EFFECT OF WOOD-BASED BIOCHAR AND SEWAGE SLUDGE AMENDMENTS FOR SOIL PHOSPHORUS AVAILABILITY

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Abstract: This study investigated the effects of two biochars (pyrolysed wood chips and garden clippings) on phosphorus (P) availability in a heavy-metal contaminated soil poor in phosphorus. Short-term 14-days incubation experiments were conducted to study how applications of biochars at different rates (1 and 5 %) in combination with (1:1) and without dried sewage sludge from a municipal waste water treatment plant (WWTP) affected the content of soil extractable P. For P-availability analyses deionized water, calcium acetate lactate (CAL), Mehlich 3 and Olsen extraction protocols were applied. In addition, the content of total and mobile forms of potentially toxic heavy metals (PTHM) was studied. Application of both biochars caused a significant decrease of PTHM available forms in sewage sludge amended soil samples. The concentration of total and available P increased with higher biochar and sewage sludge application rates.

Key words: biochar, sewage sludge, availability, heavy metals, phosphorus, soil

1. Introduction

Phosphorus represents a non-substitutable element that serves vital functions in all living organisms. However, the remaining natural resources of this important macronutrient have rather limited availability and decreasing quality (EGLE *et al.*, 2014). A considerable amount of phosphorus (P) is removed from field soils by harvesting crops and another significant amount of phosphorus is stored in residual plant biomass with low use efficiency (ZHAI *et al.*, 2015). A continued large demand for this plant nutrient in agriculture will lead to a foreseeable depletion of natural resources (VAN VUUREN *et al.*, 2010). The search for alternatives for rock phosphate as a basic raw material for P fertilizers has become a burning issue in recent discussions about global food production. The processing of phosphorus-rich municipal and agricultural wastes could contribute to the closing of the geochemical phosphorus cycle and to the conservation of the remaining rock phosphates. Sewage sludge as a product of municipal waste water treatment plants represents a heterogeneous mixture of beneficial and hazardous compounds, micro-/macroelements and organic matter (FRIŠTÁK *et al.*, 2014a). Concentrations and availability of heavy metals and other contaminants from sewage sludge restrict the agricultural applications as fertilizers (ŠUŇOVSKÁ *et al.*, 2013). However, the abundant availability of such phosphorus-rich material opens a new option in the search for effective recovery of the valuable sewage sludge components with nutrient effects when used as soil amendment.

Several studies have shown that the application of biochar as high porous material produced by pyrolysis of lignocellulosic biomass can positively influence basic soil

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properties, such as pH, water holding capacity, microbial diversity or content of available nutrients (LEHMANN *et al.,* 2015). Thermo-chemical conversion processes provide the key for the transfer of phosphorus from waste materials to stabilized products. Additionally, pyrolysis as a carbonization technology converts biomass thermochemically into stable, recalcitrant organic carbon compounds that can serve as nutrient carriers to be applied as fertilizer for agricultural soils (GLASER *et al*., 2015). The phosphorus content of biochar can increase by 2- or 3-fold during the pyrolysis process as the phosphorus in the biomass is enriched with inorganic phosphates and pyrophosphates (ATKINSON *et al*., 2010). Reversibility of phosphorus binding represents the crucial parameter of biochar utilization as an appropriate fertilizer.
The combination of pyrolysed plant residues with sewage sludge might on the one hand enrich nutrient-poor biochars and on the other hand provide a slow release of the nutrients to avoid a rapid leaching.

Therefore the main aim of our study was to assess the effectivity of wood-based biochar and its mixture with municipal sewage sludge with respect to phosphorus availability.

2. Materials and methods

2.1 Soil samples

Top soil samples (0-20 cm) of a mixed type Cambisol and Rendzina were collected from locality Arnoldstein (AS; Fig. 1), Austria (46º33'09.5"N, 13º41'21.5"E). The soil samples were air-dried, homogenised and sieved through a 2 mm mesh sieve.

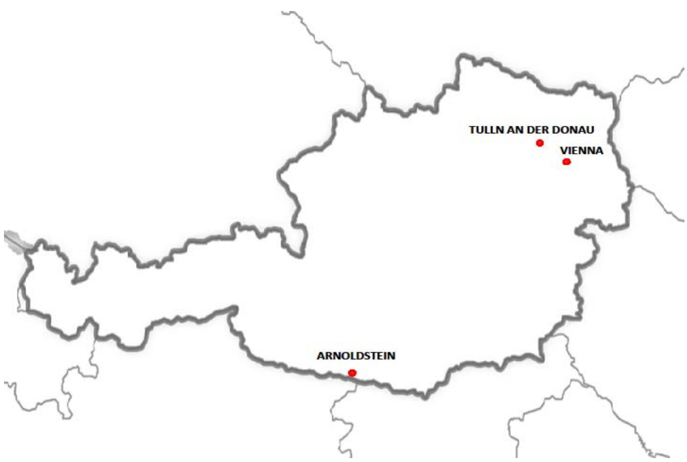

Fig. 1. Sampling sites of studied soil and sewage sludge.

2.2 Biochar and sewage sludge amendments

Biochar samples were produced in slow pyrolysis process from two different feedstocks: beech wood chips (BC A) and garden green waste residues (BC B).

Procedure and production conditions were described in our previous work (FRIŠTÁK *et al*., 2014b). For soil experiments the particle size 0.5 - 1 mm was used. Municipal sewage sludge (SS) was obtained from aeration tank of waste water treatment plant (WWTP) in Tulln an der Donau (Fig. 1). After sampling, the sludge was filtered, 2 times rinsed with deionized water, oven dried at 60 °C and 24 h, ground and sieved. For soil experiments also the particle size fraction of 0.5 - 1 mm was used.

2.3 Amendments characterization

The active and potential pH values of BC A, BC B and SS were measured after stirring the biochars and sewage sludge with deionized water and 1.0 mol L^{-1} KCl (ratio 1:2.5) for 1 h and stabilization for 1 h (inoLab pH level 2P, Weilheim, Germany). The electrical conductivities (EC) of BC A, BC B and SS were measured in 1:10 deionised water extracts after 24 h mixing (inoLab pH level 2P, Weilheim, Germany). The anion exchange capacities (AEC) of biochars and sewage sludge were determined using bromide as an index anion (LAWRINENKO, 2014). Surface areas (SA) were estimated by the titration method with NaOH according to MELICHOVÁ and HROMADA (2013) and confirmed by methylene-blue adsorption method (EL-GEUNDI *et al.*, 2014). The total C, N and H contents of biochars were measured by an elemental analyzer (CHNS-O EA 1108, Carlo Erba Instruments, Italy). Initial concentrations of Cd, Cu and Pb as models of potentially toxic heavy metals (PTHM) in biochar and sludge samples were determined after HNO_3 – H_2O_2 digestion (ENDERS and LEHMANN, 2012) by ICP-MS. Total P content was measured in the same digests by malachite green microplate UV-VIS method.

2.4 Experimental design

For incorporation into the experimental soil 1 and 5 % (w/w) amendments of BC A, BC B, SS, BCA + SS (1:1), BCB + SS (1:1) were applied. For comparison the commercial fertilizer superphosphate (SP, 42 % P_2O_5) was used. Amended soil samples were incubated at 19 ± 2 °C and 65 % water content for 14 days under greenhouse conditions.

2.5 Soil samples characterization and P determination

The amended soil samples were characterized by determination of active and potential pH, electrical conductivity (EC), anion exchange capacity (AEC), surface area (SA), total and water extractable content of Cd, Cu, Pb, total and available forms of phosphorus. For determination labile forms Calcium-Acetate-Lactate (CAL), deionized water (DW), Mehlich 3 (M3) and Olsen (OL) extraction protocols were used. For total phosphorus content modified HNO_3 – H_2O_2 digestion method (ENDERS and LEHMANN, 2012) was applied. For determination of heavy metals in soil extracts the mass spectrometry with inductively coupled plasma (ICP-MS, Perkin Elmer, Elan DRCe 9000, USA) and atomic absorption spectrometry with flame atomization (FAAS, AA 400, Perkin Elmer, USA) was used and malachite green microplate UV-VIS method was used for phosphorus determination in soil extracts.

3. Results and discussion

3.1 Characterization of soil and soil amendments

The physico-chemical properties of the studied soil sample from Arnoldstein (AS), two biochar (BCA, BCB) and sludge amendments (SS) were analysed and are summarised in Table 1. Levels of pH, AEC and SA are major determinants of the behaviour of organic and inorganic contaminants in soil (KABATA–PENDIAS, 2011). Nevertheless, pH value affects not only xenobiotic availability, but also controls the process of micro- and macronutrient uptake by plant root systems. The determination of actual and potential pH confirmed a slightly acidic character of the studied soil and dried sewage sludge. A similar character of dried SS was also found in our previous study (FRIŠTÁK *et al.*, 2014a).

Table 1. Physico-chemical characteristics of the studied soil (AS), biochar amendmends (BCA, BCB) and sewage sludge amendment (SS). Intervals denote standard deviations (n=4).

	BCA	**BCB**	**SS**	**AS**
pH_{act}	8.78 ± 0.02	9.03 ± 0.01	6.94 ± 0.01	6.29 ± 0.02
pH_{pot}	8.46 ± 0.02	8.77 ± 0.02	6.71 ± 0.01	5.45 ± 0.03
EC (mS cm^{-1})	0.54 ± 0.03	1.67 ± 0.03	0.87 ± 0.05	0.05 ± 0.04
AEC (cmol kg^{-1})	0.63 ± 0.01	0.73 ± 0.01	2.89 ± 0.01	1.05 ± 0.01
SA (m^2 g^{-1})	28.04 ± 1.55	31.79 ± 1.98	3.87 ± 0.12	18.02 ± 0.54
C (%)	80.30 ± 1.02	79.78 ± 2.41	n.a.	n.a.
H (%)	1.60 ± 0.08	1.59 ± 0.05	n.a.	n.a.
N (%)	0.40 ± 0.01	0.65 ± 0.01	n.a.	n.a.
P_{TOT} * (mg kg^{-1})	2 153 ± 89	6197 ± 369	34 685 ± 488	196 ± 6
Cd	0.20 ± 0.01	0.21 ± 0.01	0.56 ± 0.02	9.60 ± 0.58
Cu	15.70 ± 0.85	21.00 ± 1.15	360.02 ± 10.54	104.19 ± 4.78
Pb	2.10 ± 0.15	0.80 ± 0.01	35.27 ± 2.47	1 607.40 ± 98.45

*P_{TOT} = total concentration of phosphorus

Both biochar amendments showed an alkaline reaction which was related to their production conditions and type of feedstock. Wood-based biochars tend to have a higher pH compared to other types of biomass such as crop residues or manures (GAL *et al.*, 2015). The values of AEC decreased in the order SS > AS > BC B > BC A. The very low ability of biochar-based amendments to exchange the anionic forms was caused by the negative character of the surface charges. The feedstock quality and content of mineral components (Ca, Na, Fe) can catalyse the formation of oxygen functional groups which are responsible for the negative charges of biochar-based amendments (GASKIN *et al.*, 2008). For the increase of AES, surface modifications with certain Fe- or Al-oxides, -hydroxides or -chlorides may be effective (MORENO-JIMÉNEZ *et al.*, 2012; ZHANG and GAO, 2013). The determination of SA values confirmed the more porous character of biochar materials compared to sewage sludge.

The parameter SA is crucial for assessing the volume and distribution of micro- and mesopores in carbon-based material (GALAMBOŠ *et al.*, 2015). The determination of selected PTHM (Cd, Cu and Pb) revealed 20 times higher total concentrations in municipal sewage sludge and 85 times higher concentrations in the studied soil compared to biochar-based amendments. The high level of PTHM in the soil sample AS was related to the specific sampling site that was located in an area of historic mining and ore processing. Similar results were described by HORAK and FRIESL-HANL (2007). The determination of total P confirmed phosphorus deficiency in AS soil. The concentration of P in potential amendments increased in the order BC A < BC B < SS. Our analysis confirmed that sewage sludge as a heterogeneous mixture of chemical substances including plant nutrients represents a phosphorus-rich material with a potentially fertilizing effect.

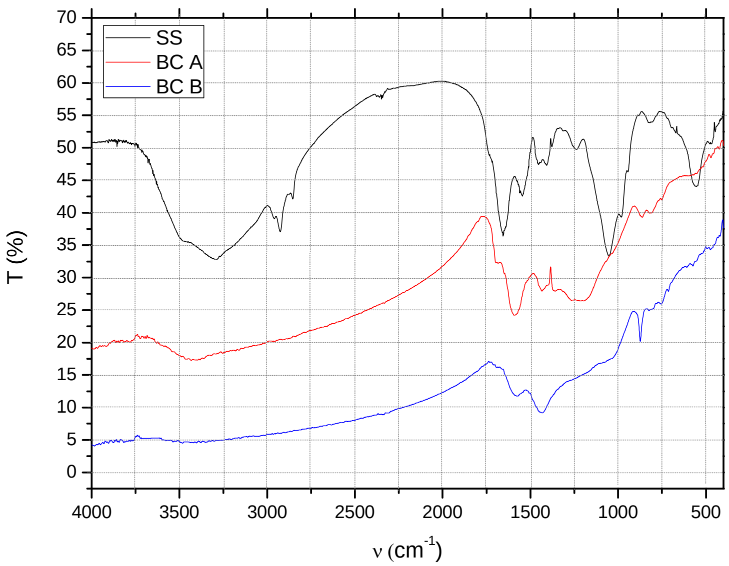

Fig. 2. FT-IR spectra of BC A, BC B and SS.

The spectral analysis in the infrared region belongs to the most important structural qualitative and semiquantitative analyses (DE LA ROSA *et al.*, 2014). FTIR spectra of BCA, BCB and SS (Fig. 2) showed typical shape and peaks of functional groups. The spectrum of SS compared to biochars is more complicated, reflecting the complex character of dried sludge biomass obtained from the activation tank of a municipal WWTP. Despite the complexity of spectra some characteristic peaks can be recognized that reflect the relative concentration of functional groups. The shape and position of wide peaks at σ 3 295 cm^{-1} for SS and at 3 420 cm^{-1} for BC A represent self-associated –OH groups. This peak was not recognized in BC B spectrum. Narrow peaks at σ 2 930 cm^{-1} and 2 812 cm^{-1} are due to C-H stretching vibration in CH, CH_2 and CH_3 functional groups in SS sample. Strong peaks in the vicinity of σ

1 650-1 695 cm^{-1} and 1 550-1 530 cm^{-1} were attributed to asymmetric and symmetric stretching vibration of C=O, C-C and C-N groups in BCA, BCB and SS. The broad peak at σ 1 045 cm^{-1} reflects the C-H bending in the sludge amendment. Similar peaks were recognized and in detail described in study of FRIŠTÁK *et al.* (2014a) and DE LA ROSA *et al.* (2014).

3.2 Effect of soil amendments incorporation

The short-term incubation experiments after incorporation of 1 % and 5 % (w/w) BC A, BC B and SS amendments into soil AS led to significant differences in physico-chemical properties and structural characteristics of the substrate (Table 2-3). Pedological analyses revealed a decrease of soil pH in the order superphosphate > SS > BC A + SS > BC B + SS > BC A > BC B for both application rates.

Table 2. Physico-chemical characteristics of amended soil with 1 % (w/w) BC A, BC B, SS, BC A+SS, BC B+SS and SP after short-term incubation (14 d, 19 °C, 65 % water content, greenhouse conditions). Intervals denote standard deviations (n=4).

	BCA	**BCB**	**SS**	**BCA+SS**	**BCB+SS**	**SP**
pH_{act}	6.61 ± 0.01	6.64 ± 0.00	6.30 ± 0.02	6.58 ± 0.01	6.60 ± 0.02	6.18 ± 0.01
pH_{pot}	5.61 ± 0.01	5.79 ± 0.02	6.08 ± 0.02	5.61 ± 0.00	5.64 ± 0.02	5.42 ± 0.02
EC (mS cm^{-1})	0.06 ± 0.00	0.07 ± 0.00	0.05 ± 0.00	0.08 ± 0.00	0.11 ± 0.01	0.18 ± 0.01
AEC (cmol kg^{-1})	0.99 ± 0.01	0.98 ± 0.02	1.59 ± 0.02	1.12 ± 0.01	1.19 ± 0.00	1.08 ± 0.03
SA (m^2 g^{-1})	22.45 ± 0.65	26.74 ± 0.45	18.58 ± 0.21	20.12 ± 0.38	23.87 ± 0.44	18.41 ± 0.41
P_{TOT} * (mg kg^{-1})	205 ± 8	219 ± 5	498 ± 5	364 ± 4	381 ± 4	822 ± 9
∑ PTHM **(mg kg^{-1})	1 721	1 721	1 739	1 727	1 728	1 721

*P_{TOT} = total concentration of phosphorus
** ∑ PTHM = Cd_{TOT} +Cu_{TOT}+Pb_{TOT}

An increase of soil alkalinity following biochar amendment has been reported for many soil types (FARRELL *et al*., 2014; STEWART *et al*., 2013; XU *et al.,* 2013). As mentioned before, this effect is due to the alkaline character of biochar because of the presence of negatively charged phenolic, carboxyl and hydroxyl functional groups on surfaces (BREWER *et al*., 2012). These groups create active sites for binding H^+ ions from soil solution and increase alkalinity of soil matrix. Additionally STEWART *et al.* (2013) described the significant role of biochar composition such as carbonates and silicates in binding and removal of H^+ ions from soil solutions. Our study confirmed the positive effect of BC A and BC B on SA values of amended soils caused by the porous character of amendments. Municipal sewage sludge as a soil amendment decreased values of soil pH but on the other side increased AEC. Generally, the composition of sewage sludge from municipal WWTP is variable concerning their chemical and biochemical components (ŠUŇOVSKÁ *et al.*, 2013); this can result in higher concentrations of exchangeable anions compared to pyrolysis products. Additionally, soil samples amended by SS showed an increase of total P but also in selected PTHM concentrations. This fact is very often the limitation for the deployment of sewage sludge in agricultural soil management. For this reason we investigated the potential effect of mixed biochar/sewage sludge additives.

Table 3. Physico-chemical characteristics of amended soil with 5 % (w/w) BC A, BC B, SS, BC A+SS, BC B+SS and SP after short-term incubation (14 d, 19 °C, 65 % water content, greenhouse conditions). Intervals denote standard deviations (n=4).

	BCA	**BCB**	**SS**	**BCA+SS**	**BCB+SS**	**SP**
pH_{act}	6.72 ± 0.02	6.92 ± 0.02	6.39 ± 0.03	6.62 ± 0.01	6.62 ± 0.02	6.16 ± 0.00
pH_{pot}	5.72 ± 0.01	6.13 ± 0.01	6.12 ± 0.01	5.70 ± 0.02	6.12 ± 0.05	5.32 ± 0.02
EC (mS cm^{-1})	0.09 ± 0.0	0.13 ± 0.01	0.09 ± 0.00	0.08 ± 0.01	0.12 ± 0.01	0.48 ± 0.02
AEC (cmol kg^{-1})	0.95 ± 0.01	0.92 ± 0.04	1.98 ± 0.12	1.19 ± 0.04	1.24 ± 0.09	1.02 ± 0.04
SA (m^2 g^{-1})	22.45 ± 1.55	26.74 ± 1.01	19.68 ± 1.17	21.04 ± 0.98	23.41 ± 0.91	18.49 ± 0.28
P_{TOT} * (mg kg^{-1})	253 ± 14	321 ± 9	1 525 ± 87	621 ± 17	649 ± 24	1031 ± 61
∑ PTHM ** (mg kg^{-1})	1 735	1 737	1 826	1 801	1 803	1 720

* P_{TOT} = total concentration of phosphorus
** ∑ PTHM = Cd_{TOT} +Cu_{TOT}+Pb_{TOT}

Mixed amendments of both biochar types and sewage sludge in both application rates showed a significant increase of total P concentrations compared to biochar only. On the other hand application of 1 % or 5 % BC A + SS and BC B + SS decreased the total PTHM concentration in comparison with single SS amendment. However, for better assessment of this effect the extractable and available forms of P and PTHM were quantified.

Application of 4 different extraction agents (Calcium-Acetate-Lactate (CAL), deionized water (DW), Mehlich 3 (M3) and Olsen (OL) extraction mixture) revealed differences in the labile and removable fractions of phosphorus in the amended soil samples. For all extraction protocols the same trend was confirmed (Fig. 3, 4). Extractable P concentration increased in the order BC B < BC A < control < BC B + SS < BC A + SS < SS < SP for both application rates.

For better explanation of the obtained results about the effects of the main soil characteristics on total and available P concentrations, a correlation analysis was performed. In the case of BC A amendment the Pearson correlation coefficients calculated at α = 0.05 (Tab. 4) showed a statistical significance for the positive correlation of total P with EC and a negative correlation with AEC, SA and available Σ PTHM, obtained by $CaCl_2$ extraction.

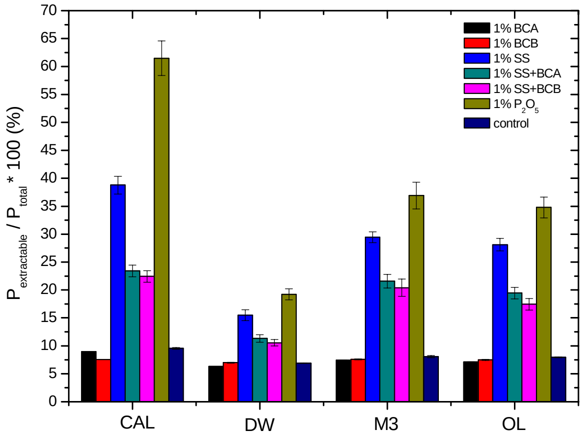

Fig. 3. Labile fractions of P extracted by Calcium-Acetate-Lactate (CAL), deionized water (DW), Mehlich 3 (M3) and Olsen (OL) extraction protocols from Arnoldstein soil amended with 1 % BC A, BC B, SS, BC A + SS, BC B + SS and SP (P_2O_5). The error bars show the mean of standard deviation (n=4).

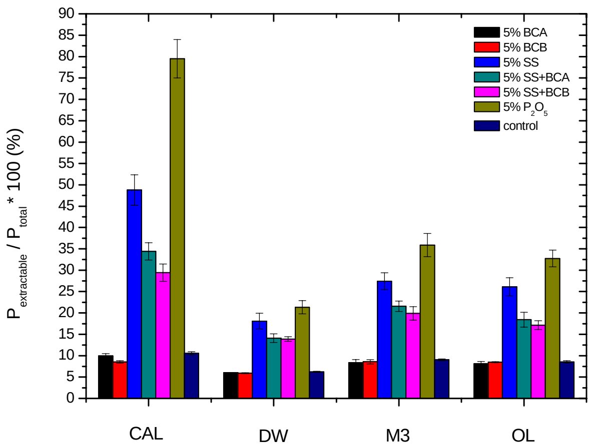

Fig. 4. Labile fractions of P extracted by Calcium-Acetate-Lactate (CAL), deionized water (DW), Mehlich 3 (M3) and Olsen (OL) extraction protocols from Arnoldstein soil amended with 5 % BC A, BC B, SS, BC A + SS, BC B + SS and SP (P_2O_5). The error bars show the mean of standard deviation (n=4).

For soil samples amended by BC B, the positive correlation between total P and EC was significant. Similarly to BC A, also for BC B a significantly negative correlation between total P and available Σ PTHM was confirmed. SS as a soil amendment showed significances of the positive correlations between total P and EC, total P and total Σ PTHM and also P total and available Σ PTHM. Additionally, also the positive correlation of available P with total Σ PTHM and available Σ PTHM was significant. Soil samples amended with mixed BC A/SS and BC B/SS exhibited a positive correlation between total P and total Σ PTHM and a negative one between total P and available Σ PTHM. For superphosphate fertilizer as soil amendment there was a significantly positive correlation between total P and EC.

Table 4. Pearson correlation coefficients (r) between soil characteristics (A - pH, B - EC, C - AEC, D - SA, E - ∑ PTHM (Cd_{TOT} +Cu_{TOT}+Pb_{TOT}), F - 0.01 M $CaCl_2$ extractable ∑ PTHM) and total and available phosphorus content in amended soil samples. Level of significance α = 0.05.

	A	B	C	D	E	F
BCA						
P_{TOT}*	0.41	**0.95**	**-0.86**	**-0.95**	0.23	**-0.96**
P_{AVAIL}**	0.57	0.76	-0.78	-0.63	0.31	-0.63
BCB						
P_{TOT}*	0.42	**0.88**	-0.57	-0.67	0.26	**-0.92**
P_{AVAIL}**	0.53	0.73	-0.28	-0.55	0.36	-0.53
SS						
P_{TOT}*	0.48	**0.87**	-0.17	-0.45	**0.98**	**0.89**
P_{AVAIL}**	0.37	0.38	-0.13	-0.37	**0.95**	**0.98**
BCA+SS						
P_{TOT}*	0.54	0.58	-0.78	-0.69	**0.87**	-0.48
P_{AVAIL}**	0.51	0.14	-0.71	-0.68	0.81	-0.42
BCB+SS						
P_{TOT}*	0.62	0.60	-0.81	-0.78	**0.88**	**-0.89**
P_{AVAIL}**	0.60	0.59	-0.80	-0.79	0.80	-0.58
SP						
P_{TOT}*	0.74	**0.89**	0.12	0.18	0.41	0.23
P_{AVAIL}**	0.78	0.77	0.11	0.21	0.32	0.23

* P_{TOT} –total concentration of phosphorus in soil samples
** P_{AVAIL} – CAL-extractable concentration of phosphorus in soil samples

The obtained results showed the relations between increasing P levels and decreasing levels of available PTHM when mixed biochar/sewage sludge amendments were applied. ZHAO *et al.* (2014) highlighted the effect of maize straw-derived biochar on soil phosphorus leaching from amended Alluvial and Red soils. The authors confirmed the increase of labile forms of soil P after biochar incorporation and short-term incubation. On the other hand, the application of a single woody biochar amendment could improve soil P retention that in parallel decreased the eutrophication risk to aquatic system (ZHANG *et al.*, 2014). LAIRD *et al.* (2010) also showed the reducing effect of a typical wood-derived biochar to migrations of soil nutrients in typical Midwestern agricultural soils. However, for detailed assessments of the biochar effect on soil P levels in terms of feedstock material, feedstock pre-treatment, combinations of feedstocks, processing conditions, and biochar application rates further studies will be required.

4. Conclusions

This paper illuminates the utilization of biochar as a potential tool for soil phosphorus management. In short-term incubation conditions, the application of woody biochar, sewage sludge from municipal waste water treatment plants and its mixtures with a studied soil could significantly alter the soil physico-chemical characteristics and available P levels. Our study confirmed the applicability of two types of biochar (wood chips-derived biochar and garden residues-derived biochar) for reducing leachable phosphorus and for decreasing eutrophication risk. The combinations of biochar and sewage sludge used as soil amendments confirmed their ability to increase soil P levels and to decrease heavy metal availability.

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