivňáková et al., 2011). The ΔpH values were calculated out of the measured values of soil pH in H_2O and KCl according to the equation 1.

$$\Delta pH = pH_{H2O} - pH_{KCl} \qquad (1)$$

Table 1. Experimental treatments

Dolná Streda – sandy soil	Veľké Uľany – loamy soil
Biochar substrates	
1. Control – unfertilized control (Co-NF)	1. Control – unfertilized control (Co-NF)
2. BS1 at rate of 10 t ha^{-1}	2. BS1 at rate of 10 t ha^{-1}
3. BS1 at rate of 20 t ha^{-1}	3. BS1 at rate of 20 t ha^{-1}
4. BS2 at rate of 10 t ha^{-1}	4. BS2 at rate of 10 t ha^{-1}
5. BS2 at rate of 20 t ha^{-1}	5. BS2 at rate of 20 t ha^{-1}
Biochar substrates together with fertilization	
1. Control – fertilized control (Co-F)	1. Control – fertilized control (Co-F)
2. BS1 at rate of 10 t ha^{-1} + fertilization (F)	2. BS1 at rate of 10 t ha^{-1} + fertilization (F)
3. BS1 at rate of 20 t ha^{-1} + fertilization (F)	3. BS1 at rate of 20 t ha^{-1} + fertilization (F)
4. BS2 at rate of 10 t ha^{-1} + fertilization (F)	4. BS2 at rate of 10 t ha^{-1} + fertilization (F)
5. BS2 at rate of 20 t ha^{-1} + fertilization (F)	5. BS2 at rate of 20 t ha^{-1} + fertilization (F)

BS1 – biochar substrate *effeco 50/50*
BS2 – biochar substrate *effeco 30/30/30*

Consequently, the obtained results of the soil pH were evaluated by the one-factor analysis of variance. The average values of the individual treatments with the biochar substrates and also their combination with the additional fertilization were assessed by LSD test at the significance level of 95%. The simple linear correlation analysis was used for the determination of the dynamics of changes of the soil pH in H_2O during the period of both experiments, and also for the assessment of the zero charge of soil particles, and the dependence between C_{org} and soil pH in H_2O.

RESULTS AND DISCUSSION

The average values of the soil pH in H_2O and KCl as a result of the application of both tested substrates, either individually or combined with other fertilization, on both soil types are summarized in Figures 1 and 2. Overall, the average values of the soil pH (pH_{H2O}) in sandy soil varied in the interval from 7.21 to 7.89, i.e., from neutral to alkaline during the period of 2018–2020. In the whole monitored period, the values of pH_{H2O} were statistically significantly affected by the application of the biochar substrates into the soil, in comparison with the unfertilized control (Fig. 1A). On the other hand, the combination of the biochar substrates, along with the additional fertilizing compared with the fertilized control, did not have any considerable effect on the changes of the average pH_{H2O} values in sandy soil in the period of 2018–2020 (Fig. 1B). Only the application of the substrate BS2 in two doses increased the average values pH_{H2O} statistically significantly, in comparison with the unfertilized control. The average values of the soil pH in KCl (pH_{KCl}) were not statistically significantly changed after the application of the biochar substrates themselves, while the soil pH_{KCl} was changed substantially after their application along with the additional fertilizing. However, only the application of the BS2 substrate in a dose of 20 t ha^{-1} in combination with additional fertilizing increased the pH_{KCl} values

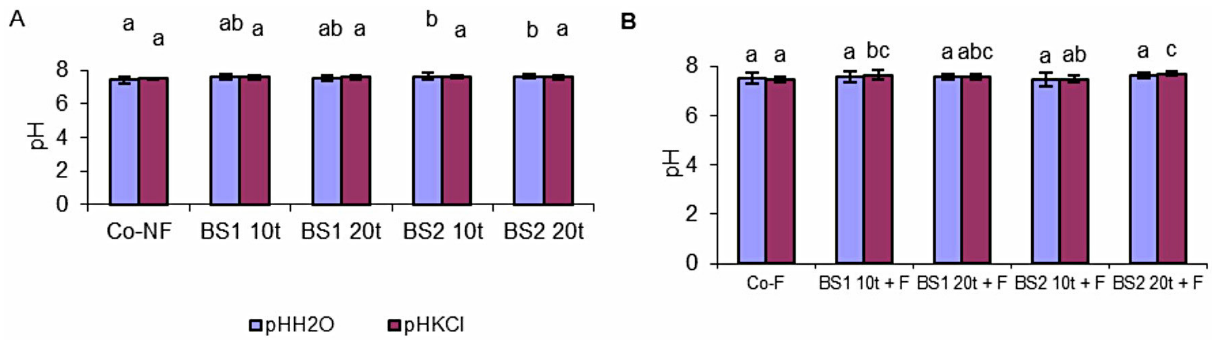

Figure 1. Soil pH in H_2O and in KCl after application of A) biochar substrates, and B) biochar substrates together with fertilization in sandy soil. Different letters between columns in the same color indicate that treatment means over the sampling dates are significantly different at P < 0.05 according to the least significant difference (LSD) multiple-range test

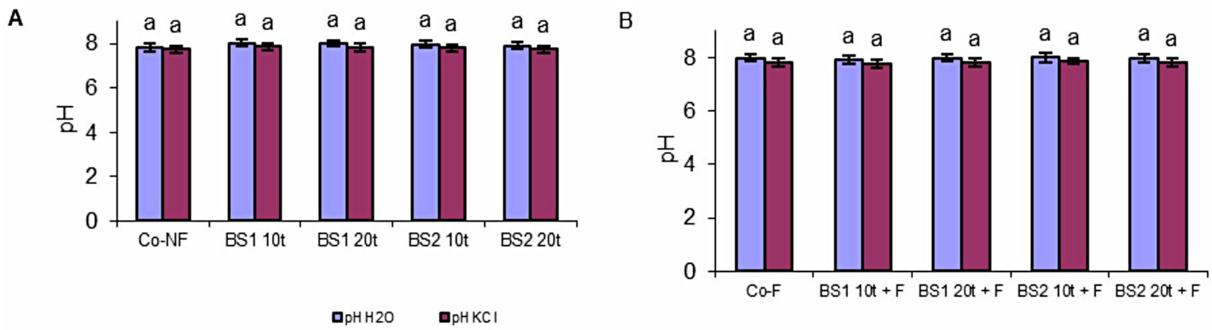

Figure 2. Soil pH in H_2O and in KCl after application of A) biochar substrates, and B) biochar substrates together with fertilization in loamy soil. Different letters between columns in the same color indicate that treatment means over the sampling dates are significantly different at P < 0.05 according to the least significant difference (LSD) multiple-range test

statistically significantly, compared with the fertilized control in sandy soil (Fig. 1B). The statistically significant differences of the average pH_{H2O} and pH_{KCl} values were not detected, neither in the case of the application of the biochar substrates themselves (Fig. 2A) nor in the case of their combination with the additional fertilization (Fig. 2B) in comparison with the particular controls. The obtained results comply with the published results of several authors (Horák, 2015; El – Naggar et al., 2019). El – Naggar et al. (2019) claim that a stronger effect of the applied biochar on the changes of soil pH is observed in sandy rather than loamy soils, mainly in the acidic soils. Overall, in the conducted experiment, the values of the pH_{H2O} and pH_{KCl} were lower in sandy soil than in loamy soil, but a slightly higher growth of the pH_{H2O} and pH_{KCl} values was recorded just in sandy soil than in loamy soil, as a result of the application of the biochar substrates. These findings are related to the initial pH of both soils (neutral pH_{H2O} in sandy soil and slightly alkaline pH_{H2O} in loamy soil in the control treatments). Besides, both soil types contained carbonates, and similarly, both tested biochar substrates comprised alkali cations and had alkaline pH.

According to the results, it is evident that the biochar substrates had an impact on the changes of the average values of soil pH, predominantly in sandy soil. However, it is important to also identify the rate of changes in soil pH after the application of the tested substrates, because the scientific studies prove that by the time the biochar application decreases their liming effect in acidic (Šimanský et al., 2018a), but also of neutral or alkaline soils (Šimanský et al., 2019). The dynamics of changes of the pH_{H2O} after the application of BS and also their combinations with the additional fertilization in both soils in the period 2018–2020 is documented in Figures 3 and 4. The values of pH_{H2O} were statistically significantly linearly decreased by 0.07, 0.09 and 0.07 pH units in each sample in Co-NF, BS2 10 t ha^{-1} and BS2 + F 20 t ha^{-1} during the investigated period. In the case of other treatments in sandy soil and all treatments in loamy soil, the considerable unstableness of soil pH values in H_2O was registered; therefore, it was not possible to identify any statistically significant linear trend over the period of three years.

The biochar (Fisher and Glaser, 2012) and also biochar substrates (Šrank and Šimanský, 2020), or their combinations with other manures and mineral fertilizers constitute the important sources of organic substances through which the carbon content in soils can be increased under certain conditions. Therefore, the mutual linear relations were studied between the soil organic carbon (C_{org}) and soil pH in H_2O. The statistically significant linear dependences were not observed between the contents of C_{org} and $pH_{H2O,}$ neither with the application of the biochar substrates themselves nor in their combination with the additional fertilizing in sandy soil (Fig. 5A). On the contrary, in loamy soil in both cases, i.e., after the application of BS and BS + F, the statistically significant negative linear trends were detected between C_{org} and pH_{H2O} (Fig. 5B). These facts approve the diametrically different impact of BS and their combination in the soils of different textures, but also in comparison with the dynamics of change of the pH_{H2O} (Fig. 3 and 4), similarly in the changes of the average values during the whole monitored period. C_{org} did not affect the changes of soil pH, but mainly the presence of alkali cations contained in both biochar substrates and the additional fertilization (in sandy soil the impact of urea and AMOFOS, in loamy soil the impact of the Italpollina manure and NPK fertilizer) influenced the changes.

The difference between the pH in KCl and pH in H_2O was also calculated. Based on it, so-called ΔpH can be determined (Hanes, 1999). If ΔpH < 0, it means that the surface of soil particles (organic substances and clay minerals) is negative. The result is that on the surface, the cations are absorbed from the soil solution. As Zołotajkin et al. (2011) stated, ΔpH depends on the content of organic substances in soil, then it is obvious that the application of biochar substrates (because they are the considerable source of organic carbon) can influence the ΔpH values (Šimanský et al., 2019a), and in this way also the soil sorption properties (Liang et al., 2006; Novak et al., 2009; Šimanský et al., 2022). Overall, the average difference was distinct in both sandy and loamy soils during the period of 2018–2020. In sandy soil in the treatments with BS applied separately, the positive difference between pH_{H2O} and pH_{KCl} was recorded, apart from the treatments Co-NF and BS1 20 t ha^{-1}, which indicates that the positively charged ions dominated on the surface of particles. It can result in the influence of sorption, mainly anions. In the treatments with the additional fertilization

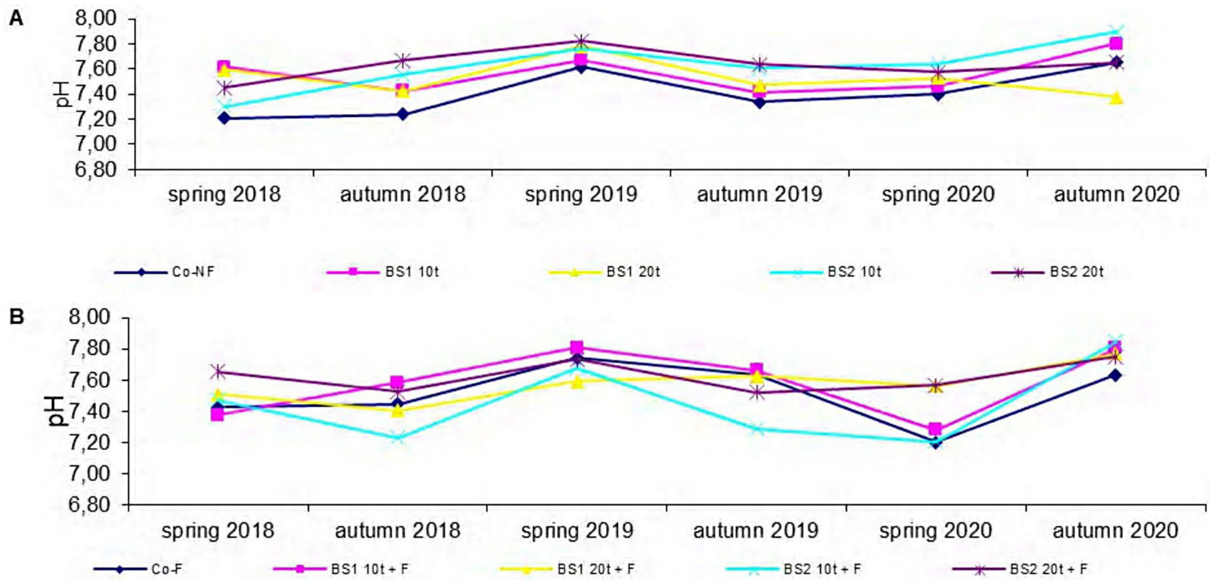

Figure 3. Dynamics of changes in soil pH_{H2O} after application of A) biochar substrates, and B) biochar substrates together with fertilization in sandy soil

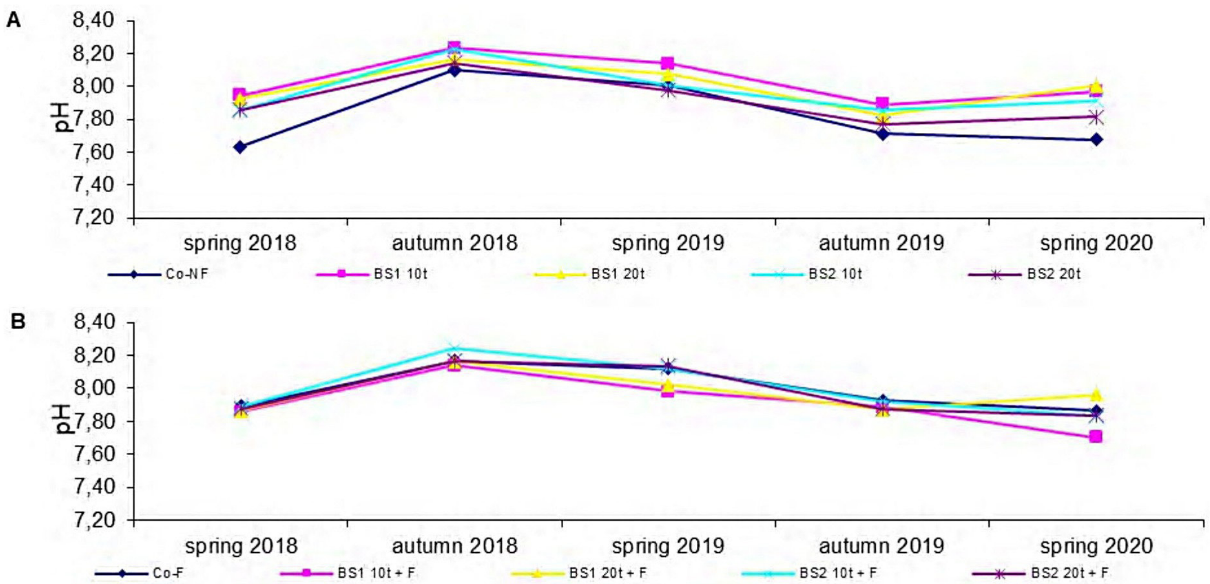

Figure 4. Dynamics of changes in soil pH_{H2O} after application of A) biochar substrates, and B) biochar substrates together with fertilization in loamy soil

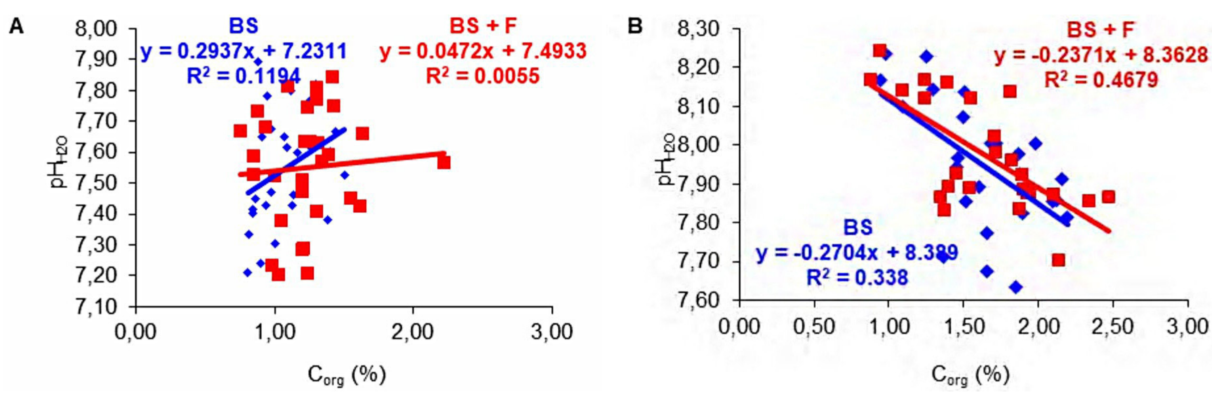

Figure 5. Linear relationships between soil organic carbon and soil pH_{H2O} A) in sandy soil and B) in loamy soil

in sandy soil, the negative difference was registered between the pH_{H2O} and pH_{KCl}, which indicates that the positively charged ions dominate on the surface of soil particles. It can lead to an impact on the sorption of cations. On the basis of the mutual relation between pH_{H2O} and ΔpH, the values of zero charge were determined, i.e., ΔpH = 0 for both soils and all the studied treatments during the analysed period (Fig. 6 and 7). The values ΔpH = 0, sandy soil achieved for controls: pH_{H2O} for unfertilized control and the fertilized control = 7.48. The application of BS and also BS + F increased the pH_{H2O} value for the achievement of the zero charges in the case of both doses, whereby it was more significant in BS2 than BS1, compared with the unfertilized control (pH_{H2O} for BS1 10 and 20 t ha^{-1} = 7.56 and for BS2 10 and 20 t ha^{-1} = 7.61). A similar trend was observed also in the treatments where the biochar substrates were combined with the additional fertilization in sandy soil (Fig. 6).

Overall, in loamy soil, the positive difference between pH_{H2O} and pH_{KCl} was determined, which indicates that the positively charged ions dominated on the suface of soil particles. The ΔpH = 0 values, were achieved in loamy soil for controls: pH_{H2O} for the unfertilized control = 7.76 and the fertilized control = 7.91. The values of zero charges were increased in comparison with the unfertilized control – they were more significant as a result of a lower rather than higher dose, but also more considerable in BS1 than BS2. ΔpH = 0 after the application of BS + F was not changed markedly compared with the fertilized control (Fig. 7). In all of them, if the individual values pH_{H2O} for the zero charges are exceeded in the particular treatments, then the opposite trend related to the sorption properties can be assumed, i.e. in this case the sorption of cations is decreased at the expense of the sorption of anions in both soils.

CONCLUSIONS

Overall, the values of the soil pH were lower in sandy rather than loamy soil; however, slightly higher growth in values of the soil pH was detected just in sandy than loamy soil as a result of the application of the biochar substrates. The most significant changes were identified in the higher rather than lower dose, and with the substrate *effeco 50/50* rather than *effeco 30/30/30* in sandy soil. The values of the soil pH in H_2O were decreased considerably after the initial application of the biochar substrates in sandy soil in the following years. The application of the additional fertilization to the biochar substrates eliminated the significant decrease of the soil pH in H_2O in both soils during the studied period.

The relationships between the content of organic carbon and soil pH in H_2O were diametrically opposed, depending on the soil texture and the application of the biochar substrates, or their combination with the additional fertilization. The mechnism having impact on the soil pH after the application of the biochar substrates was different in sandy and loamy soil. In sandy soil, the pH was considerably regulated by the content of alkali cations themselves in the tested substrates, but in loamy soil it was a result of the increase of content of organic carbon after the application of the biochar substrates.

The changes between the soil pH after the application of the biochar substrates and also their combinations with the additional fertilization affected considerably the changes of charges on the surface of soil particles in both soils. In sandy soil, the application of the biochar substrates themselves, owing to the change of the surface charge, had an impact mainly on the sorption of anions. Conversely, the additional fertilization to BS treatments influenced the sorption of cations. In loamy soil the application of BS and their combination with fertilization, as a consequence of the change of surface charge, did not have any significant impact on the soil sorption – the recorded positive effect on the sorption of anions, that is, however, neglectable compared with the sorption of cations; thus, it is not demonstrated considerably in the total soil sorption. The change of zero charge was affected predominantly by the type itself of the biochar substrates applied into both soils. In the loamy soil these substrates and lower dose played a more significant role in comparison with a higher dose.

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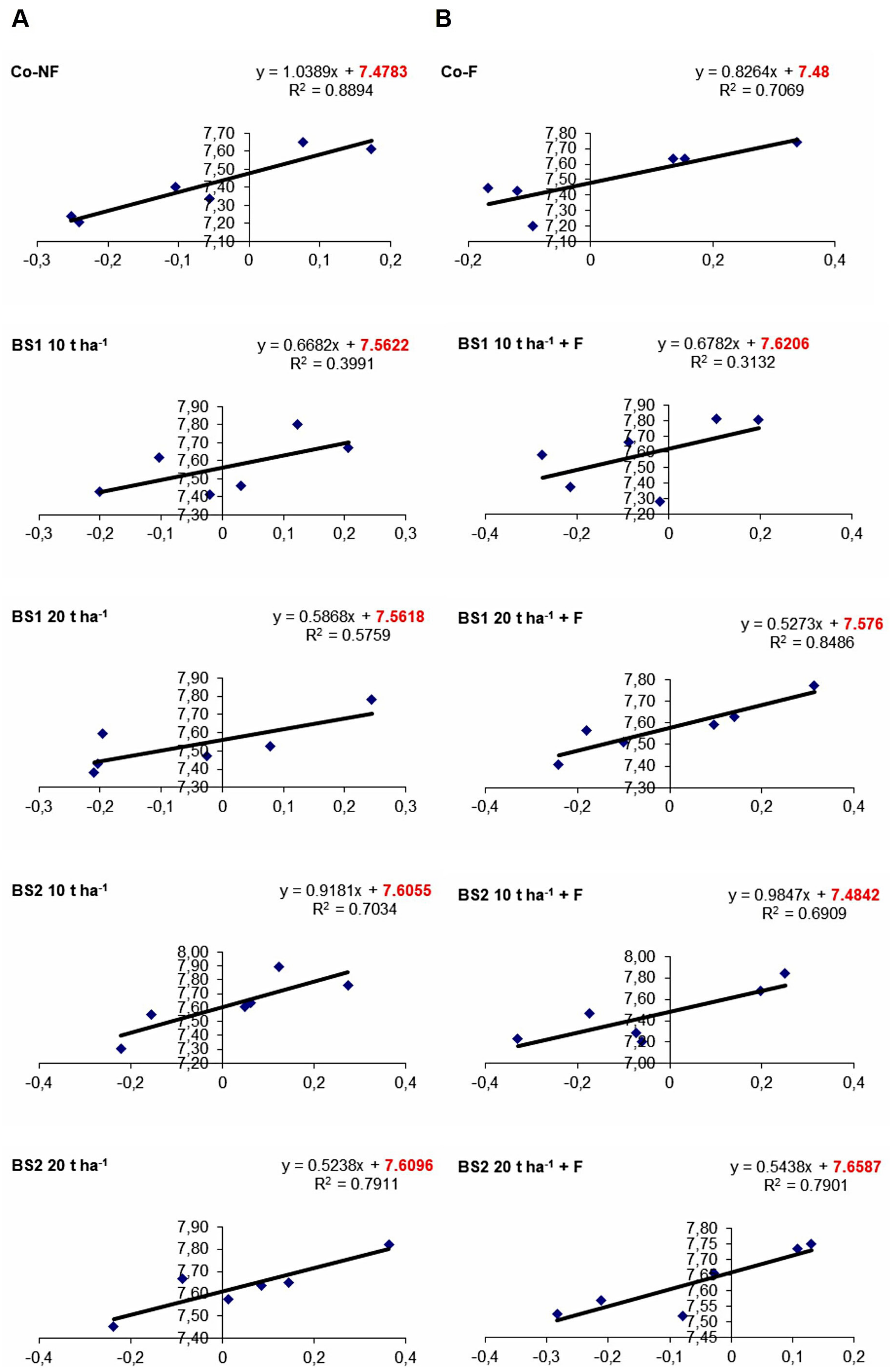

Figure 6. Zero change values after application of A) biochar substrates, and B) biochar substrates together with fertilization in sandy soil

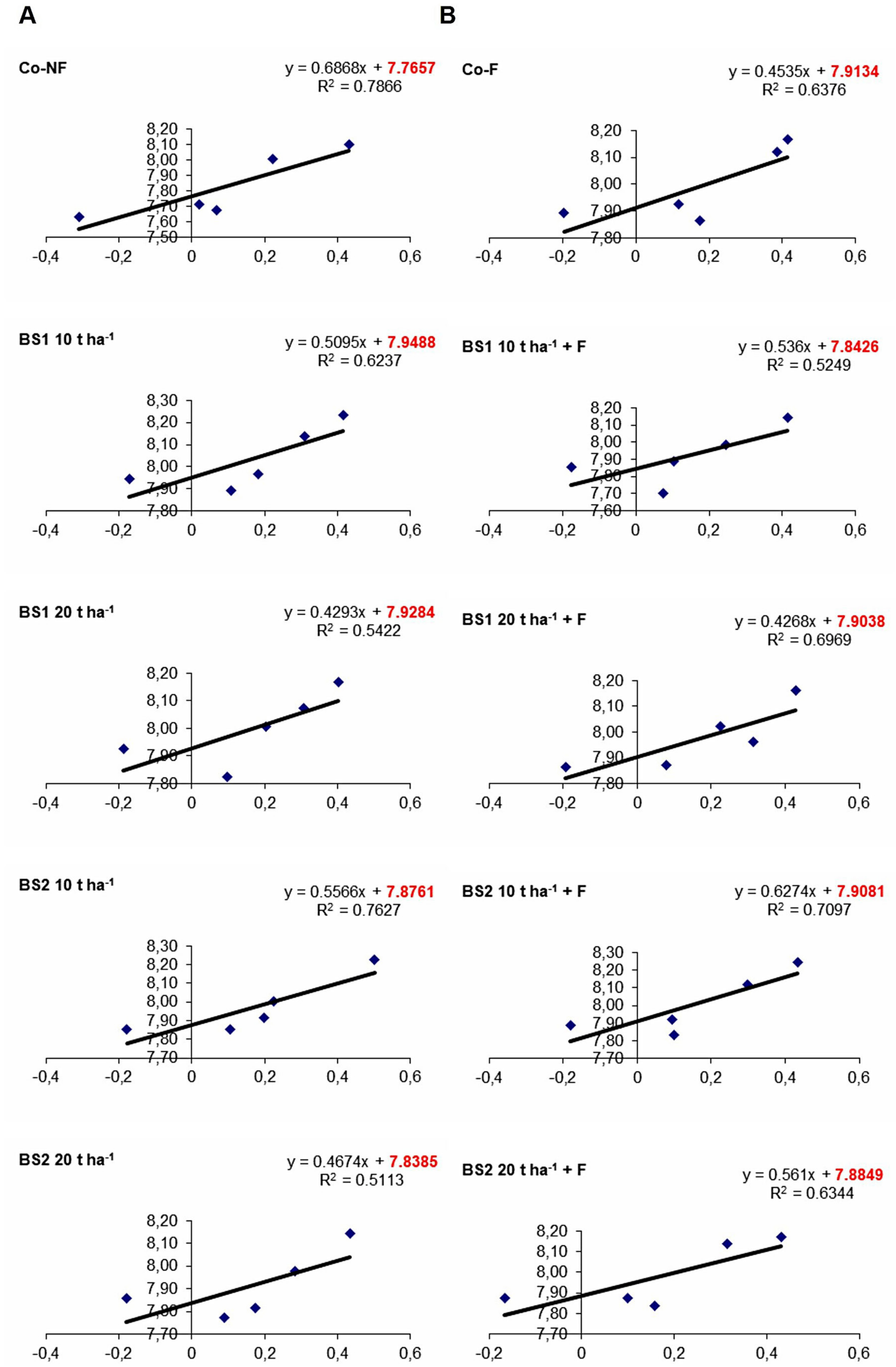

Figure 7. Zero change values after application of A) biochar substrates, and B) biochar substrates together with fertilization in loamy soil

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