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Ability of Biochar to Modify Availability of Soil Nutrients

Schopnost biocharu regulovat podíl dostupných živin v půdě

Doctoral dissertation work

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Declaration

Declaration

I declare that this diploma thesis work **Ability of Biochar to Modify Availability of Soil Nutrients** is my own work and all the sources cited here are listed in the References.

Prague, 2021

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Niguss Solomon Hailegnaw

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1. Introduction

The use of biochar, which is byproduct from energy plant and/or from sewage handling and/or biochar primarily produced for agriculture purpose to improve soil fertility is highly affected by two most important biochar factors; feedstock used for biochar production and pyrolysis conditions (Ok et al., 2015). Biochar can be of animal origin (poultry litter, swine litter or cow manure, slaughterhouse waste, etc.) or plant origin of any agricultural residue and forest waste. The production temperature could differ from very low 200 °C to very high above 700 °C.

The capability of biochar to mitigate global warming, improve degraded soil, prevent loss of nutrients in soils, serving as a source of nutrients for plants and its benefit as an efficient way of bio-waste handling urges the study of biochar to be all-inclusive (Meyer et al., 2011). One of the major contributor of global warming is the release CO_2 (Gupta et al., 2020). Based on the estimation of Woolf et al. (2010), the wide use of biochar could mitigate around 12% of the total CO_2 emission per annum. This is mainly attributed due to the recalcitrant nature of biochar carbon, which have very low rate of returning to the atmosphere and its additional use as renewable energy source. Further, the second contributor of greenhouse gasses (N_2O) is mainly released from agriculture due to the application of organic and inorganic nitrogen fertilizers to the soil. However, biochar has shown to decrease emission of N_2O by 54% in both field and laboratory studies (Cayuela et al., 2014). The adsorption of NO_3^- and NH_4^+ by biochar can result in the reduction of N_2O emission by biochar (Van Zwieten et al., 2014). Depending on the type of feedstock used and production temperature; biochar is known to decrease and increase soil pH, cation exchange capacity, dissolved organic carbon (DOC), inorganic nitrogen (both NO_3^- and NH_4^+). For example (Jien and Wang, 2013) reported an increment of soil pH after application of biochar with pH value of 9.94 to soil with pH value of 3.95, while (Shenbagavalli and Mahimairaja, 2012) reported decline in soil pH after the application of biochar having pH value of 7.57 to soil with pH value of 8.42. Both the increment and decline of soil cation exchange capacity (CEC) was presented when biochar applied to soil (Prommer et al., 2014; Jien and Wang, 2013). The mineralization, immobilization and nitrification of nitrogen and adsorption of both NO_3^- and NH_4^+ has been also reported (Martos et al., 2020; Jiang et al., 2020; Qin et al., 2020; Clough et al., 2013).

Soil degradation due the repeated use of land for agricultural production has imposed greater challenge to sustain crop production. Generally, acidic pH, low fertility, low nutrient retaining capacity are the major characteristics of degraded soils (Jien and Wang, 2013). However, biochar is known to release considerable amount of nutrients, has ability to retain nutrients (and serve as the slow release fertilizer), increase soil pH, to increase soil cation exchange capacity, improve microbial activities and increase soil water holding capacity (Aamer et al., 2020; Jiang et al., 2020; Lehmann and Joseph, 2015). The necessity of avoiding ground water contamination from wastewater containing both organic and inorganic contaminants initiate the need of wastewater treatments and this producing sewage sludge, which needs further safe handling. Sewage sludge contains wide range of contaminants such as risk elements, polycyclic aromatic hydrocarbons (PAHs) (Cai et al., 2007), pharmaceuticals (Radjenović et al., 2009), personal care products (McClellan and Halden, 2010). However, the conversion of sewage sludge to biochar has shown to reduce the concentrations of the organic pollutants in great extent. For example, the production of biochar from sewage sludge at 600 °C were able to remove 99.8% of polychlorinated biphenyls, polycyclic aromatic hydrocarbons and pharmaceuticals (Moško et al., 2021).

The above all mentioned events are expected to cause an increment of biochar production in the near future. However, the studies working on the effect of specific biochar on properties of soils with wide range of original properties is lacking. Therefore, it is important to consider a wide range of soil with varied properties in the study of biochar effect and screen soils according to their response to biochar application for the further application of biochar at the field level.

2. Literature Review

2.1. Biochar

Biochar is a carbonaceous material resulting from biomass pyrolysis under either very low presence or total absence of oxygen. Biochar feedstock, which refers the material used to produce biochar may include organic material like forestry wastes (woodchips, sawdust, etc.), crop residues, animal manures, household waste, urban yard waste, industrial byproducts, or sewage sludge. In the case of sewage sludge, the potential contamination of this material by risk elements should be taken into account (Duku et al., 2011).

Biochar from the same feedstock but different production condition (pyrolysis temperature, heating rate, heating time and particle size) may produces different biochar yield with varied properties (Williams and Besler, 1996). Biochar yield is directly related to particle size and lignin content of feedstock material. For example, the yield of biochar from olive husks (high lignin contained material) was higher than the biochar prepared from corncobs (Demirbas, 2004). It was again confirmed that, the pyrolysis of herbaceous rice straw results in high biochar yield with unique chemical properties as compared to woody material (Jindo et al., 2014). As that of biochar yield physico-chemical property of biochar is also dependent on both pyrolysis condition and type of biomass used for biochar production (Demirbas, 2004). Thus, biochar from different feedstock and production conditions (residence time, temperature, heating rate and reactor type) are different in physico-chemical properties and it is difficult to generalize their chemical composition. It is proved that biochar produced from the same feedstock under different pyrolysis temperature could produce biochar of very different properties (Lehmann and Joseph, 2015).

Most often the higher the temperature and the higher heating rate of biochar production will result in lower biochar yield (Demirbas, 2004; Zhao et al., 2017; Cao and Harris, 2010: Keiluweit et al., 2010). For example, Zhao et al. (2017) showed that biochar yield clearly decreased as biochar production temperature increased from 300 to 600 °C (Table 1).Similarly, the substantial reduction in biochar yield after the production of biochar from pine wood shavings and tall fescue grass, respectively (Table 1), was explained by the increment of biochar production temperature from 100 to 700 °C (Keiluweit et al., 2010).

Table 1. The fluctuation of biochar yield and biochar properties under growing pyrolysis temperature.

Biochar production temperature (°C)		**100**	**200**	**300**	**400**	**500**	**600**	**700**	**800**	
Biochar yield (%)	ATBB	-	-	47.9	35.5	31.7	28.5	-	-	(S.-X. Zhao et al., 2017)
	PWSB	99.8	95.9	62.2	35.3	28.4	23.9	22.0	-	(Keiluweit et al., 2010)
	TFGB	99.9	96.9	75.8	37.2	31.4	29.8	28.8		(Shen et al., 2020)
	PM	-	-	67.5	54.1	50.0	49.4	43.4	-	
pH (H_2O)	ATBB	-	-	-	7.02	9.64	10.0	10.0	10.0	(Jindo et al., 2014)
	OTB	-	-	-	6.43	8.10	9.54	8.85	9.68	
	RHB	-	-	-	6.84	8.99	9.41	9.52	9.62	
	RSB	-	-	-	8.62	9.82	10.2	10.4	10.5	
	PM	-	-	8.43	9.5	9.77	10.1	11.0	-	(Shen et al., 2020)
Carboxyl groups (mmol g^{-1})	WRB	-	-	0.74	0.35	0.20	0.16	0.17	0.10	(Chun et al., 2004)
Acidic functional groups (mmol g^{-1})	WRB	-	-	2.83	1.13	0.42	0.35	0.30	-	
Base functional groups (mmol g^{-1})	WRB	-	-	0.04	0.11	0.19	0.26	0.29	-	
Surface area (m^2 g^{-1})	WRB	-	-	116	189	309	438	363	-	

Feedstock materials

ATBB: apple tree branches biochar
PWSB: pine wood shavings biochar
TFGB: tall fescue grass biochar
OTB: oak tree biochar
RHB: rice husk biochar
RSB: rice straw biochar
WRB: wheat residue biochar
PM: pig manure

The detailed molecular and structural changes of feedstocks (plant biomass), biochar yield, volatile matter and non-volatile matter with increasing production temperature are presented on Fig 1a and 1b (Keiluweit et al., 2010). The results clearly demonstrate the decline in biochar yield as production temperature increases from 250 to 300 °C and above production temperature of 500 °C biochar yield remains constant.

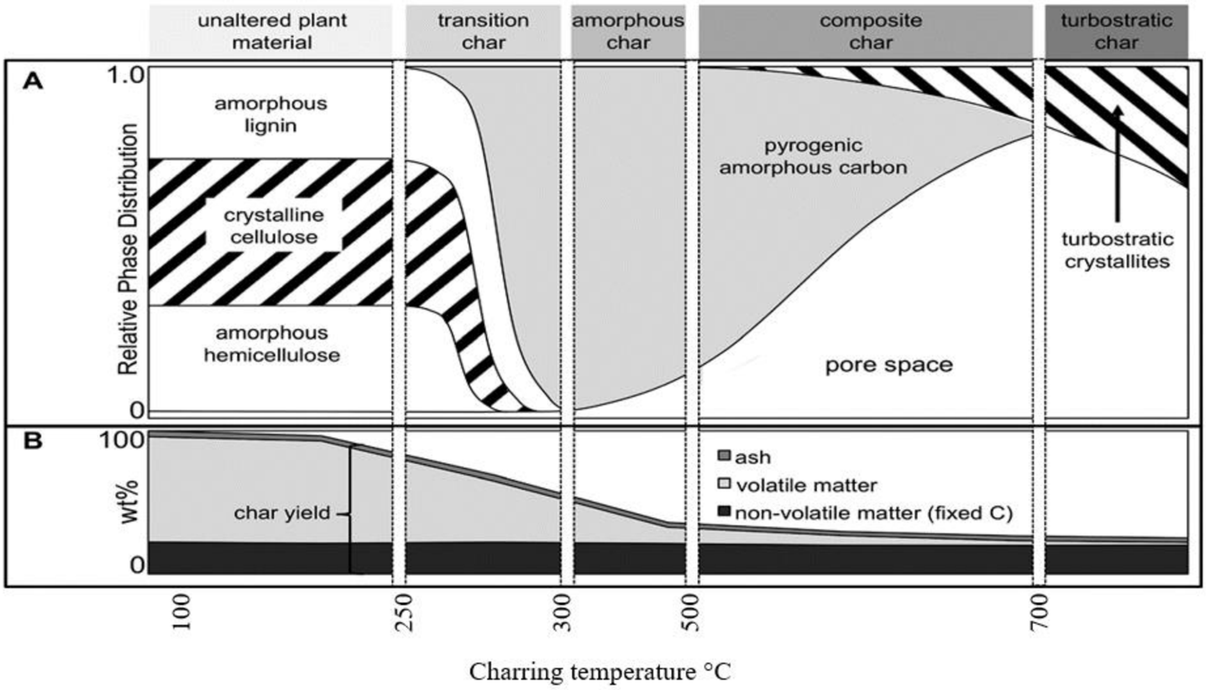

Figure 1. Dynamic molecular structure changes in plant biomass and plant biomass–derived biochar. (a) Physical and chemical characteristics of organic phases. (b) Char composition as inferred from thermogravimetric analysis (Keiluweit et al., 2010).

At the first stage of pyrolysis, there would be only the loss of water and initial dehydration reactions preserving the chemical structures of the original feedstock used for the biochar production. At the stage of transition char phase, there would be dehydration and depolymerization of plant biopolymers. At the transition stage, which is nearly from 230 – 290 °C formation of aldehydes and ketones will be dominating due the dehydration biomass and decompositions of polysaccharides and long-chain aliphatic compounds (Zhang et al., 2020). The formation of labile C, volatile organic carbon and boxyl C is also evident at this stage. At the third phase (aromatic biochar), there would be the increased aromatic C contents of biochar. The fourth stage (amorphous phase of biochar) is characterized by high degree of condensation and formation of turbostratic crystallites. The last phase of biochar production (graphite biochar) is known by the production of turbostratic biochar due to increased condensation of aromatic component of biochar.

2.1.1. Biochar pH

Biochar pH values could vary from 4 to 12 depending on feedstock used and production conditions (Cao and Harris, 2010). Various studies (Guo et al., 2020; Liu et al., 2020; Jindo et al., 2014 and Shen et al., 2020) clearly showed increasing soil pH with the rising pyrolysis temperature (Table 1). The increment in biochar pH is registered with an increment of biochar production temperature from 200 to 500 °C (Cao and Harris, 2010). The increment in biochar pH with growing production temperature was also observed on four biochars produced from peanut hull, pecan shell, poultry litter and switchgrass (Novak et al., 2009). Similarly, Gray et al., (2014) reported the increment in pH of two biochars produced from hazelnut shells and douglas fir chips as production temperature increased from 370 to 620 °C. This the main reason for the increment of biochar pH with biochar production temperature is potentially due to the increased biochar ash content, which is source of base cations at higher biochar production temperature (Břendová et al., 2012). Carbonates are reported as the main sources of biochar alkalinity at higher production temperature, while functional groups like $-\mathrm{COO}^- \ (-\mathrm{COOH})$ and $-\mathrm{O}^-(-\mathrm{OH})$ are responsible for the alkalinity at lower production temperatures (Yuan et al., 2011). An increment in pyrolysis temperature could generally result in the increment of biochar ash content and this increases total biochar alkalinity (Suliman et al., 2016). Feedstock used for biochar production have also significant effect on pH of biochar produced at the same production temperature. From this regard, Novak et al. (2009) found higher pH in poultry litter biochar compared to biochar produced from plant origin at the same temperature. This is again due to the presence of high level of ash content in poultry litter from 24 – 52% at 400 and 500 °C, respectively compared to very low ash content, which was less than 10% in plant origin (such as peanut hull, pecan shell and switchgrass in this case) biochar (Novak et al., 2009).

2.1.2. Cation exchange capacity of biochar

The total capacity of biochar to retain and exchange positively charged ions could be considered as CEC of biochar (Carrier et al., 2012). The main sources of biochar CEC are surface oxygenated functional groups (carboxylic, phenolic and lactonic) and high surface area (Suliman et al., 2016;Li et al., 2018). On top of that negative surface charge of biochar (due to negatively charged acid functional groups), high charge density of biochar and the release of surplus content of Ca^{2+} from biochar contributes for the CEC of biochar (Liang et al., 2006). As that of biochar pH, feedstock used and production temperature highly affects biochar CEC (Table 2). It is also very true that herbaceous plant materials have comparably higher CEC than hard wood materials. This is due to the reason that lignocellulose fragment of herbaceous or grassy feedstock are oxidized efficiently and cycloreversion oxidation occurs more rapidly than hard wood to form carboxylic acids (Harvey et al., 2012). Manure based biochar has higher cation exchange capacity than wood based biochar (Singh et al., 2010). Biochar, which was produced from switch grass under fast pyrolysis condition was found to have low surface area between 7.7 $\mathrm{m^2g^{-1}}$ and 7.9 $\mathrm{m^2g^{-1}}$, resulting in the reduction of biochar ability to retain cations (Boateng, 2007).

Table 2. Fluctuation of CEC with biochar feedstock and production temperature

Biochar production temperature (°C)		**250**	**350**	**450**	**550**	**700**	
CEC (mmol$_+$ kg^{-1})	PMB	103	157	145	138	80	(Mandal et al., 2018)
	GWB	115	69	66	47	34	
	SCB	-	280	200	166	169	(Conz et al., 2017)
	RHB	-	158	166	171	165	
	PLB	-	320	203	106	105	
	SDB	-	207	113	86	91	

Feedstock materials

PMB: poultry manure biochar
GWB: green waste compost biochar
SCB: sugarcane straw biochar

RHB: rice husk biochar
PLB: poultry litter biochar
SDB: sawdust biochar

CEC of biochar potentially increases with increment of pyrolysis temperature up to 550 °C, while above 550 °C the CEC of biochar start to decline with an increment in the pyrolysis temperature (Table 2). For example, from Table 2 we can clearly observe that the production of biochar at 350 °C resulted in higher CEC as compared to biochar produced at 700 °C in all feedstock except rice husk. The optimum biochar production temperature range for moderate and/or high CEC of biochar is production temperature in the range between 250 – 550 °C (Harvey et al., 2012). Yuan et al. (2011) documented that the exchangeable base cations content of biochar produced from four feedstock's (canola straw, corn straw, soybean straw and peanut straw) increased as pyrolysis temperature increased from 300 to 700 °C, which consequently increase CEC of biochar. The main source of CEC at lower temperature are oxygen containing functional groups (carbonyl, carboxyl and hydroxyl groups, etc.) and they are reported to be gradually removed as pyrolysis temperature increases (Yuan et al. 2011; Chun et al. 2004).

2.1.3. Anion exchange capacity

Opposite to CEC of biochar, very little is known about anion exchange capacity (AEC) of biochar. In some studies, it was almost unable to detect AEC of biochar. For example, Mukherjee et al. (2011) observed that AEC of biochar near to neutral pH was close to zero on biochars produced from oak (*Quercus lobata*), pine (*Pinus taeda*) and grass (*Tripsacum floridanum*) at 250, 400 and 650 °C. On the contrary, Lawrinenko and Laird (2015) found AEC of maize stover, cellulose, alfalfa meal, and albumin at 500 and 700 °C ranging from 6 to 278 mmol kg^{-1}. Biochar produced at higher temperature 700 °C in their case always acquired higher AEC than biochar produced at lower production temperature 500 °C of the same feedstock. They were also able to observe the effect of biochar pH on AEC of biochar, where the decline in pH of biochar resulted in the increment of biochar AEC. On average AEC of biochar was 25, 74 and 180 mmol kg^{-1} at the pH values of 8.0, 6.0 and 4.0, respectively. The main source of AEC of biochar are pyridinium groups, oxonium groups and protonated aromatic rings (Lawrinenko and Laird, 2015). Pyridine have pKa value of 5.2 and the aromatic carbon in the pyridinic groups in the same range. This indicates that the equilibration of biochar pH value to 4 can result in the protonation of pyridine and aromatic carbon contributing to AEC, while at pH value of 8 pyridine groups and aromatic carbon should deprotonate and could not contribute for AEC. At pH value of 8 the oxonium heterocycles, which carry pH independent positive charge could contribute for AEC of biochar (Lawrinenko and Laird, 2015).

2.1.4. Sorption property of biochar

The next unique property of biochar is its sorption property. Biochar is able to sorb both inorganic contaminants like risk elements and organic contaminants like benzene and nitrobenzene (Chun et al., 2004; Li et al., 2017). The major mechanisms of metals sorption by biochar include complexation, cation exchange, precipitation, electrostatic interaction, and chemical reduction. The sorption of benzene and nitrobenzene by high temperature biochar is mainly linked to the surface adsorption on carbonized surface of biochar and at low temperature due to surface sorption and smaller portion by residual organic-matter phase of biochar (Li et al., 2017). The sorption property of biochar could be affected by physicochemical properties of biochar such as surface area, porosity, pH, surface charge, functional groups and mineral content. Micropores could be formed during the dehydration phase of pyrolysis. The increment in biochar production temperature leads to large number of pores and this increase surface area of biochar (Li et al., 2017). Porosity of the biochar increased from 0.056 to 0.099 cm^3 g^{-1} and surface area from 25.4 to 67.6 m^2 g^{-1} due to the increase in biochar production temperature 500 to 900 °C (Chen et al., 2014). The increment in porosity of biochar due to production temperature can be also clearly seen on Fig 1a (Keiluweit et al., 2010). The increment in surface area of biochar as pyrolysis temperature increase from 300 to 600 °C and slight decline at temperature of 700 °C, as evident from the Table 1 (Chun et al.2004). Surface area of manure biochar increases as production temperature increases from 200 to 500 °C (Cao and Harris, 2010). In other study both surface area and porosity of biochars produced from two feedstock (hazelnut shells and Douglas fir chips) increased as the production temperatures increases from 370 °C to 500 °C, and to 620 °C (Gray et al., 2014).

2.1.5. Nutrient content of biochar

Similar to other properties of biochar, nutrient content of biochar is also highly variable depending on the feedstock used for biochar production and pyrolysis conditions. Depending on feedstock used biochar organic portion is high in carbon, while inorganic portion (ash) contains elements such as Ca, K, Mg and inorganic carbonates (Lehmann and Joseph, 2015). Carbon content of biochar usually ranges between 172 $g\ kg^{-1}$and 905 $g\ kg^{-1}$, nitrogen 1.8 $g\ kg^{-1}$ to 56.4 $g\ kg^{-1}$, total phosphorous 0.2 $g\ kg^{-1}$ to 73 $g\ kg^{-1}$ and total potassium 1.0 $g\ kg^{-1}$ to 58 $g\ kg^{-1}$, varying with the type feedstock used for biochar production Lehmann and Joseph, (2015). The link between nutrient content of feedstock and the subsequent content in biochar documented also Yuan et al. (2011). Based on their finding's biochar produced from feedstock with high amount of specific nutrient was able to produce biochar rich in that specific nutrient. For example, high content of P in peanut straw compared to canola straw, corn straw and soybean straw resulted in much higher P content in peanut straw biochar than the rest three biochar. The effect of feedstock used for biochar production was particularly magnificent on biochar content of N and P. Biochar produced from animal origin (sewage sludge and broiler litter) had higher total P and N content as compared to plant origin (wood, green waste) biochar. Biochar produced from manure was rich in N, P, Ca, Mg and K (Cao and Harris, 2010). There is also higher concentration of N and P in wastewater sludge biochar.

On the other side, even if feedstock is highly linked to nutrient content of biochar, the temperature of pyrolysis also have a significant effect. Biochar produced at lower charring temperature is characterized by high content of easily decomposable substrates as compared to biochar produced at higher temperature. Low charring temperature helps biochar to retain volatile and labile compounds (Jindo et al., 2014). An increment in temperature also caused smaller, less structured fragments of biochar with less O, H and aliphatic C functional groups, but increased aromatic carbon rings (Peng et al., 2011). The effect of biochar production temperature on the elemental and nutrient content of biochar is clearly presented in Table 3. The percentage of C increases, while the percentage of H and O decrease with the increment of biochar production temperature (Shen et al., 2020; Wang et al., 2020; Zhao et al., 2017; Keiluweit et al., 2010). Significant increment in percentage of K and P with production temperature, while stabilized amount of P above 500 °C was observed (Zhao et al., 2017). There was also significant increment in the content of Ca, Mg, Fe and Zn with production temperature of biochar. On the other side Mn and Cu content of biochar increase from production temperature of 300 to 500 °C, while declined at 600 °C (Zhao et al., 2017).

The increment in aromatic carbon rings of biochar with pyrolysis temperature decreases mineralization rate of C and this subsequently reduces the release of N, P and S bound on organic structure of biochar. In addition, content of N and C could decrease with increasing pyrolysis temperature due to volatilization. Decline in water-soluble P, Ca and Mg was reported at higher production temperature due to the crystallization of Ca-Mg-P and the formation of white-lockite $(\mathrm{Ca, Mg})_3(\mathrm{PO}_4)_2$ at temperature 500 °C and above (Cao and Harris, 2010).

Table 3. The elemental and nutrient content in biochar as affected by the pyrolysis temperature.

Biochar production temperature (°C)		**300**	**400**	**500**	**600**	**700**	
C (%)	ATBB	62.2	71.1	74.9	80.0	-	(Zhao et al., 2017)
	PWSB	54.8	74.1	81.9	89.0	92.3	(Keiluweit et al., 2010)
	TFGB	59.7	77.3	82.2	89.0	94.2	
	PM	36.0	30.5	28.1	28.9	27.9	(Shen et al., 2020)
H (%)	ATBB	5.18	4.03	2.88	2.72	-	(Zhao et al., 2017)
	PWSB	6.50	4.95	3.54	2.99	1.62	(Keiluweit et al.' 2010)
	TFGB	6.64	4.7	3.32	2.47	1.53	
	PM	3.53	2.25	1.42	0.86	0.81	(Shen et al., 2020)
N (%)	ATBB	1.69	1.94	1.77	1.28	-	(Zhao et al., 2017)
	PWSB	0.05	0.06	0.08	0.06	0.08	(Keiluweit et al. 2010)
	TFGB	1.02	1.24	1.09	0.99	0.70	
	PM	3.14	2.53	2.22	1.59	1.41	(Shen et al., 2020)
O (%)	ATBB	24.2	15.1	10.4	6.59	-	(Zhao et al.,2017)
	PWSB	38.7	20.9	14.5	8.0	6.0	(Keiluweit et al. 2010)
	TFGB	32.7	16.7	13.4	7.60	3.60	
	PM	10.7	7.5	3.6	2.24	4.43	(Shen et al., 2020)
K (%)	ATBB	0.57	0.89	1.1	1.14	-	(Zhao et al., 2017)
P (%)		0.21	0.28	0.34	0.34	-	
Ca (g kg^{-1})		12.9	16.8	20.2	20.9	-	
Mg (g kg^{-1})		3.01	4.04	4.69	5.64	-	
Fe (mg kg^{-1})		268	361	480	583	-	
Mn (mg kg^{-1})		56.9	79.3	103	89.4	-	
Cu (mg kg^{-1})		20.3	50.5	85.1	58.9	-	
Zn (mg kg^{-1})		33.1	53.3	60.5	61.1	-	

Feedstock materials:
ATBB: apple tree branches biochar
PWSB: pine wood shavings biochar
TFGB: tall fescue grass biochar
PM: pig manure

On the contrary, Yuan et al., (2011) reported the increment in total base cations, exchangeable base cations, soluble base cations, carbonate and total P on canola straw, corn straw, soybean straw and peanut straw biochar as production temperature increased from 300 to 700 °C. The main reason for these different results of these two studies could be the feedstock used. Cao and Harris (2010) tested the biochar of animal origin (cow manure) and Yuan et al. (2011) used four biochars of plant origin. This could indicate the strong effect of both feedstock and production conditions in determining properties of biochar. However, this relatively moderate nutrient content of biochar and improved soil properties after the addition of biochar alone could not make biochar suitable to fertilize soils due to very low content of plant available nutrients especially N and P. For this combination of biochar with mineral fertilizers and/or treatment of feedstock to boost biochar elemental content have been imperative (Xie et al., 2015).

Besides of the production temperature of biochar, holding time also had a significant impact on the biochar elemental composition (Table 4). The prolongation of biochar holding time at both lower and higher pyrolysis temperature could increase the content of C, while decreasing the content of H and O. (Wang et al., 2020).

Table 4. The effect of holding time on the elemental content of biochar produced from pig manure (adapted from Wang et al., 2020).

Pyrolysis temperature (°C)	**300**					**700**				
Holding time (min.)	**0**	**15**	**30**	**60**	**120**	**0**	**15**	**30**	**60**	**120**
C (%)	33.6	35.7	37.6	35.9	34.9	31.6	34.8	36.1	37.8	38.5
H (%)	4.60	3.80	3.60	3.30	3.20	0.90	1.00	1.00	1.10	1.00
O (%)	26.5	15.0	11.7	10.9	11.7	7.50	3.30	3.20	1.60	0.50
N (%)	1.90	2.00	2.10	2.00	2.00	1.50	1.50	1.40	1.40	1.40

2.2. Impact of biochar on agro-chemical properties of soil

Biochar is able to change both physical and chemical properties of soil. This ability of biochar could arise from its unique physio-chemical property (Sohi et al., 2010). Both properties of biochar used and soil amended with biochar determine degree and magnitude of biochar effect on soil properties (Haefele et al., 2011).

2.2.1. Soil pH

Application of biochar to soil could increase or decrease soil pH, the effect depends on both original pH of soil and pH of the biochar used. The application of biochar to soil with lower pH than applied biochar clearly increased soil pH (Aamer et al., 2020; Jiang et al., 2020; Jing et al. 2020; Cooper et al. 2020; Tang et al., 2020; Ronsse et al., 2013). Jien and Wang (2013) reported an increment of soil pH from 3.9 to 5.1 after application of wood biochar with pH of 9.94 to highly weathered soil. It is expected that the increment in pH of soil after biochar addition is simply the function of initial pH of both soil and biochar, keeping in mind many other factors affecting (organic carbon content of soils, soil content of Al^+, H^+, Ca^{2+}, K^+ and Mg^{2+}, soil minerals, soil texture etc.) the increment of pH (Xie et al., 2015).

For instance, the replacement of soil exchangeable $\mathrm{Al^{3+}}$ and $\mathrm{H^+}$ by base cations such as $\mathrm{Ca^{2+}}$ and $\mathrm{K^+}$ from biochar could result in the increment of soil pH (Masud et al., 2014). The binding of surplus soil solution $\mathrm{H^+}$ by negatively charged functional groups (phenolic, carboxylic and hydroxyl) present at the surface of biochar could also result in the increment of soil pH (Gul et al., 2015). The decarboxylation of organic anions after the addition of biochar due to the increased attack of organic anion by microbes could consume surplus $\mathrm{H^+}$ (according to the following equation) (Barekzai and Mengel, 1993) from soil solution and this result in the increment of soil pH.

$$\mathrm{R-CO-COO^- + H^+ \rightarrow R-CHO + CO_2}$$

In addition to decarboxylation of organic anions, the association of $\mathrm{H^+}$ ions with oxygen containing functional groups $(\mathrm{-COO-}, \mathrm{-C=O}, \mathrm{-OH-})$ and $\mathrm{CO_3^{2-}}$ of biochar could increase soil pH. Further biochar decreased soil $\mathrm{NO_x-N}$, which consume soil $\mathrm{H^+}$ and increase soil pH. Based on their report addition of wheat, rice and peanut biochar (pH = 7.1, 8.4, 9.2 respectively) to soil with pH value of 4.7 was able to decrease N cycle contribution to acidity by 0.12, 0.17 and 0.15 $\mathrm{cmol\ kg^{-1}}$ respectively (Wang et al., 2014). Shenbagavalli and Mahimairaja (2012) applied the *Prosopis* sp. biochar with pH value of 7.57 to soil with pH value of 8.42 and observed decreased soil pH to 7.92 at 90th day of incubation. The reduction was at all biochar application rates (1, 2, 3, 4 and 5 %) and all periods of incubation (30, 60 and 90 days). The main reason for the reduction in soil pH was the release of protons (H^+) from the exchangeable sites of biochar, proliferation of acid producing soil microorganisms and the production of organic acids during the decomposition of organic matter present in soils (Shenbagavalli and Mahimairaja, 2012).

2.2.2. Cation exchange capacity and exchangeable cations

Cation exchange capacity of soil refers to the ability of soil to retain weakly bound cations like ammonium, potassium, calcium, magnesium and others. This property of soil, which is very valuable, could be improved by application of biochar (Liang et al., 2006). Jien and Wang (2013) reported increment of soil CEC from 74.1 $mmol_{(+)}$ kg^{-1} to 9.26 and 108 $mmol_{(+)}$ kg^{-1} after application of 2.5 and 5 % biochar (with CEC of 223 $mmol_{(+)}$ kg^{-1}), respectively. Increment of CEC from 179 to 194.7 $mmol_{(+)}$ kg^{-1} after application of 5% biochar was also evident (Shenbagavalli and Mahimairaja, 2012). Effect of the same biochar on soil CEC and exchangeable cations may vary from soil to soil. For instance El-Naggar et al., (2018) has reported the high effectiveness of three biochar (amur silvergrass residue, paddy rice straw, and umbrella tree) in increasing both CEC and exchangeable cation contents of sandy soil with very low CEC and low exchangeable cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) compared to sandy loam soil.

The ability of biochar to increase soil CEC mainly arises from its high porosity, high surface, variable surface charges and the presence of oxygenated functional groups ($-COO-, -C=O, -OH-$) and CO_3^{2-} present on the surface of biochar (Glaser et al., 2002). The adsorption Al and Fe oxides and the reduction in soil point of zero charge can result in the reduction of soil CEC (Trakal et al., 2016). On the other hand, the deprotonation of functional groups from minerals like kaolinite could increase the development of greater surface negative charge and soil CEC (Sparks, 2003). Biochar induced soil pH increment in acidic soil may also raise soil CEC as biochar could make H^+occupied exchangeable site free (Atkinson et al., 2010). It has been suggested that at lower production temperature of biochar the presence of non-carbonized (un burned) organic matter is mainly responsible for the majority of CEC (Mukherjee et al., 2011). The highest increment in exchangeable K^+ as compared to other cations has been reported after application of three biochar types (amur silver grass residue, paddy rice straw, and umbrella tree) in two different soils and this was mainly due to the high amount of K^+ in all three biochars (El-Naggar et al., 2018).

2.2.3. Inorganic nitrogen stabilizattion/immobilization

The effect of biochar on soil N can be multidimensional. This means that biochar can induce or reduce ammonia volatilization, nitrogen sorption (Aghoghovwia et al., 2020), mineralization, immobilization (Horák et al., 2020), nitrification and increment in soil NO_3^--N (Jing et al., 2020b). The positive effect of biochar on mitigating ammonia volatilization, prevention of nitrous oxide emission, and reduction of nitrate leaching is clearly described in Fig 2 (Ok et al., 2015). Therefore, biochar could reduce ammonia NH_3 volatilization through sorption of NH_4^+ by surface functional groups and by adsorption into micro-pores of biochar. On the other hand, biochar could reduce nitrous oxide (N_2O) emission by adsorption of N_2O, complete denitrification to N_2, inhibition of nitrification, reducing denitrification by adsorption of NH_4^+ on the negatively charged surface of biochar and NO_3^- by base functional groups of biochar. The adsorption of NO_3^- by biochar could be due to base functional groups like chromenes, ketones and pyrones on biochar (Al-Wabel et al., 2018). In addition to this the unconventional H-bonding between NO_3^--N ions and the biochar surface could be responsible for the adsorption of NO_3^--N (Mukherjee et al., 2011). Biochar effect on soil inorganic nitrogen can vary from biochar to biochar. The variation of biochar effect in nitrogen mineralization and immobilization is due to the effect of feedstock used and pyrolysis temperature on biochar carbon content and its lability (Clough et al., 2013). For example, the high effectiveness of low temperature biochar in reducing volatilization of NH_3 from soil as compared to high temperature biochar is evident. Biochar produced at lower temperature could be more effective in reducing NH_3 loses by combination two mechanisms. The first one is through having low pH than high temperature biochar, where there will be low NH_3 volatilization after application of low temperature biochar due to lower pH as compared to high temperature biochar.

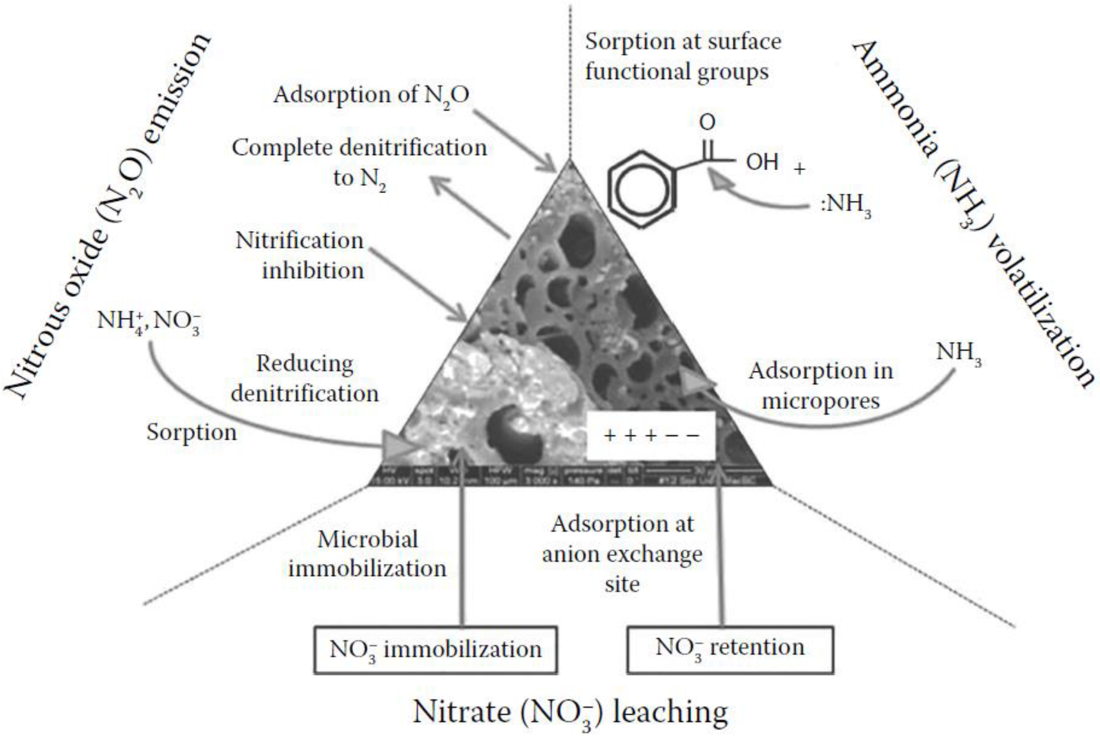

Figure 2. Schematic diagram of mechanisms for biochar-induced mitigation of nitrate leaching, ammonia volatilization and nitrous oxide emission (Ok et al., 2015).

The second mechanism could be through retaining N by its functional groups. This is because biochar produced at low temperature is rich in carboxylic, phenolic, amine and other functional groups, which are responsible for high CEC of biochar (Mandal et al., 2018). The effect of fast and slow pyrolysis wheat straw biochar has been compared for their consequent effect on mineral N (Bruun et al., 2012). In their findings biochar from slow pyrolysis resulted in facilitated mineralization, while fast pyrolysis biochar caused immobilization of mineral N. The main reason for the immobilization of N after the addition of fast pyrolysis biochar was due its labile and un-pyrolysed carbohydrate content. Biochar could also facilitate N mineralization due to its priming effect stimulating microorganisms to mineralize recalcitrant soil organic matter (Zimmerman et al., 2011).

Adsorption of $\mathrm{N-NO_3^-}$ by high temperature biochar has been reported in several studies (Kameyama et al., 2012, 2016; Yao et al., 2012). The adsorptive property of biochar depends on both production temperature and type of feedstock used. Biochar produced at high-temperature (600–700 °C) reported to have lower $\mathrm{N-NH_4^+}$ adsorption capacity compared to low temperature biochar (400–500°C) (Gai et al., 2014). This could be due to low polarity (low O/C ratio) and conversion of acidic functional groups on the biochar surface, especially in the carboxyl group to neutral or basic fused aromatic group after losing their oxygen-containing functional groups, which could reduce their $\mathrm{NH_4^+}$adsorption ability. Other study also indicated the decline in surface functional groups with negative charge $(\mathrm{-COO^-, -COH\ and - OH})$ at high production temperature, which could reduce sorption of $\mathrm{N-NH_4^+}$ and increase sorption of $\mathrm{N-NO_3^-}$ (Yuan et al., 2011). Yao et al. (2012) recorded 34% reduction in $\mathrm{NO_3^-}$ in leachate following the addition of biochar produced from pepperwood at 600 °C, and similarly addition of apple branch biochar at the rate of 2 and 4% reduced soil nitrate content, particularly in N-rich soils (Li et al, 2017). Biochar produced at lower temperature always had a higher CEC, implying the higher adsorption effect on $\mathrm{NH_4^+}$. Biochar with a CEC of 190–686 $\mathrm{mmol_{(+)}\ kg^{-1}}$ acquired higher $\mathrm{N-NH_4^+}$ sorption capacity than biochar with CEC of 3–85 $\mathrm{mmol_{(+)}\ kg^{-1}}$ (Gai et al., 2014). It is also evident that the type of feedstock used for biochar production could determine whether $\mathrm{N-NH_4^+}$ or $\mathrm{NO_3^-}$ to be predominantly adsorbed. As clearly reported by (Harvey et al., 2012), woody biochar exhibited less adsorption effects on $\mathrm{NH_4^+}$ in comparison to grassy biochar. This was mainly due to the higher concentration of carboxylic functional groups on the surface of grassy biochar than woody biochar, but the effect of soil itself on the effectiveness of biochar has been also reported. High effectiveness of biochar to reduce $\mathrm{N-NH_4^+}$ in coarse texture soils than medium textured soils was reviewed by Nguyen et al. (2017). On the contrary, the release of $\mathrm{N-NO_3^-}$ have been reported after the application of wheat straw biochar (450 °C) in a paddy rice field in very recent study (Jing et al., 2020b). Thus, this pattern could be due to the decomposition of organic carbon and the dissolution of minerals in the biochar.

2.2.4. Dissolved organic carbon

Both decline and increment in mineralization of C has been reported, the effect depending on both feedstock used and pyrolysis condition. For example the release DOC by biochar produced between pyrolysis temperature of 400 to 500 °C is reported (Uchimiya et al., 2013). Zimmerman et al., (2011) obtained higher C release in soil amended by low temperature pyrolysed biochar compared to high temperature pyrolysed biochar. In addition to this, they have noticed enhanced mineralization of C in biochar produced from grass than hardwood biochar. Magnitude and degree of carbon mineralization after the addition of biochar could be also affected by properties of soil and interaction with biochar (Zimmerman et al., 2011). For example soil organic matter (SOM) could be stabilized on mineral surface of silt-clay fraction of soil (Lützow et al., 2006). In addition to this, application of biochar to soils rich with oxide/hydroxide of Al and Fe could result in the adsorption of biochar originated hydrophobic (dissolved organic matter) DOM by Al and Fe oxide/hydroxide minerals (Lin et al., 2012). The increment in soil pH after biochar addition is able to increase organic matter solubilization and increment of negative charge on soil organic matter. In this context, the surface negative charge leads to highly stable organic matter by adsorbing positively charged cations (Whittinghill and Hobbie, 2012). Additional mechanism for increased stabilization and SOM after the addition of biochar is the formation of micro aggregates between biochar and SOM, which provide physical protection for SOM from solubilization and microbial attacks (Cheng et al., 2008). On the other hand, high positive priming effect on the mineralization of soil native SOC has been reported after the addition of manure based biochars (Singh and Cowie, 2014) and increment of organic matter content of soil after the application of rice straw biochar produced at 500 °C (Tang et al., 2020). Generally, biochars produced from herbaceous materials showed improved mineralization effect than biochar produced from woody materials (Zimmerman et al., 2011).

2.2.5. Effect of biochar on soil microorganisms

Microorganisms, which are present in soils, are very important indicators of soil health conditions. Soil microorganism could be affected by any crop management including, fertilizer application and amendments added to soil. Therefore, it is important to identify possible effect of biochar addition to soil on soil microorganisms (Geisseler et al., 2017). Biochar support the improving effect of microorganisms on soil ecosystem stability, nutrient cycling and soil carbon change (Zhu et al., 2017). The effect of biochar on soil microbes and native soil organic carbon is summarized in Fig 3. Biochar could interfere in soil microbial activity possibly in 7 different ways, where both positive and negative effects can be found: (1) Biochar could provide shelter or physical protection of microorganisms. It is true that biochar is more porous in structure than soil, thus microbes can attach to this structure (Quilliam et al., 2013). (2) Biochar could improve soil CEC, sorb positively charged nutrients and, therefore, maintains the availability of nutrients for microbial use. (3) Biochar could release free radicals and volatile organic carbons, which could be toxic to microbes (Ghidotti et al., 2017: Truong et al., 2010). (4) Biochar is able to improve soil properties like pH, water holding capacity and soil aeration, these providing suitable conditions for microbial reproduction and multiplication. (5) Biochar could reduce the enzymatic activities and elemental cycles of N (Tang et al., 2020; Bailey et al., 2011). This could be linked to the direct adsorption of the enzymes by biochar, release of toxic substrate and subsequent killing of microbes and the blockage of soil reactions (Tang et al., 2020). (6) Biochar could also adsorb and/or favor the hydrolysis of microbe signal molecule; this affects communication of microbes (Masiello et al., 2013). (7) biochar could reduce toxicity of soil contaminants (Zhu et al., 2017: Brendova et al., 2015). For example Koltowski et al. (2017) reported that biochar produced from willow tree under 700 °C was able to reduce mortality of microbes and improved the proliferation of *Folsomia candida* in soil. This is due to the immobilization of risk elements Al, Cd, Co, Cr, Mn, Ni, and organic pollutants like polycyclic aromatic hydrocarbons (PAH) by biochar. In another study, the increment of biochar (coconut shell) application rate (10, 30 and 50 t ha^{-1}) increased the gram negative and positive bacterial phospholipid fatty acid (Dangi et al., 2020). This is was linked to the supply of labile carbon to the soil bacteria. Similarly, Guo et al. (2020) revealed the increment of microbial biomass carbon and nitrogen after the application of low temperature biochar (350

°C) produced from peels of *Carya cathayensis*, directly linked to the biochar induced increment of microbial biomass.

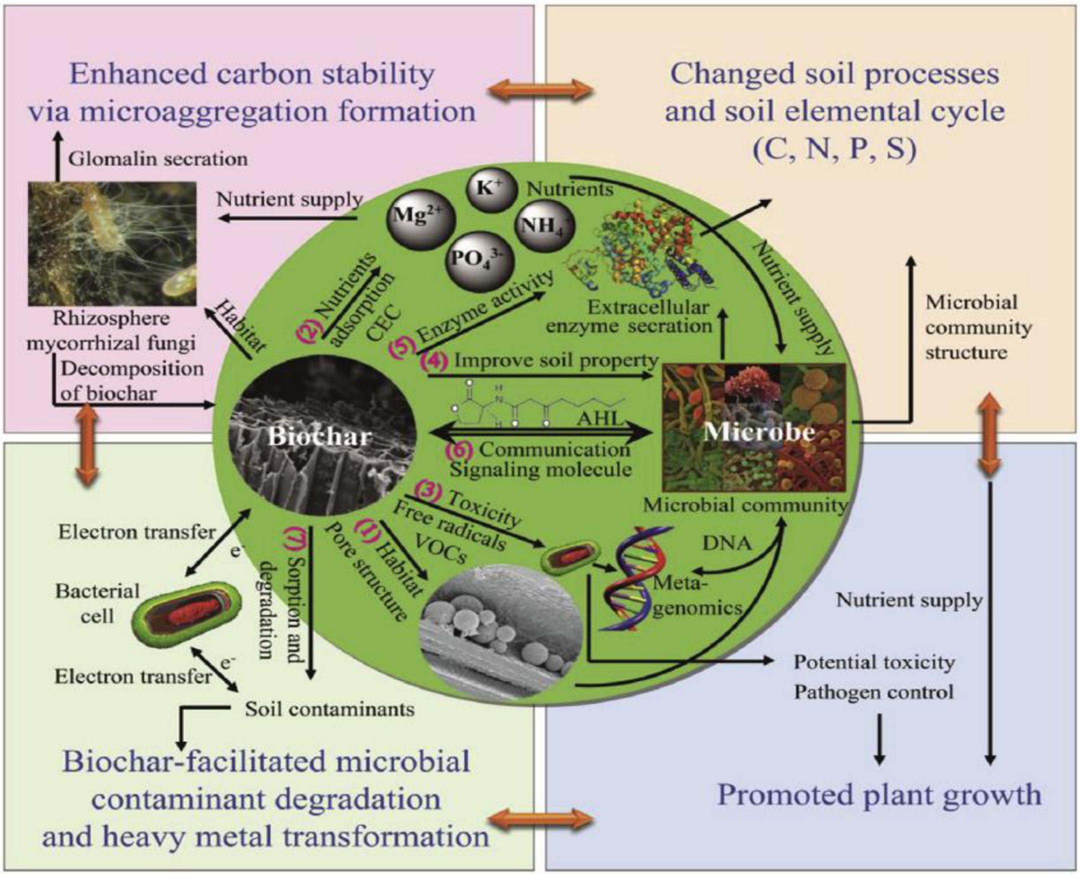

Figure 3. Proposed mechanisms of biochar-microbe interactions and the environmental effects of biochar. The central circular area illustrates the interaction between biochar and microbes, while the enclosing four boxes represent the effects of their interaction on carbon sequestration, soil processes (elemental cycling), contaminant degradation, and plant growth (Zhu et al., 2017).

2.2.6. Risk elements

The high occurrence of risk elements above certain limit in crop production farmland induce both physiological and biochemical effect on plants and by doing this affect crop yield and quality (Wuana and Okieimen, 2011). Biochar ability to reduce the availability of risk elements is evident (Jing et al. 2020; Xu et al., 2020; Yang et al., 2016; Park et al., 2011; Liang et al., 2014).

Biochar could reduce availability of metals in soil by three main mechanisms: i) adsorption, ii) precipitation, and iii) redox reaction, as presented in Fig. 4 (Ok et al., 2015). The increment of soil pH, cation exchange capacity of biochar, physical adsorption by biochar, precipitation with metals and in general the improvement of soil properties after the addition of biochar are the main mechanisms for the decline of metals after the addition of biochar to soil (Gomez-Eyles et al., 2013). The increment in soil pH decreases mobility of metals by sorption of metals to the surface of biochar and precipitation with hydroxide, phosphate and carbonate. The mineral components of biochar such as Ca, K, Mg and P are responsible for the reduction of risk elements after the addition of biochar to soil through ion exchange and precipitation with metals. Furthermore, the oxygen containing functional groups (carboxyl, hydroxyl and carbonyl groups) are responsible for high surface negative charge and high CEC of biochar, while this increasing biochar ability to decrease availability of soil risk elements (Li et al., 2017). But this ability of biochar to decrease availability and mobility of risk elements is affected by both feedstock used and production temperature (Gai et al., 2014). The increment in biochar production temperature reduces oxygen containing functional groups due to high degree of carbonization resulting in low atomic ratio of H/C, O/C and N/C (Li et al., 2017). On the contrary the production of biochar at lower temperature can result in higher proportion of non-carbonized organic matter and this enables biochar to release DOC to soil solution, while co-mobilization of metals with high affinity for organic carbon (Cu, Pd, Hg) could be expected (Uchimiya et al., 2011). Additionally, Xu et al. (2020) observed that the ability of biochar to reduce Cr(VI) into Cr(III) has declined with the increment of biochar production temperature (400 to 600 °C) and then increased when the production temperature increased from 600 to 800 °C. This was due to the reason that O-containing functional groups of biochar are mainly responsible for the reduction of Cr(VI) into Cr(III) at the lower production temperature < 600 °C, and their decline with the increment of production temperature. However, above 600 °C the Cr(VI) reduction capacity of biochar could again start to increase due to the emergence of conjugated aromatic structure, which are responsible for the adsorption of metals at the higher production temperature. Furthermore the benefit of converting sewage sludge to biochar in reducing the mobility of risk elements has been confirmed (Liu et al., 2014; Figueiredo et al., 2019) .

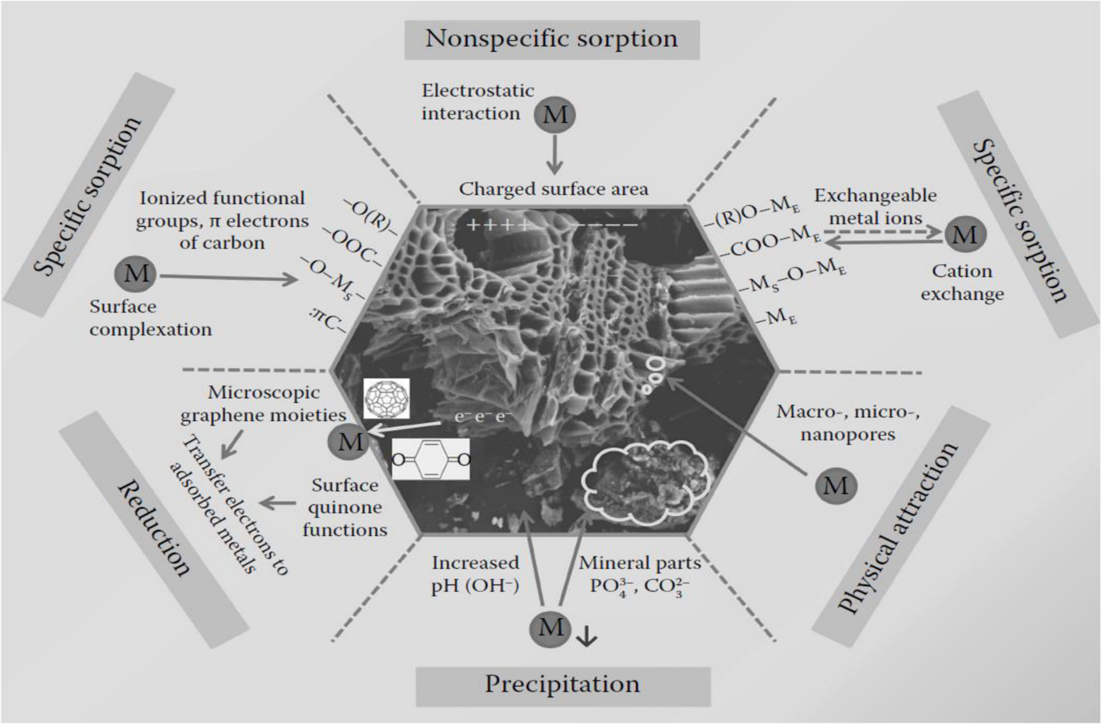

Figure 4. Schematic diagram for biochar reducing concentration of metals in soil (Ok et al., 2015).

2.3. Influence of biochar on crop production

Biochar effect on crop yield is very different from soil to soil and type of biochar used. Based on the specific soil and biochar properties, biochar may have positive, negative or no effect on crop yield. The general mechanisms of soil benefit from biochar for increased crop production was summarized in Fig 5 (Ok et al., 2015). Biochar could induce either direct positive effect through release of nutrients to soil and their subsequent uptake by crops (Jing et al., 2020) or the indirect effect by upgrading soil quality (soil pH, soil CEC, microbial activity, soil structure, porosity, water holding capacity) and efficient use of applied fertilizers (Lehmann and Joseph, 2015).

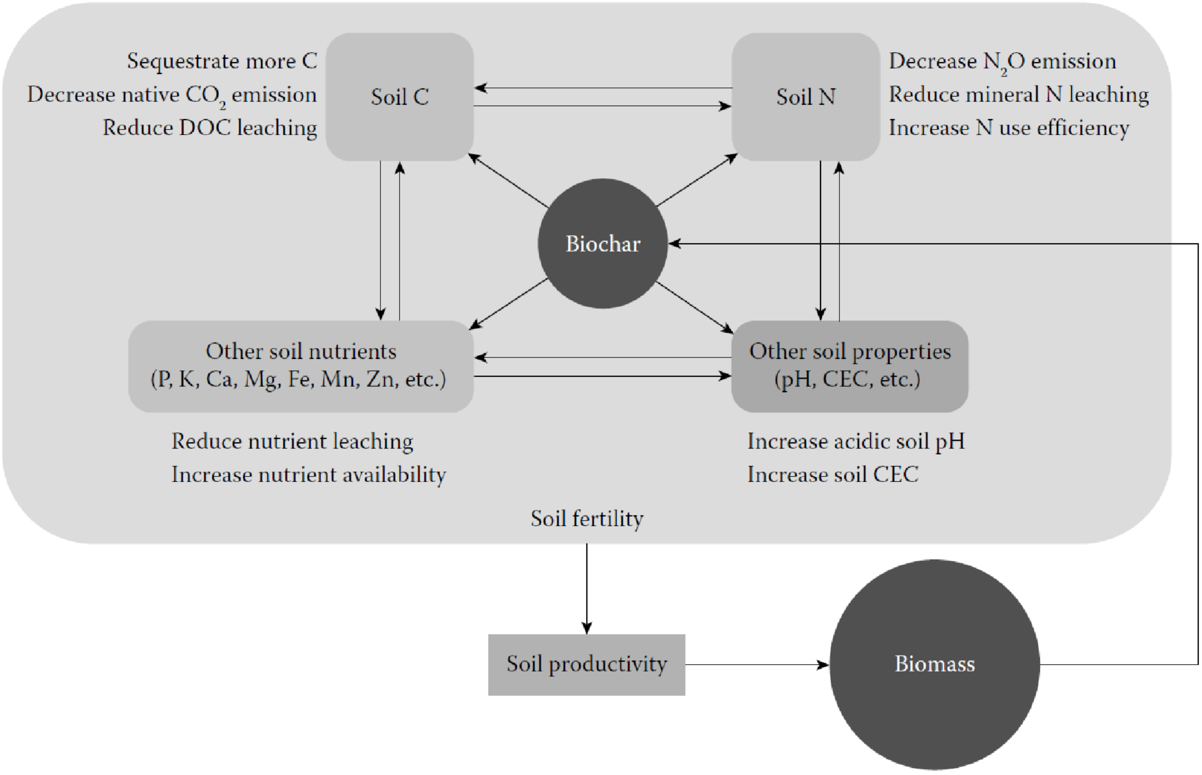

Figure 5. Schematic diagram of biochar role in improving soil fertility (Ok et al., 2015).

The increment in the crop yield after biochar application have been reported to be due to direct supply of nutrient by biochar and/or by conditioning of soil (Glaser et al., 2002). For example, the application of cacao shell biochar (22.5 t h^{-1}) to very acidic (pH_{KCl} = 3.6) Utisol increased maize yield due to the improvement of soil pH and the decline in the available content of Al^{3+} (Hale et al., 2020). Similarly, the application of cow manure biochar at the rate of 15 and 20 t ha^{-1} on dry land sandy soil was able to significantly improve nutrient uptake of maize and to increase yield by 150 and 98% as compared to control respectively (Uzoma et al., 2011). Biochar improved P availability resulting in increased maize yield (Zhu et al., 2014). The effect of biochar on crop yield may be affected by nutrient status of the soil. For example, biochar increased crop yield up to 35 % on low fertile agricultural soils and reduce crop yield in fertile soil at the first three seasons of crop production (Haefele et al., 2011). The application of biochar with organic fertilizer could result in higher crop yield than application of organic fertilizer alone. Similarly co-application of 1% biochar with NPK (0.15 $\mathrm{g\,kg^{-1}}$ N, 0.1 $\mathrm{g\,kg^{-1}}$ $\mathrm{P_2O_2}$ and 0.15 $\mathrm{g\,kg^{-1}}$ $\mathrm{K_2O}$ increased maize biomass by 146 % (Peng et al., 2011). The effect of feedstock used for biochar production has been reported (Cornelissen et al., 2018), where the application of cacao shell biochar was more effective in increasing crop yield compared to rice husk biochar. This was mainly attributed due to high pH and high acid neutralizing capacity of cacao shell biochar, which decreased acidity of soil more effectively as compared to rice husk biochar.

Even though majority of field studies reported increment of crops yield, there were also studies reported the negative effect of biochar. Application of switchgrass biochar decreased wheat shoot biomass from 17.7 to 9.1 g per pot, most probably due to the altering soil microbial community structure in the treated soil. This effect could be sustaining unless measures is taken to add supplemental N and labile carbon (C) (Kelly et al., 2015). On their study, the decline in the wheat biomass was mainly attributed due the decline in the availability of nutrients after the addition of biochar in an alkaline Aridisol soil (pH = 8.1), because of further pH increment to 8.33 after the addition of 10% biochar. Therefore, the application of biochar in neutral or alkaline soil further increases soil pH and this limits the availability of nutrients to the plant.

3. Scientific Hypotheses and Objectives

Four major hypothesis and objectives were set for PhD dissertation.

3.1.Hypotheses

The effect of biochar on soil pH, CEC and exchangeable cations (Ca^{2+}, K^+ and Mg^{2+}) could be highly dependent on soil specific properties.

Biochar could efficiently reduce the mobility of metals (Al, Cu, Zn, Mn, and Cd) in soils and the efficiency varies per specific soil properties.

The application of biochar to soil could influence content of soil NO_3^-, NH_4^+ and DOC.

Co-application of biochar with nitrification inhibitors treated ammonium sulfate soils could maximize crop yield and the uptake of nutrients by the reduction of N losses.

3.2.Objectives

To determine the effect of soil properties on biochar induced changes of soil pH, CEC and exchangeable cations (Ca^{2+}, K^+ and Mg^{2+}).

To evaluate the efficiency of biochar to reduce the mobility of metals (Al, Cu, Zn, Mn, and Cd) in soil.

To investigate the effect of biochar application on NO_3^-, NH_4^+ and DOC.

To determine the effect of biochar co-application with nitrogen fertilizers treated by nitrification inhibitors on crop yield and yield components.

4. Published papers

4.1. High temperature-produced biochar can be efficient in nitrate loss prevention and carbon sequestration

Authors: Niguss Solomon Hailegnaw, Filip Mercl, Kateřina Pračke, Jiřina Száková, Pavel Tlustoš

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High temperature-produced biochar can be efficient in nitrate loss prevention and carbon sequestration

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ABSTRACT

The effects of biochar on soil properties including nutrients have been reported in previous studies, but few studies targeted on soil nitrogen. Moreover, there remains a lack of studies considering the liberation of ammonia during the ammonium (N-NH_4^+) adsorption process. Our study aimed to fill this research gap. A pot incubation experiment was conducted for 84 days, with ten different soils and four rates of wood chip-based biochar (0.5, 2, 4, and 8%). Biochar's effect on soil ammonium was inconsistent and insignificant in most of the incubated soils at all biochar rates. This finding contradicted our Langmuir model, which estimated maximum ammonium adsorption capacity of biochar as 6.66 mg of N-NH_4^+ per g of biochar. Soil response in nitrate (N-NO_3^-) and dissolved organic carbon (DOC) followed a similar declining trend in all soils in both incubation periods, with the effect boosted according to the biochar application rate. The Langmuir isotherm estimated the maximum N-NO_3^- adsorption capacity of our biochar as 11.3 mg g^{-1}. Soil original properties determined amount of nitrate and DOC reduction after biochar addition. Our result also indicated poor estimation of ammonium adsorption by biochar due to the liberation of ammonia. As a result, we strongly recommend that ammonia liberation should be considered during adsorption experiments and more studies in this field.

1. Introduction

Nitrogen is the most important growth and development-limiting nutrient for plants. This nutrient is also the most challenging to reduce losses to water and/or air to achieve improved crop yield (Zebarth et al., 2009). Given that soil contains around 2344 gigatons of organic carbon globally, it can simultaneously be a source of atmospheric CO_2 and a medium for C sink (Stockmann et al., 2013). It would be economical to simultaneously attain or alleviate these two challenges (nitrogen loss and release carbon to the atmosphere) and to devise a measure or method to improve or reduce the effects of these global challenges. Biochar is a widely discussed, carbon-rich residue resulting from the thermal decomposition (pyrolysis) of organic material under the partial or total absence of oxygen (Lehmann and Joseph, 2015). The biochar alters the nutrient balance of the soil and simultaneously it may be considered as a source of nutrients such as Ca, P and K. However, the nitrogen content and availability in biochar-treated soil is questionable due to the heterocyclization of N during pyrolysis (Zheng et al., 2013). Contemporary studies have reported both negative and positive effects of biochar on the binding of the soil's inorganic nitrogen and dissolved organic carbon (DOC) depending on the biochar type (feedstock and pyrolysis conditions), soil type and the period in which the measurements are taken (Zimmerman et al., 2011; Cely et al., 2014; Speratti et al., 2018). Based on the findings of Cely et al. (2014), the effect of biochar on soil carbon mineralization depends on both the properties of feedstock and the pyrolysis conditions. In this context, the application of apple branch biochar at rates of 2% and 4% increased the C-mineralization rate, while biochar amendment at 1% reduced the C-mineralization rate. The nitrogen loss was significantly reduced in biochar-amended soils with increasing pyrolysis temperature (Cheng et al., 2018). A negative priming effect was identified in the soil following the addition of wood biochar (slow pyrolysis at 620 °C), and a positive priming effect in the case of the same soil amended with paper sludge + wheat husk biochar (slow pyrolysis at 500 °C). Other studies have proposed the application of biochar as an efficient method for carbon sequestration owing to its ability to reduce soil organic carbon decomposition and to adsorb significant amounts of soil-dissolved C by biochar (Lu et al., 2014). Biochar may adsorb, release and/or stimulate the mineralization of nitrogen (Clough et al., 2013). A 12% decline in mineralization of N at 128 t ha^{-1} of wood biochar (slow pyrolysis at 620 °C) application rate on sandy loam soil has been reported. In contrast, a 35% increment in net N mineralization after the application of

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the same amount of biochar produced from a mixture of paper sludge and wheat husk (slow pyrolyzed 500 °C) on the same soil has also been identified (Cely et al., 2014). Based on the comparative experiment of Ameloot et al. (2015), poultry litter biochar increased the mineralization of N in both high and low soil organic matter (SOM) contained soils. However, that of pine wood biochar (pyrolysis temperature of 400 and 500 °C) induced a significant decline in N mineralization of SOM rich soil. The negative effect of pine wood biochar on N mineralization could be due to N immobilization or to the preclusion of microbial activity induced by toxic biochar compounds (Clough and Condron, 2010; Ippolito et al., 2012). In general, studies up to date reported both positive and negative effects of biochar on soil soluble carbon and inorganic nitrogen, depending on both soil and biochar factors; pyrolysis temperature (high or low), feedstock ranging from herbaceous to woody materials and/or from animal (poultry litter, cow dung) to plant origin (Gul and Whalen, 2016). Consequently, our study aimed to fill gaps in the existing biochar research.

- Evaluating the effect of biochar on nitrate, ammonium and DOC content in soils with diverse properties and defining the most limiting soil factor.
- Comparing the actual decline of soil nitrate and ammonium with the adsorption capacity of biochar from the adsorptive solution.
- Control possible loss of nitrogen during the ammonium adsorption experiment and determine the maximum adsorption capacity

2. Material and methods

2.1. Soil and biochar sources and characteristics

Soils were selected to achieve a wide range of their main properties (pH, cation exchange capacity (CEC), nutrient content and textural classes) from 10 different agricultural sites in the Czech Republic. Each soil was collected at the top layer 0–20 cm, air-dried and passed through a 2 mm sieve prior to use. Biochar was produced from wood chips at 700 °C. The localization and specific properties of soils and biochar are presented in Table 1.

2.2. Chemical analyses

The biochar and soil pH were determined following extraction with 0.01 M $CaCl_2$ (w/v = 1/5) by using an Argus pH meter (Sentron) with transistor CupFET probe. Determination of the CEC was undertaken according to Gillman (1979) using a three-step saturation of samples with $BaCl_2$ and the subsequent release of Ba^{2+} using $MgSO_4$. Dissolved organic carbon, nitrate nitrogen, ammonium nitrogen were determined after extraction for 2 h with 0.01 M $CaCl_2$ (w/v = 1:10), and measured using a continuous flow analyzer (Skalar San+) according to the method used by Jaszberenyi et al. (1994). The total C and N were determined by a CHNS Vario MACRO cube (Elemental Analyzer system GmbH, Hanau, Germany) analyzer. The total organic carbon (TOC) was determined according to Sims and Haby (1971) spectrophotometrically following the oxidation of organic matter (OM) with $K_2Cr_2O_7$.

2.3. Batch sorption experiment

A sorption experiment was conducted according to the procedure used by Yao et al. (2012) with NH_4NO_3 solution. 0.1 g of biochar was mixed with 30 ml of NH_4NO_3 solution with various concentrations of N-NO_3^- and N-NH_4^+ (2–900 mg L^{-1} and 1–140 mg L^{-1}, respectively) in three replicates. The mixtures (Biochar, NH_4NO_3) were agitated at 200 rpm for 24 h to reach equilibrium, centrifuged and supernatant filtered. The remaining N-NO_3^- and N-NH_4^+ was measured from the filtrate using a continuous flow analyzer (Skalar San+). The amount of adsorbed N-NO_3^- or N-NH_4^+ per unit mass of biochar was calculated as Eq. (1).

Table 1
The main physiochemical properties of soils and biochar.

Properties	Malín	Suchdol	Kbely	Poděbrady	Hněvčeves	Červený Újezd	Lhota	Humpolec	Žamberk	Lukavec	Biochar
Localization	49°58′N, 15°17′E	50°7′N, 14°22′E	50.133870 N, 14.565645E	50°7′N, 15°9′E	50°18′N, 15°43′E	50°4′N, 14°10′E	49°42′N, 13°59′E	49°33′N, 15°21′E	50.1443247 N, 16.5138989E	49°33′N, 14°58′E	–
Soil type	Luvisol	Chernozem	Chernozem	Fluvisol	Luvisol	Luvisol	Fluvisol	Cambisol	Cambisol	Cambisol	
pH	7.10	6.90	7.01	6.10	5.90	6.20	5.91	4.50	4.80	5.30	9.50
CEC (mmol kg^{-1})	356.3 ± 0.8	249.3 ± 4.0	217.7 ± 0.3	150.3 ± 1.0	145.7 ± 12.6	146.2 ± 6.8	129.5 ± 4.7	90.3 ± 2.0	74.9 ± 3.7	48.5 ± 6.0	102 ± 5.2
Organic carbon (%)	2.80 ± 0.0	1.61 ± 0.1	1.90 ± 0.0	1.50 ± 0.0	1.21 ± 0.1	1.70 ± 0.1	2.20 ± 0.2	1.30 ± 0.0	1.60 ± 0.0	1.20 ± 0.0	–
Total N (%)	0.37 ± 0.01	0.16 ± 0.00	0.20 ± 0.01	0.19 ± 0.02	0.14 ± 0.05	0.22 ± 0.00	0.25 ± 0.01	0.16 ± 0.00	0.20 ± 0.00	0.16 ± 0.01	0.40 ± 0.02
Total C (%)	4.28 ± 0.09	2.14 ± 0.09	2.95 ± 0.2	1.90 ± 0.03	1.40 ± 0.63	2.42 ± 0.01	2.67 ± 0.04	1.60 ± 0.09	1.98 ± 0.09	1.48 ± 0.13	87.55 ± 0.2
C/N ratio	11.60 ± 0.13	13.23 ± 0.16	14.65 ± 0.61	9.81 ± 0.01	9.74 ± 0.84	10.98 ± 0.1	10.65 ± 0.26	10.00 ± 0.16	9.96 ± 0.16	9.30 ± 0.23	219.98 ± 12.9
N-NO_3^- (mg kg^{-1})	82.8 ± 1.1	39.1 ± 6.0	113.3 ± 5.8	69.1 ± 9.3	23.6 ± 1.6	45.9 ± 7.7	97.1 ± 2.1	98.2 ± 3.0	32.4 ± 7.3	36.1 ± 1.2	–
N-NH_4^+ (mg kg^{-1})	16.5 ± 1.5	5.7 ± 0.8	4.2 ± 1.0	15.0 ± 1.3	2.0 ± 0.8	1 ± 0.8	23.7 ± 2.2	2.0 ± 0.3	23.5 ± 3.2	3.9 ± 0.7	–
DOC (mg kg^{-1})	120.2 ± 1.7	13.4 ± 4.3	138.4 ± 2.6	100.9 ± 4.5	75.9 ± 9.9	62.4 ± 3.8	76.3 ± 2.4	11.7 ± 0.6	63.6 ± 2.0	63.4 ± 2.1	–
$Al_{(Cacl2)}$ (mg kg^{-1})	0.98 ± 0.05	0.50 ± 0.00	0.81 ± 0.33	1.19 ± 0.0	0.82 ± 0.30	0.50 ± 0.00	0.66 ± 0.14	5.97 ± 0.28	3.04 ± 0.31	5.04 ± 0.98	–
$Fe_{(Cacl2)}$ (mg kg^{-1})	1.14 ± 0.04	0.05 ± 0.00	0.25 ± 0.16	0.41 ± 0.03	0.39 ± 0.18	0.07 ± 0.03	0.19 ± 0.07	0.75 ± 0.03	0.20 ± 0.11	0.55 ± 0.19	–
Sand (%)	11.6	13.16	14.92	56.57	4.29	25.72	39.64	30.22	26.08	27.18	–
Silt (%)	61.2	60.05	60.16	24.5	67.14	48.81	45.5	48.38	59.82	61.20	–
Clay (%)	27.18	26.77	24.9	18.93	28.55	25.45	14.85	21.4	14.08	11.60	–
Textural class	Silt clay loam	Silt clay loam	Silt loam	Sandy loam	Silt clay loam	Loam	Loam	Loam	Silt loam	Silt loam	–

All data are presented as arithmetic means ± standard deviation (n = 3).

$$Q_e = (C_i - C)\frac{V}{M} \tag{1}$$

where, Q = amount of $N\text{-}NO_3^-$ or $N\text{-}NH_4^+$ adsorbed by biochar ($mg\ g^{-1}$); C_i = amount of $N\text{-}NO_3^-$ or $N\text{-}NH_4^+$ in the initial or original solution ($mg\ L^{-1}$); C = concentration of $N\text{-}NO_3^-$ or $N\text{-}NH_4^+$ in the equilibrium solution ($mg\ L^{-1}$), V = volume of solution (L) and M = mass of biochar (g).

These sorption data were subsequently applied to Freundlich and Langmuir adsorption models Eqs. (2) and (3), respectively (Limousin et al., 2007).

$$Q_F = FC^n \tag{2}$$

where Q_F = amount of adsorbed $N\text{-}NO_3^-$ or $N\text{-}NH_4^+$ by biochar ($mg\ g^{-1}$); F = Freundlich isotherm constant ($mg\ g^{-1}$); C = the equilibrium concentration of $N\text{-}NO_3^-$ or $N\text{-}NH_4^+$ and n = adsorption intensity ($mg\ L^{-1}$).

$$Q_L = Q_{max}\frac{LC}{1 + LC} \tag{3}$$

where Q_L = amount of adsorbed $N\text{-}NO_3^-$ or $N\text{-}NH_4^+$ by biochar ($mg\ g^{-1}$); Q_{max} = maximum biochar coverage capacity ($mg\ g^{-1}$); L = Langmuir isotherm constant; C = the equilibrium concentration of $N\text{-}NO_3^-$ or $N\text{-}NH_4^+$ ($mg\ L^{-1}$).

2.4. Capturing liberated ammonia

The amount of N, which is liberated as ammonia (NH_3) from a solution of NH_4NO_3 and biochar mixture during our sorption experiment, was estimated via the titration method using boric acid as a receiving solution and titrated with a standard solution of 0.1 $mol\ L^{-1}$ HCl. The amount captured was calculated using the following formula:

$$N_{ammonia}(mg\ L^{-1}) = \frac{f_t * c(HCl) * (V_t - V_s) * M(N) * 10^3}{V_v} \tag{4}$$

where

f_t: Titration factor = 1
c(HCl): Concentration of HCl used for titration ($mol\ L^{-1}$)
V_t: Amount of HCl added to titrate sample (ml)
V_s: Amount of HCL added to titrate control (ml)
M(N): Molar mass of Nitrogen (14.007 $mol\ g^{-1}$)
V_v: Amount of receiving boric acid with indicator solution (ml).

2.5. Experimental design

The incubation experiment was initiated by adding 200 g soil in 500 ml holding plastic pots for 12 weeks under controlled environmental conditions. The experiment was designed with 5 treatments: control (200 g soil + No biochar); soil + 0.5% biochar; soil + 2% biochar; soil + 4% biochar; and soil + 8% biochar (w/w ratio). Each treatment was set in three replications. Soil was thoroughly mixed with biochar (0.5, 2, 4, and 8%) and filled to individual pots. Once the experiment started each pot with soil and soil biochar mixture was regularly irrigated every other day to reach 60% of soils water holding capacity. Soils 60% water holding capacity was calculated after determining the maximum water holding capacity of each soil. This was done by filling Mitscherlich columns with air-dried soils of known weight and moisture content. The columns were then soaked in water for 2 h and the water drained for 12 h according to the procedure used by Mercl et al. (2016). Samples of the incubated soil and/or soil-biochar mixtures were collected at the 7th (week 1) and 84th days (week 12) of incubation. Each sample was divided in two halves in order to determine the moisture content, and the other half was frozen at −28 °C for nutrient analysis.

2.6. Statistical analyses

The one-way analysis of variance (ANOVA) was used to determine the effect of biochar under Tukey's significance of difference test. A multivariate analysis of variance was employed to investigate the general effects of biochar application rate, incubation period and soil type, and their interactions with soil properties. Correlation tests were undertaken between values of biochar-induced decline (percentage) in $N\text{-}NO_3^-$, $N\text{-}NH_4^+$ and DOC of soil and soil parameters with the Pearson two-tailed test at $p = 0.05$. Multiple linear regression was performed for soil content of $N\text{-}NO_3^-$, $N\text{-}NH_4^+$ and DOC including all treatments ($n = 300$).

The percentage of $N\text{-}NO_3^-$, $N\text{-}NH_4^+$ and DOC that declined or increased due to biochar addition was calculated using Eq. (5).

$$X\,(\%) = \left(\frac{C_0 - C_n}{C_0}\right)100 \tag{5}$$

where X denotes change in percentage of $N\text{-}NO_3^-$ or $N\text{-}NH_4^+$ or DOC, C_0 concentration in the control $mg\ kg^{-1}$ and C_n concentration in the biochar-amended treatments $mg\ kg^{-1}$.

The Freundlich adsorption and Langmuir adsorption models were fitted using Sigma plot for Windows version 11.0. In this paper mean values differences at $p = 0.05$ were considered statistically significant and all statistical analyses were performed using SPSS 17.0 software.

3. Results and discussion

3.1. Nitrate and ammonium adsorption isotherms

In order to understand the nitrate and ammonium adsorption mechanism and maximum adsorption capacity of the applied biochar, we investigated sorption isotherms for both, $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$ (Figs. 1 and 2) by attaching them to Freundlich and Langmuir models. In the case of both nitrate and ammonium, the Langmuir model was more effective ($R^2 = 0.92$ for $N\text{-}NO_3^-$ and $R^2 = 0.91$ for $N\text{-}NH_4^+$) than the Freundlich model ($R^2 = 0.83$ and $R^2 = 0.79$ for $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$, respectively) in estimating the maximum adsorption.

The maximum $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$ adsorption capacity of our biochar as calculated by the Langmuir model was 11.3 $mg\ g^{-1}$ and 6.66 $mg\ g^{-1}$, respectively. These results indicate that our biochar have a higher nitrate adsorption capacity compared to the adsorption of ammonium. This difference is possibly due to the higher production temperature of our biochar. The elevated production temperature of our biochar could have resulted in the removal of the O-carrying functional groups. This could result in low polarity (i.e., low O/C ratio) due to the decline in the surface functional groups with negative charge ($-COO^-$, $-COH$ and $-OH$), at high production temperatures and this could reduce sorption of ammonium (Gai et al., 2014), while increasing sorption of nitrate (Yuan et al., 2011).

In a further sorption study of sawdust biochar produced at 600 °C, the maximum $N\text{-}NO_3^-$ adsorption capacity was estimated as 8.94 $mg\ g^{-1}$ and for biochar produced at 300 °C the maximum $N\text{-}NH_4^+$ adsorption capacity was estimated as 5.31 $mg\ g^{-1}$ (Wang et al., 2015). This result could additionally indicate the high nitrogen adsorption or removal capacity of our biochar from nitrate and ammonium rich solution.

A further outcome worth acknowledging was the release of ammonia when NH_4NO_3 was mixed with biochar, which had a considerable effect on the determination of adsorbed ammonium by biochar. Based on our finding, without considering liberated ammonia, the maximum $N\text{-}NH_4^+$ adsorption capacity of our biochar was estimated as 7 $mg\ g^{-1}$, but this value was reduced to 6.66 $mg\ g^{-1}$ after considering liberated ammonia.

The amount of liberated ammonia is indicated in Fig. 3. The liberated $N\text{-}NH_4^+$ reached up to 26.6 $mg\ L^{-1}$ at 141 $mg\ L^{-1}$ of the $N\text{-}NH_4^+$

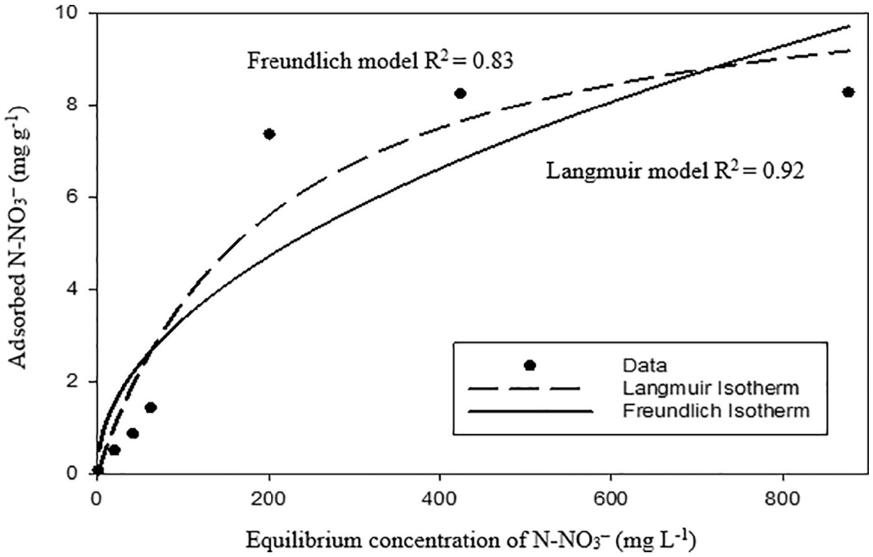

Fig. 1. Adsorption isotherm for N-NO_3^-.

containing solution. The liberated amount increased as the concentration of N-NH_4^+ increased in the solution and become almost stable at the higher concentration of N-NH_4^+. This could indicate that the results of other studies focused on evaluating the biochar effect on the adsorption of ammonium without consideration of ammonia liberation are not precise interpretation.

3.2. Effect of biochar on soil nitrate

We presented the percentage of reduced soil nitrate following biochar addition in all soils relative to nitrate content of control in Fig. 4. The negative effect of biochar was prominent in all investigated soils at both incubation periods, and the amount of decline increased as the rate of biochar application increased from 0.5% to 8%. The addition of 0.5% biochar resulted in the decline of nitrate by up to 35% relative to the control. However, this decline was significant only in some of the incubated soils (Supplementary Table S 1). The addition of 2% biochar induced a decline up to 70% relative to the control. This decline was significant in all soils except for two soils at the first week of incubation, which become significant at the later period of incubation (12 week) in all soils in both incubation periods. The 4% biochar addition induced a significant decline in all soils at both incubation periods, with a significant effect ranging up to 76%. Similarly, the 8% biochar addition induced significant declines in all soils, with effects ranging up to 81%. However, in most cases there was no significant difference between the 4 and 8% biochar application rate.

Adsorption of nitrate by high temperature biochar has been reported in several studies (Kameyama et al., 2012, 2016; Yao et al., 2012). Yao et al. (2012) identified a 34% reduction of nitrate in leachate following the addition of biochar produced from pepperwood at

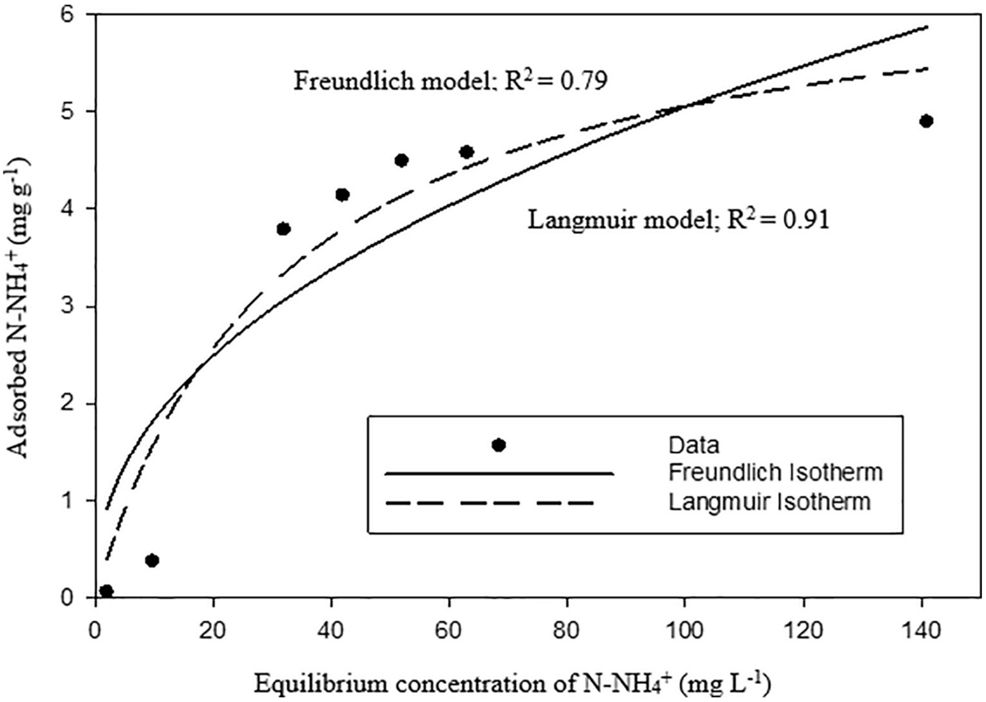

Fig. 2. Adsorption isotherm for N-NH_4^+ after consideration of liberated N-NH_4^+ due to the increment of pH after biochar addition.

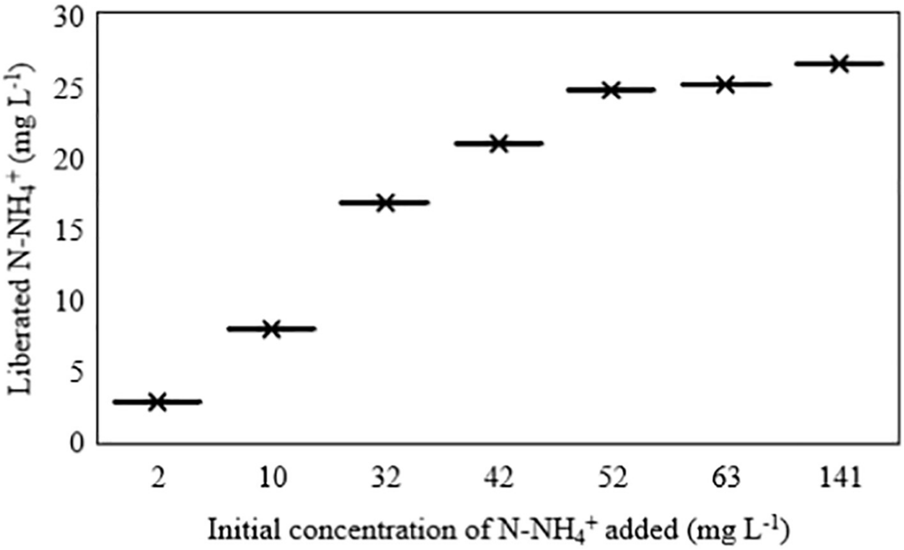

Fig. 3. Liberated N-NH_4^+ (mg L^{-1}) as ammonia during the adsorption experiment of N-NH_4^+.

600 °C, and similarly the rate of 2% and 4% of the apple branch biochar reduced the soil nitrate content, particularly in N-rich soil (Li et al., 2017). One of the reasons for the decline in our soil nitrate content could be the sorption effect of our high temperature biochar. The sorption of nitrate by biochar is potentially caused by the production of the base functional group during higher pyrolysis temperature (700 °C) (Kameyama et al., 2012). A further reason for the decline is immobilization of N due to the wide C/N ratio of our biochar (87.6). This is in agreement with Ameloot et al. (2015), who identified the immobilization of N following the addition of pine wood biochar with a high C/N ratio. The immobilization of N was also reported during the 65-day incubation study of Bruun et al. (2012). Another study saw the immobilization of mineral N of up to 43% following biochar application. In addition to the high C/N ratio of biochar, the sorption of compounds toxic to microbes by biochar may result in an increment of microbial biomass (Chen et al., 2009). The increment in pH of soil after biochar addition could increase microbial activity owing to the suitability of the pH environment, and this may lead to increased utilization and immobilization of soil nitrate. Biochar may also result in the decline of nitrates by the sorption of organic matter and microbial enzymes, this in turn preventing the decomposition of organic matter, which is the primary source of nitrogen (Kwon and Pignatello, 2005; Kasozi et al., 2010).

3.3. Effect of biochar on ammonium

Biochar increased the content of soil ammonium up to 184% and decline up to 79%. However, in most cases the effect was insignificant and inconsistent in terms of time and rate of biochar application, rendering it difficult to summarize the effects of biochar on ammonium of our investigated soils. At the first week of incubation, a significant decline in the content ammonium of four soils (Malín, Lhota, Poděbrady and Žamberk) was noted, all of which have a considerably high content of N-NH_4^+ (≥15 mg kg^{-1}) in comparison to other soils (Table S 2). At the 12th week of incubation, this effect was nullified as the content of ammonium in the control treatment decreased to the same level as biochar addition. All other soils saw insignificant change, possibly due to their low N-NH_4^+ (≤6 mg kg^{-1}). This result is in agreement with the findings of Jones et al. (2012), who reported insignificant effects at the rate of 50 t ha^{-1} of biochar application. This insignificant effect of our

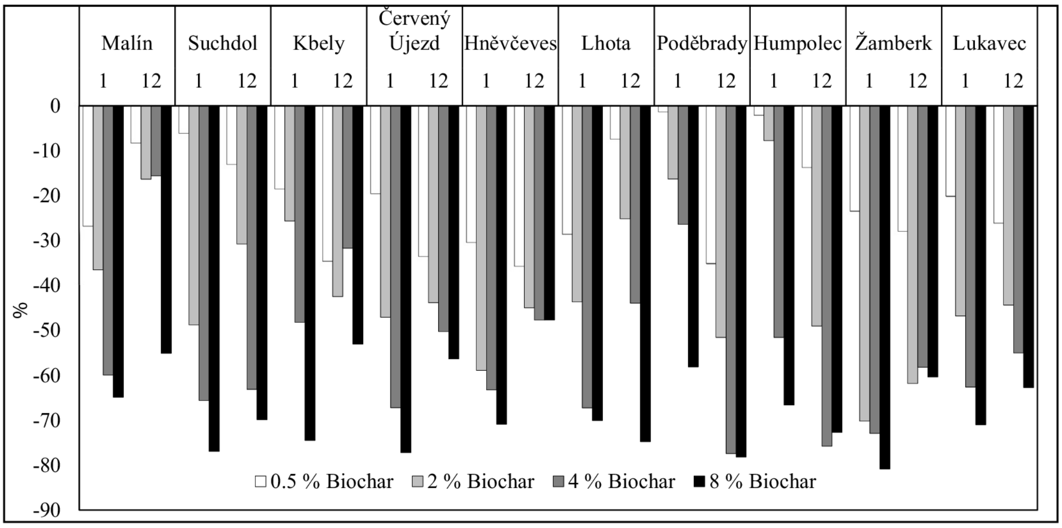

Fig. 4. The mean relative value of nitrate. Percentage expressed as the difference between biochar amended treatments and un-amended control treatment; 0% indicates as No change in amount of nitrate due to biochar addition. On the horizontal axis, 1 and 12 indicates the 1st and 12th week of incubation period or sample collection time respectively.

biochar on sorption and/or release of ammonium possibly owes to the low CEC of our biochar in comparison to most incubated soils, and due to the low level of ammonium in incubated soils. The high production temperature of our biochar could result in the low CEC of biochar. The low adsorption of ammonium by high-temperature biochars (600–700 °C) as compared to low temperature biochar (400–500 °C) has also been reported (Gai et al., 2014). This could be due to low polarity (low O/C ratio) and conversion of acidic functional groups on the biochar surface, especially in the carboxyl group to neutral or basic fused aromatic group after losing their oxygen-containing functional groups, which could reduce their ammonium adsorption ability. Biochar produced at lower temperature always had a higher CEC, implying the higher adsorption effect of ammonium. Biochar with a CEC of 190–686 mmol kg^{-1} acquired higher ammonium sorption capacity than biochar with CEC of 3–85 mmol kg^{-1} (Gai et al., 2014).

It is also evident that the type of feedstock used for biochar production could determine whether ammonium or nitrate is predominantly adsorbed. As clearly reported by Harvey et al. (2012), woody biochar exhibited less adsorption effects on ammonium in comparison to grassy biochar. This was mainly due to the higher concentration of carboxylic functional groups on the surface of grassy biochar than woody biochar. Another probable reason could be the removal of adsorbed ammonium from biochar by $CaCl_2$ during our extraction. The possible removal of ammonium by extracting medium potassium chloride was reported by Dempster et al. (2012).

3.4. *Effect of biochar on dissolved organic carbon*

The effect of biochar on DOC followed the similar declining trend as that of soil nitrate. The addition of 0.5% biochar induced a decline in DOC of up to 73% (Fig. 5). This decline in the biochar addition rate of 0.5% was not significant in most soils (Table S 3). In the case of the biochar addition rate of 2%, DOC declined by up to 75%, with this being significant in most soils but insignificant when compared to the 0.5% biochar addition rate. That of 4% biochar addition induced a decline of approximately 85%, and this effect was significant in all soils except for three. DOC significantly declined following the addition of 8% biochar, with an effect ranging up to 88%. This effect was significant in all soils but one. The application of 8% biochar was unable to induce a significant effect over the 4% biochar addition rate. The highest decline in DOC was in the acidic and low organic carbon contained soil (Humpolec), which recorded a decline of up to 88% following the addition of 8% biochar at the 12th week of incubation. A tremendous increment in the DOC of control at the 12th week of incubation was identified in the soil of Humpolec, possibly due to the decomposition of organic matter. However, the DOC of biochar treatments continued to decline, indicating the preclusion of the decomposition of organic matter and/or the sorption of DOC resulting from the decomposition. This finding agrees with Zimmerman et al. (2011), who found a decline in the mineralization of soil organic carbon at the later incubation period of lower organic matter contained soil. This soil (Humpolec) has a pH of 4–5, which is in the range of higher DOM sorption. As the pH decreases to this level the ionization of multiprotic DOM molecules also declines, and the charge on the molecule will have less negative charges, causing the soil mineral surface to adsorb more DOM molecules before the surface has become more negatively charged (Shen, 1999). This may be also due to the higher content of extractable Al and Fe (5.97 and 0.75 mg kg^{-1}, respectively), which is higher than in other soils. The decline in the amount of DOC as the rate of biochar application increases has also been reported by others (Kuhlbusch and Crutzen, 1995; Kasozi et al., 2010).

In general, the decline in DOC following the addition of biochar could indicate the effect of two components (soil and biochar) on the DOC content of the soil solution. This can be explained as the adsorption by soil minerals of soluble carbon that originated from biochar (Kaiser et al., 1996). They found sorption of hydrophobic DOC by oxide/hydroxide of soils possibly due to the higher affinity of hydrophobic DOC to oxide/hydroxide of Al and Fe. The increase in soil pH can result in the increased solubility of organic matter and growth of the negative charge of organic matter. Thus, the increment in solubility and/or negative charge on the organic matter results in the stabilization of negatively charged organic matter by sorption to positively charged cations (Whittinghill and Hobbie, 2012). Subsequently, the formation of a Ca^{2+} bridge between negatively charged particles may bind organic matter together or to minerals (Shen, 1999). This phenomenon may have occurred in our incubated soils with the addition of biochar very rich in exchangeable Ca^{2+} ions and released to the soil solution, possibly forming Ca^{2+} bridging with SOM. The decline in soil DOC was significant in at least in one of the four applied biochar rates in all soils, except for in soil Lukavec. In soil Lukavec, the amount of DOC declined at both periods of incubation in all biochar application rates, although this finding was insignificant. This soil is characterized by its relatively

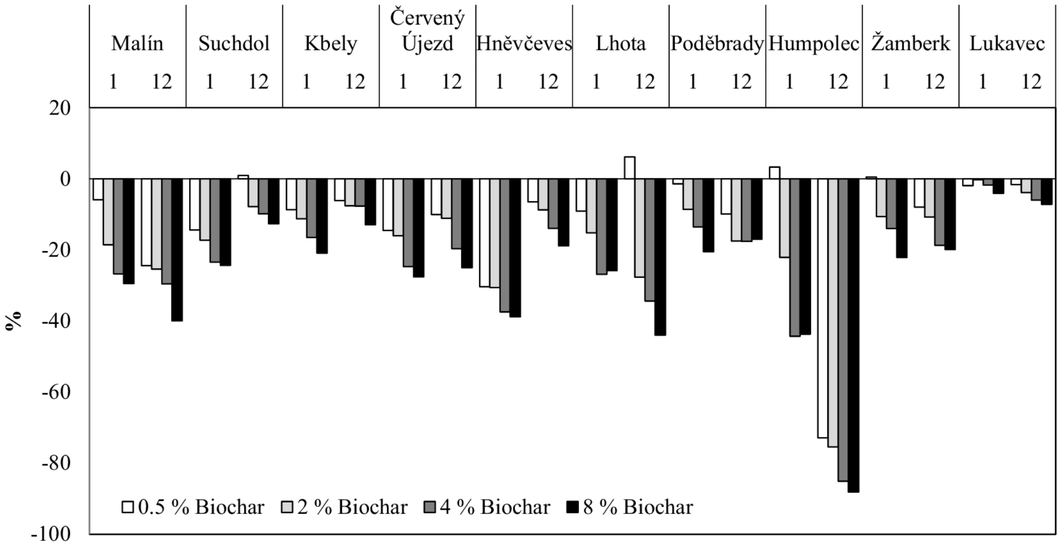

Fig. 5. The mean relative value of DOC. Percentage expressed as a difference between biochar amended treatments and un-amended control treatment; 0% indicates as No change in amount of DOC due to biochar addition. On the horizontal axis, 1 and 12 indicates the 1st and 12th week of incubation period or sample collection time respectively.

Table 2

Multivariate analysis of variance in soil N-NO_3^-, N-NH_4^+ and DOC with interaction and single effect of factors.

Soil properties		Soil type	Period of incubation	Biochar rate	Soil type * incubation period	Biochar rate * soil type	Biochar rate * incubation period	Biochar rate * incubation period * soil type
N-NO_3^-	DF	9	1	4	9	36	4	36
	F	542	5.79	564	74.5	26.5	5.33	14.6
	P	*< 0.001*	*< 0.05*	*< 0.001*	*396*	*< 0.001*	*< 0.001*	< 0.001
N-NH_4^+	DF	9	1	4	9	36	4	36
	F	443	2009	44.6	396	7.58	36.4	7.84
	P	*< 0.001*	*< 0.001*	*< 0.001*	*< 0.001*	*< 0.001*	*< 0.001*	< 0.001
DOC	DF	9	1	4	9	36	4	36
	F	1263	196	117	24.5	4.67	2.37	3376
	P	*< 0.001*	*< 0.001*	*< 0.001*	*0.054*	*< 0.001*	*< 0.001*	< 0.001

The italicized values indicate the significance level at $n = 300$.
DF; degree of freedom, F; F test and P; p value.

Table 3

Regression equations for N-NO_3^-, N-NH_4^+ and DOC including soil parameters and biochar addition rate, regression coefficients are displayed.

Content (mg kg^{-1})	Intercept value	Biochar rate (%)	pH	Organic carbon (%)	N (%)	C (%)	CEC (mmol kg^{-1})	Al_{CaCl2} (mg kg^{-1})	Fe_{CaCl2} (mg kg^{-1})	Clay (%)	
N-NO_3^-	2788.4***	−5.2***	−324.3***	153.0***	−7697***	287.2***	1.7***	−149***	732.7***	−20***	$R^2 = 0.75$
N-NH_4^+	39.7	−0.3*	−7.0	8.2	–	–	0.06*	–	−10.3	−0.5*	$R^2 = 0.39$
DOC	668.4***	−2.1***	−55.9***	−73.7***	−1641.7***	124.7***	0.7***	−33.9***	96.3**	−7.8***	$R^2 = 0.93$

All soils (10) included after addition of 4 level of biochar (0.5, 2, 4 and 8%) plus control and two Sampling periods (week 1 and week 12) with $n = 300$. The model is significant at $p > 0.0001$ for all three (N-NO_3^-, N-NH_4^+ and DOC) and for coefficients: * are significant at $p > 0.05$, *** significant at 0.0001.

low level of organic matter, nitrate nitrogen, ammonium nitrogen and dissolved organic carbon in comparison to other soils. This would suggest that the negative effect of biochar addition on soil DOC is more prevalent in soil with relatively high soil organic matter and/or inorganic nitrogen and/or DOC. The following finding is also to be expected: the very low level of mineralizable carbon from our biochar owing to the elevated production temperature of our biochar. This is possibly due to the conversion of aliphatic carbon to more aromatic carbon with high pyrolysis temperature (Rafiq et al., 2016).

3.5. Soil factors controlling the effect of biochar on soil inorganic nitrogen and DOC

Our study has discussed the contribution of these soil parameters on the amount of biochar-induced changes on both inorganic nitrogen and DOC, through analyzing the correlation coefficient between soil parameters and biochar-induced change on soil nitrate, ammonium and DOC (Table S 4). In the first week, the effect of biochar addition on the percentage of nitrate decline was not correlated with any of the soil parameters except for that of organic carbon being positively correlated at the biochar application rate of 0.5%. This result from the first week could confirm that the direct effect of biochar on soil nitrate is negative irrespective of the soil type and/or soil parameters. However, this trend was not analogous to the result of the 12th week of incubation, indicating that the effect becomes soil-specific or that the effect is contingent on specific soil properties. Soil organic carbon, total nitrogen, total carbon, CEC and the silt + clay fraction are significantly correlated in a negative way and the percentage of sand in a positive manner to the percentage of reduced soil nitrate. The higher soil organic carbon, total nitrogen and total carbon indirectly refers to the higher organic matter of soils, which could possibly result in the sorption of organic matter OM to the biochar surface, reducing nitrate sorption. In other words, this is due to the competition over the sorption site for nitrate on the biochar by soil OM. Another possible reason is the substitution of lost soil nitrate from the mineralization result of SOM, as SOM can be regarded as the major supplier of soil nitrogen and microbial activities are expected to be higher in OM-rich soils (Hadas et al., 1992). The negative correlation of soil CEC with the percentage of biochar-induced decline in soil nitrate is possibly due to the reduced potential of biochar to adsorb nitrate in soils, which have a high CEC as the biochar effect on nitrate primarily rises due to its anion exchange capacity (AEC). It is well known that soils that have low CEC are expected to have comparably higher AEC than soils with high CEC. This could contribute to the decline in soil nitrate through the adsorption effect of soil in addition to the effect of biochar. Higher fractions of sand resulted in higher rates of decline in soil nitrate after the addition of biochar. This is probably due to the direct availability of soil nitrate for biochar sorption. This finding owes to the temporary adsorption and/or the physical protection of soil nitrate by the silt + clay fraction and their subsequent removal via the extraction of the sample with 0.01 M $CaCl_2$. There was no significant correlation between the decline and/or increment in the amount of soil ammonium and all soil parameters. This is due to the low insignificant effect and the fluctuation of the biochar effect on soil ammonium with negative and positive magnitude on the same soil at different biochar application rates. When we see the percentage of the reduced amount of DOC, it is only significantly positively correlated with the Al content of the soil. This could be due to the higher affinity of hydrophobic DOC to the oxide/hydroxides of soil minerals (Kaiser et al., 1996).

On the other hand, the multivariate analysis of variance (Table 2) indicated that all evaluated factors (biochar rate, period of incubation and soil type) and their interaction effects significantly affected soil nitrate and ammonium in the treated soils. For soil DOC, all the factors and their interaction effects were significant at $p < 0.05$ except for the interaction effect of soil type and incubation period.

In addition, we deployed multiple linear regression for nitrate, ammonium and DOC to model equations integrating the biochar addition rate and other soil parameters that have a significant regression coefficient (Table 3). The biochar rate affects nitrate to the highest degree with $\beta = -5.1$, and to a lesser extent DOC and ammonium with $\beta = -0.18$, -0.12, respectively. The equation for nitrate and DOC explains 75 and 93% of the variability respectively and the entire model is significant at a p value = 0.0001. Therefore, these equations can be used to estimate the variability of nitrate and DOC content of the soil before applying biochar (high temperature) to soil. This aids in providing general insights regarding how our biochar will perform after application to the soil, and in determining whether the application is needed based on our desired purpose of biochar application to the soil.

4. Conclusion

Our study has indicated the significant role of biochar in reducing nitrate and DOC, as well as the inconsistent effect on the ammonium content of soils. The amount of adsorbed nitrate from our adsorptive solution is rather comparable with the amount of nitrate decline in the soil environment. The immediate effect of high temperature biochar on soil nitrate follows a negative magnitude irrespective of soil properties. However, over time the amount of reduced soil nitrate becomes soil specific and is primarily determined by soil original total nitrogen, total carbon, organic matter content, CEC and soil texture. The increment in soil original organic carbon, total nitrogen, total carbon, CEC and soil clay fraction content could reduce the amount of decline, whereas a high proportion of sand facilitates the decline of nitrate in the soil. However, the amount of adsorbed ammonium from the adsorptive solution was incomparable with the rate of decline in the soil environment. Biochar was able to reduce ammonium in soils that have a relatively high ammonium content. The effect of high temperature wood biochar on the soil content of DOC is clearly similar to the effect of biochar on soil nitrate content. Biochar reduced the soil's DOC and the amount of decline increased with the amount of biochar added.

In addition, we were able to identify the general neglect of N loss as ammonia during the adsorption experiment leading to an incorrect estimation of biochar maximum ammonium adsorption capacity. Based on our finding, we strongly recommend future consideration of ammonia, which could be liberated during the estimation of maximum ammonium adsorption capacity of biochar and further research regarding the adsorption of ammonium by biochar is needed.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.geoderma.2018.11.006.

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4.2. Mutual relationships of biochar and soil pH, CEC, and exchangeable base cations in a model laboratory experiment

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SOILS, SEC 3 • REMEDIATION AND MANAGEMENT OF CONTAMINATED OR DEGRADED LANDS • RESEARCH ARTICLE

Mutual relationships of biochar and soil pH, CEC, and exchangeable base cations in a model laboratory experiment

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Abstract

Purpose The majority of biochar studies use soils with only a narrow range of properties making generalizations about the effects of biochar on soils difficult. In this study, we aimed to identify soil properties that determine the performance of biochar produced at high temperature (700 °C) on soil pH, cation exchange capacity (CEC), and exchangeable base cation (Ca^{2+}, K^+, and Mg^{2+}) content across a wide range of soil physicochemical properties.

Materials and methods Ten distinct soils with varying physicochemical properties were incubated for 12 weeks with four rates of biochar application (0.5, 2, 4, and 8% *w/w*). Soil pH, CEC, and exchangeable base cations (Ca^{2+}, K^+, and Mg^{2+}) were determined on the 7th and 84th day of incubation.

Results and discussion Our results indicate that the highest biochar application rate (8%) was more effective at altering soil properties than lower biochar rates. Application of 8% biochar increased pH significantly in all incubated soils, with the increment ranging up to 1.17 pH unit. Biochar induced both an increment and a decline in soil CEC ranging up to 35.4 and 7.9%, respectively, at a biochar application rate of 8%. Similarly, biochar induced increments in exchangeable Ca^{2+} up to 38.6% and declines up to 11.4%, at an 8% biochar application rate. The increment in CEC and exchangeable Ca^{2+} content was found in soils with lower starting exchangeable Ca^{2+} contents than the biochar added, while decreases were observed in soils with higher exchangeable Ca^{2+} contents than the biochar. The original pH, CEC, exchangeable Ca^{2+}, and texture of the soils represented the most crucial factors for determining the amount of change in soil pH, CEC, and exchangeable Ca^{2+} content.

Conclusions Our findings clearly demonstrate that application of a uniform biochar to a range of soils under equivalent environmental conditions induced two contradicting effects on soil properties including soil CEC and exchangeable Ca^{2+} content. Therefore, knowledge of both biochar and soil properties will substantially improve prediction of biochar application efficiency to improve soil properties. Among important soil properties, soil exchangeable Ca^{2+} content is the primary factor controlling the direction of biochar-induced change in soil CEC and exchangeable Ca^{2+} content. Generally, biochar can induce changes in soil pH, CEC, and exchangeable Ca^{2+}, K^+, and Mg^{2+} with the effectiveness and magnitude of change closely related to the soil's original properties.

Keywords Biochar · CEC · Exchangeable base cations (Ca^{2+}, K^+, Mg^{2+}) · pH

1 Introduction

Biochar production and application to soil can serve as an environment-friendly strategy for the disposal of increasingly abundant organic waste (Zhang et al. 2018). The ability to use biochar for waste disposal and the benefits of using biochar to improve soil quality and rehabilitate degraded soils have attracted considerable attention (Berek 2014). The main mechanisms of soil improvement include the ability of biochar to increase cation exchange capacity (CEC), pH, and water holding capacity and to directly add mineral nutrients (Wang et al. 2014; Chathurika et al. 2016; Hilioti et al. 2017; Cornelissen

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et al. 2018). The high pH and CEC of biochar result in increased pH and CEC of soils (Zhang et al. 2018). The ability of biochar to increase soil pH and CEC mainly results from its composition of alkaline substances, including ash and carbonates of Ca^{2+}, K^+, and Mg^{2+} (Yuan et al. 2011; Jien and Wang, 2013); its surface properties; and the ability of biochar to reduce exchangeable acidic cations (Al^{3+} and H^+) (Masud et al. 2014).

Much of the work on biochar has focused on specific soil conditions, primarily acidic to slightly acidic, low in CEC, and degraded, poor soils. For example, work done by Martinsen et al. (2015) reported an increment in pH, CEC, and exchangeable bases after application of three biochars produced from cacao (*Theobroma cacao*) shell, oil palm (*Elaeis guineensis*) shell, and rice (*Oryza sativa*) husk on 31 soils. However, all 31 soils used for the study were acidic (pH (H_2O) ranging from 3.5 to 5.6) and had CEC ranging from low (16.1) to medium (153.9 $mmol_c\ kg^{-1}$), and the majority of the soils were very acidic with low in CEC. Increment in soil exchangeable base cations (Ca^{2+}, K^+, and Mg^{2+}) has been also reported following the application of biochar in acidic soil (pH (H_2O), 3.8) (Xu et al. 2013). Similarly, biochar significantly increased soil pH and exchangeable cations in two acidic soils with pH (H_2O) of 4.12 and 4.75 (Wang et al. 2014). In another recent study, biochar increased CEC, pH, and exchangeable K^+, Mg^{2+}, and Ca^{2+} in soil that was moderately acidic (pH ($CaCl_2$) 4.5; pH (H_2O) 5.1) with low CEC (60.5 $mmol_c\ kg^{-1}$) (Pandit et al. 2018). The increment in pH and CEC of soils after application of biochar to three acidic to slightly acidic soils (pH ($CaCl_2$) 3.95, 5.12, and 5.85) with low CEC (18.3, 27.6, 35.4 $mmol_c\ kg^{-1}$) has also been reported (Martinsen et al. 2014). Hence, additional studies are needed to investigate the effects of biochar additions on soil pH, CEC, and exchangeable base cation contents across soils with a wider range of physicochemical properties under the same environmental conditions. Based on this gap among previous studies, our work attempts to address the following objectives:

1) To elucidate the soil factors, which predominantly governs the effect of high-temperature pyrolyzed biochar (700 °C) application on soil pH, CEC, and exchangeable base cations (Ca^{2+}, K^+, and Mg^{2+})
2) To identify level of soil pH, CEC, and exchangeable base cations (Ca^{2+}, K^+, and Mg^{2+}) content for the application of high-temperature pyrolyzed biochar (700 °C) with particular characteristics for most effective alteration of the soil properties

2 Materials and methods

2.1 Soil sampling and biochar production

Soils were selected based on their individual properties (pH, CEC, nutrient content, and textural classes) from 10 different agricultural sites in the Czech Republic, namely Malin, Suchdol, Kbely, Poděbrady, Hněvčeves, Červený Újezd, Lhota, Humpolec, Žamberk, and Lukavec, with conventional crop rotation in all cases. Each soil was collected randomly from the top layer of 0–20 cm, air-dried, and passed through a 2-mm sieve prior to use. The biochar was produced from coniferous wood chips by fast pyrolysis in a fluid reactor at 700 °C and ground to 2 mm. The specified high temperature was selected to produce quite stable biochar with the highest production temperature and exploitation of the highest possible energy from the biomass. The location and specific properties of soils and biochar are presented in Table 1.

2.2 Experimental design

A 12-week incubation experiment was set up using 500-ml plastic pots to which 200 g of dry soil was added. Pots were kept in a greenhouse with room temperature (25 ± 2 °C) controlled and the moisture content in pots was kept at 60% of a given soil's water holding capacity. The experiment was designed with 5 treatments for each soil: control (soil + no biochar), soil + 0.5% biochar, soil + 2% biochar, soil + 4% biochar, and soil + 8% biochar (*w*/*w* ratio). The selected biochar application rate is in regard of considering field applicable rate 0.5 and 2% biochar rate and slightly higher biochar rate 4 and 8% to observe the highest possible biochar effect at higher rate in laboratory scale. Each soil–treatment combination was replicated three times. All pots were filled with the soil–biochar mixture and thoroughly mixed individually. Every pot was irrigated every other day in order to reach 60% water holding capacity. For the determination of soil 60% water holding capacity, first soil maximum water holding capacity was determined. It was done by filling Mitscherlich columns with air-dried soils of known weight and moisture content. Subsequently, the column was soaked in water for 2 h to fully saturate the soil in the column and after full saturation for 2 h, the water in the soil was drained for 12 h. After draining, the maximum water holding capacity was determined gravimetrically as the amount of water retained by the known amount of soil (dry weight) in the Mitscherlich columns. Samples of incubated soils and soil–biochar mixtures (50 g) were taken randomly on the 7th day (week 1) to assess the immediate response of soils on the biochar application. After taking these initial samples from each pot, the soil remaining was left to incubate until the end of our incubation period. The second samples of 50 g were taken at day 84 (week 12) of incubation after thoroughly mixing. The duration of the experiment approximated the vegetation period of many crops.

2.3 Chemical analysis

The biochar and soil pH were determined after extraction of samples with 0.01 M $CaCl_2$ ($w/v = 1/5$) according to ISO 10390 (2005) using an Argus pH meter (Sentron) with a

Table 1 Selected physicochemical properties of soils and biochar

Properties	Malín	Suchdol	Kbely	Poděbrady	Hněvčeves	Červený Újezd	Lhota	Humpolec	Žamberk	Lukavec	Biochar
Localization	49° 58′ N, 15° 17′ E	50° 7′ N, 14° 22′ E	50.133870 N, 14.565645 E	50° 7′ N, 15°9′ E	50° 18′ N, 15° 43′ E	50° 4′ N, 14° 10′ E	49° 42′ N, 13° 59′ E	49° 33′ N, 15° 21′ E	50.1443247 N, 16.5138989 E	49° 33′ N, 14° 58′ E	–
Soil taxonomy (USDA)	Fluvents	Mollisol	Mollisol	Fluvents	Alfisols	Alfisols	Fluvents	Inceptisols	Inceptisols	Inceptisols	–
pH ($CaCl_2$)	7.10	6.90	7.01	6.10	5.90	6.20	5.91	4.50	4.80	5.30	9.50
CEC ($mmol_{(+)}\ kg^{-1}$)	356 ± 0.8	249 ± 4.0	218 ± 0.3	150 ± 1.0	146 ± 12.6	146 ± 6.8	130 ± 4.7	90 ± 2.0	75 ± 3.7	49 ± 6.0	102 ± 5.2
Organic carbon (%)	2.80 ± 0	1.61 ± 0.1	1.90 ± 0.0	1.50 ± 0.0	1.21 ± 0.1	1.70 ± 0.1	2.20 ± 0.2	1.30 ± 0.0	1.60 ± 0.0	1.20 ± 0	–
Exch. Ca^{2+} ($mmol\ kg^{-1}$)	376 ± 1.2	253 ± 3.7	241 ± 3.7	150 ± 6.3	120 ± 8.1	138 ± 2.8	122 ± 4.1	90 ± 2.1	72 ± 0.6	46 ± 0.9	176 ± 13.5
Exch. K^+ ($mmol\ kg^{-1}$)	8.0 ± 0.1	4.6 ± 0.1	4.3 ± 0.1	5.8 ± 0.5	6.5 ± 0.1	12.3 ± 0.1	5.5 ± 0.2	4.3 ± 0.2	1.6 ± 0.1	5.2 ± 0.1	50.4 ± 0.3
Exch. Mg^{2+} ($mmol\ kg^{-1}$)	19.5 ± 0.0	11.8 ± 0.3	7.5 ± 0.1	8.0 ± 0.9	18.2 ± 0.2	12.7 ± 0.1	10.6 ± 0.3	7.9 ± 0.1	2.7 ± 0.1	3.3 ± 0.0	23.2 ± 7.3
Sand (%)	11.6	13.6	14.92	56.57	4.29	25.72	39.64	30.22	26.08	27.18	–
Silt (%)	61.2	60.05	60.16	24.5	67.14	48.81	45.5	48.38	59.82	61.20	–
Clay (%)	27.18	26.77	24.9	18.93	28.55	25.45	14.85	21.4	14.08	11.60	–
Textural class	Silt clay loam	Silt clay loam	Silt loam	Sandy loam	Silt clay loam	Loam	Loam	Loam	Silt loam	Silt loam	–
Agricultural use	Conventional crop rotation										–

Exch., exchangeable

transistor CupFET probe. For the determination of CEC, 2.5 g sample was added in 50-ml Nalgene tube agitated for 1 h and the supernatant collected after centrifugation. The saturation was done three times filling the supernatant to 100-ml flask for the determination of exchangeable cations (Ca^{2+}, K^+, and Mg^{2+}). After the three-step saturation of the soil sample with 0.1 mol L^{-1} $BaCl_2$ solution, the exchanged Ba^{2+} was released by agitating the centrifuged pellet with 0.02 mol L^{-1} $MgSO_4$ solution for 2 h. After 2-h agitation, the solution was centrifuged and the remaining Mg^{2+} in the supernatant was determined for estimation of CEC (Gillman 1979).

2.4 Statistical analyses

One-way analysis of variance (ANOVA) was used to analyze the effect of biochar under Tukey's significance difference test. Multivariate analysis of variance was employed to investigate the general effects of biochar application rate, incubation period, soil type, and interactions with soil properties.

Relative changes (%) of CEC and exchangeable Ca^{2+}, K^+, and Mg^{2+} in biochar-amended soils were calculated using Eq. (1).

$$X\ (\%) = \left(\frac{C_n - C}{C}\right) \times 100 \qquad (1)$$

where X denotes the changes in CEC or exchangeable Ca^{2+}, K^+, and Mg^{2+} (%); C is the concentration in the control soils mmol kg^{-1}; and C_n is the concentration in the biochar-amended treatments mmol kg^{-1}.

Pearson correlation tests were performed among values of biochar-induced changes in CEC, pH, and exchangeable Ca^{2+}, K^+, and Mg^{2+} of soils using the Pearson two-tailed test with $\alpha = 0.05$.

In this paper, mean value differences at $\alpha = 0.05$ were considered statistically significant and all statistical analyses were performed using SPSS 17.0 software.

3 Results

3.1 Effect of biochar on soil pH

The application of 0.5% biochar to soil did not induce significant changes to soil pH at either incubation period (1 and 12 weeks), with the exception of a few cases after 1 week (Table 2). Significant pH increment began with a 2% biochar application rate in seven soils, which had a pH ≤6.2 (Poděbrady, Hněvčeves, Červený Újezd, Lhota, Humpolec, Žamberk, and Lukavec). A pH rise of up to 1.17 units was observed in these seven soils. For the remaining three soils with pH > 6.2 (Malín pH = 7.1, Suchdol pH = 6.9, and Kbely pH = 7.01), 8% biochar induced a significant increase at both

Table 2 Effect of biochar on soil pH

Soil	Malín		Suchdol		Kbely		Poděbrady		Hněvčeves	
DOI	7	84	7	84	7	84	7	84	7	84
Control	7.06 ± 0.10 B	7.33 ± 0.01 C	6.71 ± 0.19 C	7.13 ± 0.01 B	6.99 ± 0.02 C	6.06 ± 0.02 D	6.23 ± 0.04 D	5.71 ± 0.02 D	5.95 ± 0.07 D	4.15 ± 0.06 C
0.5% biochar	7.24 ± 0.03 AB	7.34 ± 0.05 BC	6.80 ± 0.02 B	7.14 ± 0.15 B	6.99 ± 0.02 C	6.15 ± 0.01 D	6.32 ± 0.02 D	6.01 ± 0.09 C	5.98 ± 0.08 D	4.22 ± 0.07 BC
2% biochar	7.27 ± 0.02 AB	7.40 ± 0.05 BC	6.82 ± 0.03 B	7.16 ± 0.04 AB	7.30 ± 0.08 BC	6.28 ± 0.06 C	6.50 ± 0.04 C	6.13 ± 0.08 BC	6.27 ± 0.03 C	4.36 ± 0.04 B
4% biochar	7.32 ± 0.05 AB	7.46 ± 0.03 AB	6.83 ± 0.02 B	7.18 ± 0.08 AB	7.33 ± 0.08 AB	6.42 ± 0.06 B	6.73 ± 0.0 6 B	6.34 ± 0.14 B	6.48 ± 0.03 B	4.40 ± 0.10 B
8% biochar	7.47 ± 0.24 A	7.57 ± 0.07 A	6.92 ± 0.03 A	7.35 ± 0.02 A	7.42 ± 0.06 A	6.75 ± 0.05 A	6.95 ± 0.01 A	6.65 ± 0.13 A	6.90 ± 0.04 A	5.28 ± 0.10 A
Soil	Červený Újezd		Lhota		Humpolec		Žamberk		Lukavec	
DOI	7	84	7	84	7	84	7	84	7	84
Control	6.06 ± 0.02 D	6.23 ± 0.04 D	5.71 ± 0.02 D	5.95 ± 0.07 D	4.15 ± 0.06 C	4.87 ± 0.02 D	4.38 ± 0.06 D	4.93 ± 0.03 D	5.02 ± 0.01 D	5.11 ± 0.02 D
0.5% biochar	6.15 ± 0.01 D	6.32 ± 0.02 D	6.01 ± 0.09 C	5.98 ± 0.08 D	4.22 ± 0.07 BC	4.95 ± 0.03 D	4.46 ± 0.14 CD	4.97 ± 0.03 D	5.07 ± 0.08 D	5.17 ± 0.04 D
2% biochar	6.28 ± 0.06 C	6.50 ± 0.04 C	6.13 ± 0.08 BC	6.27 ± 0.03 C	4.36 ± 0.04 B	5.21 ± 0.02 C	4.61 ± 0.02 BC	5.22 ± 0.06 C	5.30 ± 0.02 C	5.42 ± 0.07 C
4% biochar	6.42 ± 0.06 B	6.73 ± 0.0 6 B	6.34 ± 0.14 B	6.48 ± 0.03 B	4.40 ± 0.10 B	5.44 ± 0.02 B	4.68 ± 0.03 B	5.46 ± 0.01 B	5.60 ± 0.04 B	5.65 ± 0.06 B
8% biochar	6.75 ± 0.05 A	6.95 ± 0.01 A	6.65 ± 0.13 A	6.90 ± 0.04 A	5.28 ± 0.10 A	5.78 ± 0.08 A	4.98 ± 0.03 A	5.85 ± 0.03 A	6.05 ± 0.01A	6.14 ± 0.04 A

Mean value of soil pH ± standard deviation ($n = 3$), the same letters indicating insignificant effect of biochar addition at $P = 0.05$ within the same sample collection period per each soil

DOI, day of incubation

incubation periods, and a 4% biochar addition also increased pH in these soils in some cases. In these three neutral soils, the addition of the highest amounts of biochar (8%) increased soil pH only to a maximum of 0.4 units. We have also calculated the theoretical expected increment of pH by considering the percentage of biochar added to the incubated soils and comparing with the effect of tested biochar in our incubation experiment. The results revealed that the calculated pH of the soil–biochar mixture was in most cases lower than the actual pH, with the variation reaching up to 0.69 units.

3.2 Effect of biochar on soil CEC

Both a significant increase and a decrease in the CEC of incubated soils were observed following the addition of biochar to soils. The "break point" of the change in the direction of biochar effect on soil CEC was identified (Fig. 1). Biochar addition increased the CEC of seven soils (Poděbrady, Hněvčeves, Červený Újezd, Lhota, Humpolec, Žamberk, and Lukavec), which all had a lower original content of exchangeable Ca^{2+} compared with biochar. In these seven soils, the relative increment of CEC compared with the control treatment ranged between 0.2 and 35.4%. This group of soils was characterized by lower CEC, lower exchangeable Ca^{2+}, and lower pH relative to the remaining three soils. The addition of 0.5 and 2% biochar induced a considerable change only in a few cases, and the higher biochar rates (4 and 8%) induced a significant increase in all seven soils.

A decline in CEC was observed in soils that had a higher original exchangeable Ca^{2+} content than the biochar, namely the Malín, Suchdol, and Kbely soils. The relative decline of soil CEC compared with the control treatment in these three soils varied from 0.2 to 7.9%. Application of 0.5% biochar did not induce a significant CEC decrease in all soils (Table S1, Electronic Supplementary Material—ESM). The biochar addition rate of 2% induced significant CEC decreases in Malín and Suchdol soils at 12 weeks of incubation, whereas 4% caused a substantial decrease in Malín and Kbely soils at both incubation periods, and in Suchdol at week 12. However, the addition of 8% biochar significantly decreased soil CEC in all three soils at both incubation periods.

We also calculated the change in CEC according to the amount (percentage) of biochar added and the properties of soil mixture incubated in order to compare with the biochar effect in soil environments. This figure was higher than the actual CEC recorded from our incubation in all soils, with a difference ranging up to 25%.

3.3 Effect of biochar on soil exchangeable cations (Ca^{2+}, K^{+}, and Mg^{2+})

The biochar addition showed the break point in the magnitude of biochar-induced change in the exchangeable Ca^{2+} content

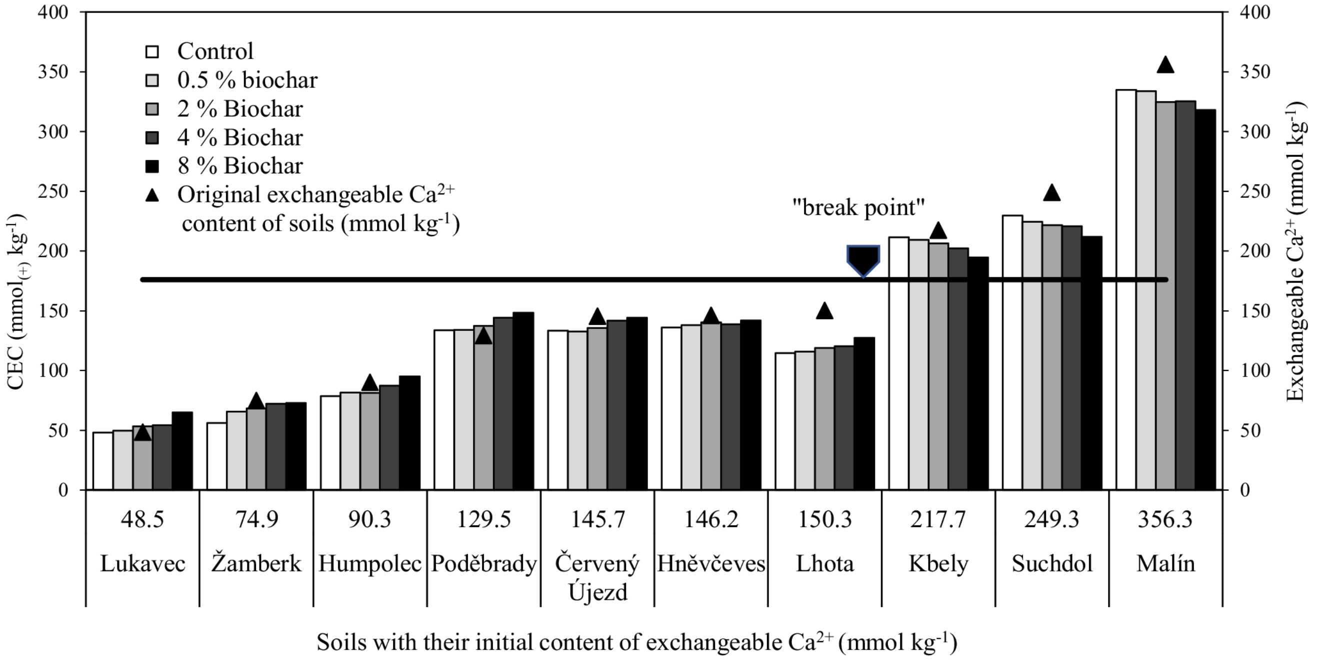

Fig. 1 Effect of elevated biochar rates on soil CEC (mmol$_{(+)}$ kg^{-1}) at the 12th week of incubation and interaction with the original content of soil exchangeable Ca^{2+} (mmol kg^{-1}). CEC of all soils after biochar addition with significance difference is stated at Table S1 (ESM); the vertical line indicates the exchangeable Ca^{2+} content of added biochar (mmol kg^{-1}); ⬟ indicates "break point," i.e., the soil original exchangeable Ca^{2+} content, where biochar-induced increment in soil CEC is altered toward decline for this particular biochar

of soils (Fig. 2). An increment in exchangeable Ca^{2+} was observed in seven soils (Poděbrady, Hněvčeves, Červený Újezd, Lhota, Humpolec, Žamberk, and Lukavec) at 4 and 8% biochar application rates. These seven soils had a lower original exchangeable Ca^{2+} content relative to the biochar. A decrease in exchangeable Ca^{2+} was found in three soils (Malín, Suchdol, and Kbely) that had a higher original exchangeable Ca^{2+} content than the biochar.

The decline in soil exchangeable Ca^{2+} content was up to 11.4% relative to the control at a biochar application rate of 8%. This decline was not significant in most cases for 0.5 and 2% biochar additions, whereas 4 and 8% biochar addition rates induced a considerable decline in all three soils (Table S2—ESM). On the other hand, a significant increment was observed in four soils (Poděbrady, Humpolec, Žamberk, and Lukavec) ranging up to 38.6% relative to the control treatment at the 8% biochar rate. In these four soils, the exchangeable Ca^{2+} increment was at 4% biochar rate in all soils except for soil Humpolec, whereas the increment was observed only in some cases for 0.5 and 2% biochar addition rate. The exchangeable Ca^{2+} contents of the remaining three soils (Hněvčeves, Červený Újezd, and Lhota) were unaffected by biochar additions. These three soils had similar contents of exchangeable Ca^{2+} as that of the added biochar.

The addition of biochar was able to increase exchangeable K^+ content in all soils except some in the 0.5% biochar addition rate treatment. At 0.5% biochar addition, the effect was significant in all soils at least at one of the incubation periods, except for the Malín and Humpolec soils (Table 3). The biochar addition rate of 2% induced significant K^+ content increases in all soils except for Humpolec after only 1 week of incubation. Biochar additions of 4 and 8% substantially increased the exchangeable K^+ of all soils at both incubation periods. The proportion of biochar-induced increment relative to the control was up to 242% at a biochar addition rate of 8% in soil with an acidic pH (pH = 4.8) and with very low exchangeable K^+ content (1.6 mmol kg^{-1}) as compared with other soils. The increment in exchangeable K^+ was as low as 0.7%, and even declined in two cases of the 0.5% biochar application rate in Suchdol and Malin soils with neutral pH (pH = 6.9 and 7.0, respectively). Biochar-induced decreases in exchangeable K^+ occurred in only two cases at the 5% biochar application rate: in Malin soil, a decrease of up to 5.4% after 1 week of incubation, and in Suchdol soil, a decrease of up to 1.6% after 12 weeks of incubation. The effect of biochar application on soil exchangeable Mg^{2+} content was inconsistent and insignificant in most incubated soils (Table S3—ESM). A significant increment was only observed in two soils (Žamberk and Lukavec), both of which were characterized by very low original exchangeable Mg^{2+} contents, were acidic, and had low CEC. This increment ranged up to a maximum of 63% compared with the control treatment at the 8% biochar addition rate.

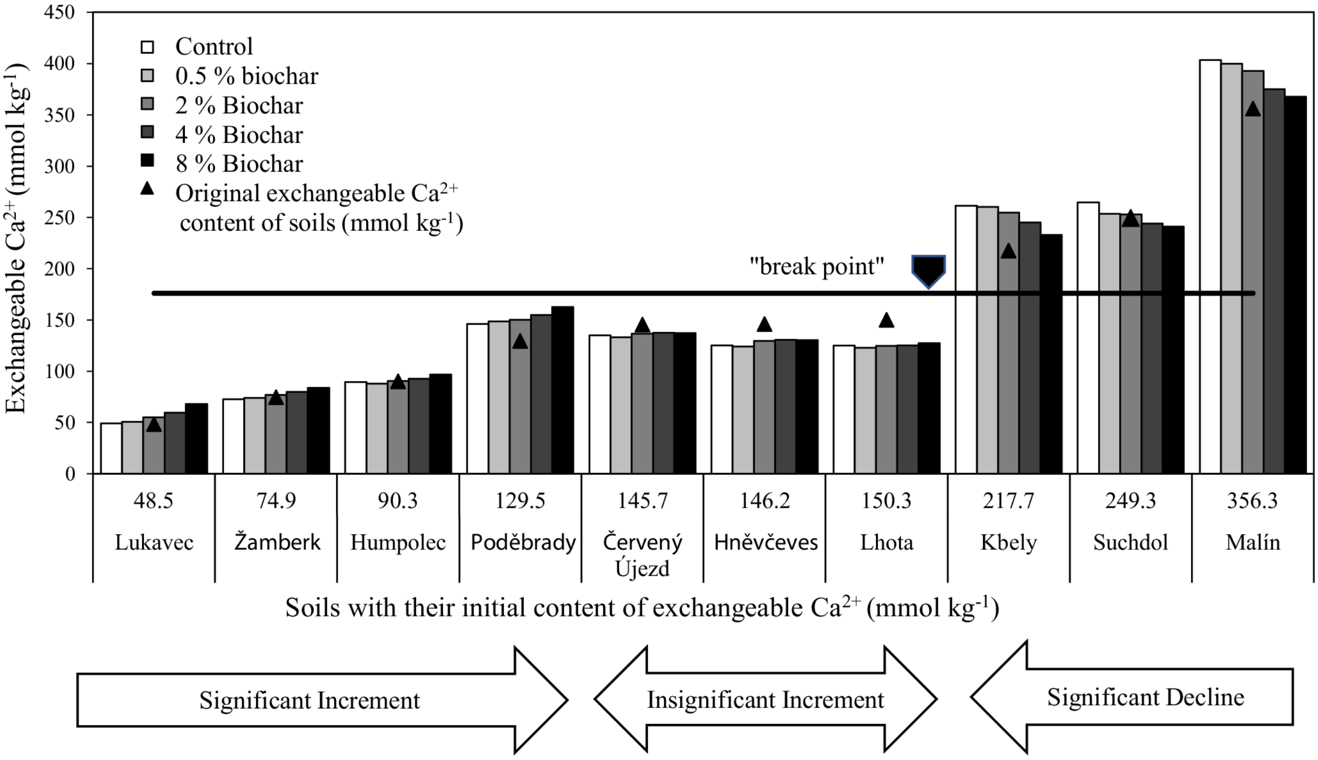

Fig. 2 Effect of elevated biochar rates on the content of soil exchangeable Ca^{2+} (mmol kg^{-1}) at the 12th week of incubation and interaction with the original content of soil exchangeable Ca^{2+} (mmol kg^{-1}). Exchangeable Ca^{2+} content of all soils after biochar addition with significance difference is stated in Table S1 (ESM); the vertical line indicates the exchangeable Ca^{2+} content of added biochar (mmol kg^{-1}); ⬟ indicates "break point," i.e., the soil original exchangeable Ca^{2+} content, where biochar-induced increment in soil CEC is altered toward decline for this particular biochar

3.4 The interrelationships of the determined soil characteristics

Based on our results from the multivariate analysis of variance (Table 4), all factors evaluated (biochar rate, period of incubation, and soil type), and in many cases their interactions, significantly affected soil pH and exchangeable Ca^{2+} ($p < 0.05$). With respect to CEC, exchangeable K^+, and exchangeable Mg^{2+}, all the evaluated factors and their interactions were significant ($p < 0.05$).

Pearson correlations among original soil properties with the amount of change in soil pH, percentage of change in CEC, and exchangeable Ca^{2+}, K^+, and Mg^{2+} relative to the control after 12 weeks of incubation were calculated (Table 5). The amount of biochar-induced change in soil pH relative to control soil was significantly and negatively correlated with the soil's original pH, CEC, exchangeable Ca^{2+} content, and percentage of soil clay fraction. The amount of biochar added had a positive significant correlation with the percentage of soil sand fraction.

The biochar-induced decline (%) in soil CEC and exchangeable Ca^{2+} at 12 weeks of incubation behaved in the same way and both parameters were negatively correlated with the original soil pH, CEC, exchangeable Ca^{2+} and Mg^{2+} content, and the percentage of soil clay fraction. In the case of K^+, the biochar rate was negatively correlated with soil exchangeable K^+ and Mg^{2+} content, and with the percentage of soil clay fraction. Exchangeable Mg^{2+} was negatively and significantly correlated only with the initial soil exchangeable Mg^{2+} content and the percentage of soil clay fraction.

The regression analysis for pH including all ten soils was used to model equations integrating the biochar addition rate and other soil parameters, which have a significant regression coefficient (Table 6). All original soil properties included were significant ($p < 0.01$). The whole model of soil pH was significant ($p < 0.001$) and could explain 97% of the variability in soil pH after the addition of biochar.

Another model for CEC and exchangeable Ca^{2+} was constructed after grouping our soils into two groups. One group contained soils with a lower exchangeable Ca^{2+} content than added biochar (Table 7), and the other contained soils with a higher exchangeable Ca^{2+} than the added biochar (Table 8). The entire model was significant ($p < 0.001$) and explained more than 99% of the variability in both CEC and exchangeable Ca^{2+}. In both cases, soil properties without a significant effect were excluded from the model. Moreover, the biochar effect on soil exchangeable K^+ and Mg^{2+} was not presented due to the insignificance of the whole model.

Table 3 Effect of biochar addition on exchangeable K^+ content of soil

Soil	Malín		Suchdol		Kbely		Poděbrady		Hněvčeves	
DOI	7	84	7	84	7	84	7	84	7	84
Control	10 ± 0.2 AB	9.0 ± 0.1A	5.6 ± 0.2 A	6.2 ± 0.2 A	5.3 ± 0.1 A	5.7 ± 0.1 A	5.1 0.2 A	5.9 ± 0.1 A	7.6 ± 0.1 A	7.8 ± 0.3 A
0.5% biochar	9.4 ± 0.3 A	9.1 ± 0.2 AB	6.1 ± 0.3 B	6.1 ± 0.2 AB	6.1 ± 0.1 B	6.0 ± 0.2 A	5.8 ± 0.1 B	6.1 ± 0.0 A	8.4 ± 0.6 B	8.2 ± 0.0 AB
2% biochar	10.7 ± 0.8 BC	9.7 ± 0.4 B	6.3 ± 0.1 B	6.7 ± 0.3 BC	6.7 ± 0.1 C	7.0 ± 0.5 B	5.9 ± 0.2 B	6.8 ± 0.1 B	8.7 ± 0.1 B	8.6 ± 0.2 B
4% biochar	11.5 ± 0.2 C	10.4 ± 0.2 C	7.3 ± 0.2 C	7.2 ± 0.2 C	7.7 ± 0.1 D	7.6 ± 0.1 C	7.4 ± 0.2 C	7.4 ± 0.2 B	9.2 ± 0.2C	9.6 ± 0. 3 C
8% biochar	13.3 ± 0.4 D	11.9 ± 0.3 D	8.5 ± 0.1 D	8.8 ± 0.3 D	9.8 ± 0.2 E	9.5 ± 0.2 D	8.2 ± 0.5 D	9.3 ± 0.5 C	10.7 ± 0.3 D	11.3 ± 0.2 D

Soil	Červený Újezd		Lhota		Humpolec		Žamberk		Lukavec	
DOI	7	84	7	84	7	84	7	84	7	84
Control	13.3 ± 0.2 A	12.4 ± 0.2 A	6.8 ± 0.2 A	6.0 ± 0.1 A	4.5 ± 0.1 A	4.1 ± 0.1 A	1.9 ± 0.2 A	2.5 ± 0.6 A	5.5 ± 0.1A	5.3 ± 0.2 A
0.5% biochar	14.1 ± 0. 2 B	12.5 ± 0.1 A	7.6 ± 0.2 B	6.3 ± 0.1 A	5.2 ± 0.2 AB	4.5 ± 0.1 AB	2.6 ± 0.2 AB	2.8 ± 0.3 B	6.5 ± 0.5 BC	5.4 ± 0.1 A
2% biochar	14.4 ± 0.1 B	13.3 ± 0.1 B	8.5 ± 0.3 C	7.1 ± 0.3 B	5.2 ± 0.1 AB	4.7 ± 0.2 B	3.3 ± 0.1 B	3.6 ± 0.2 C	6.5 ± 0.0 B	6.1 ± 0.3 B
4% biochar	15.2 ± 0.2 C	14.5 ± 0.3 C	9.8 ± 0.1 D	8.2 ± 0.2 C	5.7 ± 0.0 B	4.9 ± 0.2 B	4.4 ± 0.3 C	4.8 ± 0.1 CD	7.3 ± 0. 4C	6.8 ± 0.1C
8% biochar	16.6 ± 0.2 D	16.4 ± 0.5 D	11.5 ± 0.4 E	9.9 ± 0.2 D	6.8 ± 0.7 C	5.5 ± 0.2 C	6.5 ± 0.5 D	6.6 ± 0.6 D	8.3 ± 0.2 D	8.4 ± 0.3 D

Mean value of soil K^+ content in mmol kg^{-1} with standard deviation in italic ($n = 3$), the same letters indicating insignificant effect of biochar addition rate at $P = 0.05$ within the same sample collection period per each soil

DOI, day of incubation

Table 4 Multivariate analysis of variance in soil pH, CEC, and exchangeable Ca^{2+}, K^+, and Mg^{2+} with interaction and single effect of factors

Soil properties		Biochar rate	Period of incubation	Soil type	Biochar rate × incubation period	Biochar rate × soil type	Biochar rate × incubation period × soil type
pH	DF	4	1	9	4	36	45
	F	1084.909	1536.107	5665.431	3.055	23.662	30.587
	P	*< 0.001*	*< 0.001*	*< 0.001*	*0.323*	*< 0.001*	*< 0.001*
CEC	DF	4	1	9	4	36	45
	F	20.38	23.54	41,466.41	3.33	40.44	12.75
	P	*< 0.001*	*< 0.001*	*< 0.001*	*0.011*	*< 0.001*	*< 0.001*
Exch. Ca^{2+}	DF	4	1	9	4	36	45
	F	11.30	23.45	23,598.43	1.18	25.60	12.17
	P	*< 0.001*	*< 0.001*	*< 0.001*	*0.323*	*< 0.001*	*< 0.001*
Exch. K^+	DF	4	1	9	4	36	45
	F	313.17	7.70	640.23	2.57	1.96	3.72
	P	*< 0.001*	*0.006*	*< 0.001*	*0.039*	*0.002*	*< 0.001*
Exch. Mg^{2+}	DF	4	1	9	4	36	45
	F	18.24	22.17	4404.12	3.23	4.25	4.65
	P	*< 0.001*	*< 0.001*	*< 0.001*	*0.014*	*< 0.001*	*< 0.001*

The italicized values indicate the significance level at $n = 300$

DF, degree of freedom; *F*, *F* test; *P*, *P* value

4 Discussion

4.1 Effect of biochar on soil pH

The addition of biochar effectively increased soil pH (Table 2). Further, pH increment clearly depended on soil type and biochar application rate. In acidic to slightly acidic soils, a significant increment of pH began from a 2% biochar addition rate, while 8% biochar rate induced a significant pH increment in all soils. The increment of soil pH due to biochar addition is consistent with findings in other studies (Jien and Wang 2013; Masud et al. 2014; Wang et al. 2014; Gul et al. 2015; Hilioti et al. 2017; Kameyama et al. 2017; Al-Wabel et al. 2018; Mandal et al. 2018). For example, Jien and Wang (2013) reported an increment in soil pH after the addition of 2.5%, and 5% (*w*/*w*) biochar (from 3.9 in the control samples up to 5.1 after the addition of 5% biochar) produced from waste wood of white lead trees (*Leucaena leucocephala*). The increment in soil pH of up to 0.4 units (from 7.3 up to 7.7) was also reported after the addition of poplar leaf–based biochar produced at 650 °C (Bai et al. 2017). One of the mechanisms for the pH increment after biochar addition is likely due to the considerable amount of ash and base cations in biochar. This mechanism is evidenced by Li et al. (2018), where high-temperature

Table 5 Pearson's correlation coefficients among percentage of 8% biochar rate induced changes (CEC, exchangeable cations, and pH values) relative to control at the 12th week of incubation and soil original properties

Biochar-induced changes	Initial soil parameters						
	pH	CEC (mmol$_{(+)}$ kg^{-1})	Exch. Ca^{2+} (mmol kg^{-1})	Exch. K^+ (mmol kg^{-1})	Exch. Mg^{2+} (mmol kg^{-1})	Sand (%)	Clay (%)
Change in pH	−0.76**	−0.82**	−0.83**	−0.12	−0.50	0.75**	−0.72**
% change in CEC	−0.89**	−0.86**	−0.83**	−0.31	−0.69*	0.43	−0.83**
% change in Exch. Ca^{2+}	−0.71*	−0.80**	−0.79**	−0.21	−0.62*	0.39	−0.78**
% change in Exch. K^+	−0.41	−0.40	−0.40	−0.64*	−0.61*	0.14	−0.57*
% change in Exch. Mg^{2+}	−0.48	−0.53	−0.51	−0.45	−0.74**	0.09	−0.72**

$n = 10$

Exch., exchangeable

**Correlation is significant at $p < 0.01$

*Correlation is significant at $p < 0.05$

Table 6 Regression model for pH including soil parameters and biochar addition rate at 12th week of incubation, regression coefficients are displayed

Soil properties	Intercept value	Biochar rate (%)	Original Exch. Ca^{2+} (mmol kg^{-1})	Original Exch. K^{+} (mmol kg^{-1})	Original Exch. Mg^{2+} (mmol kg^{-1})	Original pH	Clay (%)	
pH	− 0.034	0.16***	− 0.003***	− 0.16***	0.04***	1.03***	0.02**	$R^2 = 0.973$

Exch., exchangeable

***Significant at $p < 0.001$

**Significant at $p < 0.01$

$n = 150$

biochar with high pH increased the pH of soils with its considerable ash content. The alkalinity of biochar, and the subsequent release of base cations, especially Ca^{2+} and K^+, and the replacement of soil exchangeable Al^{3+} and H^+ by these cations on the soil's negatively charged sites could greatly increase soil pH (Masud et al. 2014). In addition, negatively charged functional groups (e.g., phenolic, carboxylic, and hydroxyl) present at the surface of biochar could also contribute to the increment of soil pH by binding the surplus H^+ ions present in the soil solution (Gul et al. 2015). Another possible mechanism is the decarboxylation of organic anions initiated by biochar addition, owing to increasing attack of organic anions by microbes, which may consume surplus H^+ from the soil solution, and thus increase soil pH (Wang et al. 2014). Based on the multivariate analysis of variance (Table 4), the effect of soil type on the amount of biochar-induced pH rise was greater than the effect of incubation period, biochar addition rate, or their interaction effect. Our correlation analysis (Table 5) also confirmed the dependence of biochar effectiveness on original soil properties. Overall, the results suggest that the effectiveness of biochar amendment for increasing soil pH is greater in soils with low pH, CEC, exchangeable Ca^{2+} content, and clay fraction, and in soils with a higher sand fraction. This is due to the greater buffering capacity of soils with higher CEC than soils with lower CEC (Xu et al. 2013). The low increment in soil pH in soils with high clay contents is similarly due to the high buffering capacity of clay soils compared with sandy soils (Jones Jr 2012). Our regression model (Table 6) is applicable for testing the effect of biochars with similar properties (high-temperature wood biochar produced at 700 °C) on soil pH.

4.2 Effect of biochar on soil CEC and exchangeable cations (Ca^{2+}, K^+, Mg^{2+})

The multivariate analysis of variance (Table 4) indicated that biochar application rate and the interaction of biochar rate with both soil type and incubation period induced significant differences in soil CEC and exchangeable Ca^{2+} content. There was also clear evidence that the exchangeable Ca^{2+} content of soil was the most consequential factor for determining the magnitude of biochar-induced changes to soil CEC and exchangeable Ca^{2+}. We found no studies supporting or contradicting this generalization. However, the base of this generalization is that the increment in soil CEC and exchangeable Ca^{2+} was in seven soils (Poděbrady, Hněvčeves, Červený Újezd, Lhota, Humpolec, Žamberk, and Lukavec), which had higher exchangeable Ca^{2+} content than the biochar added. The more general finding that increment in soil CEC and exchangeable Ca^{2+} after biochar addition is in agreement with previous studies (Jien and Wang 2013; Chintala et al. 2014; Martinsen et al. 2015; Hilioti et al. 2017; Al-Wabel et al. 2018; Cornelissen et al. 2018). The primary mechanisms for biochar additions increasing CEC are likely mediated through the greater surface area, negative surface charge, and charge density of biochar (Liang et al. 2006; Li et al. 2018) and the release of surplus Ca^{2+} content from biochar, which accounted 176 mmol kg^{-1} (Table 1). The presence of oxygenated (acid) functional groups on biochar surfaces can also increase soil CEC (Glaser et al. 2003; Sohi et al. 2010). Another potential mechanism is the adsorption of oxides (Al and Fe) by biochar and the subsequent decline in soil point of zero charge (pzc) leading to an increase in soil CEC (Trakal et al. 2016). In addition, the increment in pH of acidic and weakly acidic soils after the addition of biochar could result in the deprotonation of functional groups from minerals, such as kaolinite, resulting in the development of more negative charges that contribute to the development of higher CEC (Sparks 2003). A decrease in CEC and exchangeable Ca^{2+} was observed in three soils (Malín, Suchdol, and Kbely), each of which had lower exchangeable Ca^{2+} content than the added biochar. A decline in soil CEC was reported previously. Prommer et al. (2014) observed a decline of soil CEC from 225 to 208 $mmol_{(+)}$ kg^{-1} after application of biochar (produced at 500 °C with pH value of 7.5 and an unreported CEC) to soil with a pH of 7.5 and CEC of 225 $mmol_{(+)}$ kg^{-1}. In our soils, the first cause for the decline in CEC and exchangeable Ca^{2+} content of the three soils (Malín, Suchdol, and Kbely) likely arose from their high exchangeable Ca^{2+} contents. Thus, the release of surplus exchangeable Ca^{2+} from biochar into the soils, which already had high exchangeable Ca^{2+} and organic matter contents, possibly led to the formation of aggregates between exchangeable Ca^{2+} and soil organic matter. Consequently, this formation of aggregates can lead to reductions of both CEC and exchangeable Ca^{2+} (Clough and Skjemstad 2000). This mechanism is in agreement

Table 7 Regression model for CEC and exchangeable Ca^{2+} including soil parameters and biochar addition rate at 12th week of incubation for seven soils, which have lower exchangeable Ca^{2+} than added biochar; regression coefficients are displayed

Soil properties	Intercept value	Biochar rate (%)	Original Exch. Ca^{2+} (mmol kg^{-1})	Original Exch. K^{+} (mmol kg^{1})	Original Exch. Mg^{2+} (mmol kg^{1})	Original pH	Clay (%)	
Exch. Ca^{2+} (mmol kg^{-1})	− 78.91***	1.06***	0.817***	− 1.75***	− 0.937***	17.96***	0.985***	$R^2 = 0.991$
CEC ($mmol_{(+)}$ kg^{-1})	− 97.05***	1.59***	0.57***	− 0.94***	0.76***	20.86***	1.11***	$R^2 = 0.992$

n = 105

Exch., exchangeable

***Significant at $p < 0.001$

**Significant at $p < 0.01$

with the report of Glaser et al. (2002), where they reported the binding of highly available calcium with soil organic matter (SOM). In another study, the reduction of Ca^{2+} extractability in soils containing large amounts of calcium was reported and resulted from Ca^{2+}–organic matter bridging (Shen 1999). The presence of high Ca^{2+} content in soil may also protect biochar from oxidation and decomposition (Clough and Skjemstad 2000). A second mechanism for the decrease in CEC of these three soils (Malín, Suchdol, and Kbely) could be their high organic matter content. SOM, which is a rich source of surface negative charges, could be adsorbed by biochar resulting in a decline of exchange sites on both SOM and biochar surfaces (Clough and Skjemstad 2000). This phenomenon was reported as a possible mechanism for the decline of soil CEC and exchangeable Ca^{2+} (Kwon and Pignatello 2005). Third, the humic and fulvic acids from organic matter-rich soils could block the inner pores of biochar, rendering them inaccessible for further physical adsorption and thus reducing CEC (Pignatello et al. 2006). Based on the Pearson correlation coefficients (Table 5), the effectiveness of biochar to increase soil CEC and exchangeable Ca^{2+} was high in soils with lower original exchangeable Ca^{2+}, pH, CEC, clay fraction, and exchangeable Mg^{2+}. The final content of soil exchangeable Ca^{2+} and soil CEC was estimated based on our regression model (Table 7 and Table 8). This model provides a first approximation of what to expect after the addition of biochars with different properties. In our model, we clearly presented which model should be used for which type of soil. Here, we would like to emphasize that it is important to use a specific model for soils with differing exchangeable Ca^{2+} contents.

Results from the multivariate analysis (Table 4) indicated that the paramount factor affecting exchangeable K^{+} content was soil type followed by the biochar application rate. This could simply indicate that there was considerable variability in the K^{+} content between incubated soils, and that biochar also significantly affects the overall soil exchangeable K^{+} content. Generally, biochar was effective at increasing the content of soil exchangeable K^{+} regardless of the soil properties. This was likely due to the high content of exchangeable K^{+} in our biochar, which was almost five times higher than the content of soil exchangeable K^{+} and its direct release into the soil. A high availability of K (even up to 80% of total K) was reported in biochar derived from manure, crop residue, and municipal waste (Zornoza et al. 2016). Similar results were reported by Kongthod et al. (2015), where cassava (*Manihot esculenta*) stem–based biochar-amended soils released up to 148 mg kg^{-1} of K after 7 days of incubation, and rice husk biochar treatments released up to 188 and 186 mg kg^{-1} of K after 1 and 3 days of incubation, respectively. An increment of soil K content following the application of peanut (*Arachis hypogaea*) hull and pine (*Pinus* spp.) chip biochar to the top soil was reported (Gaskin et al. 2010). In an additional study, an increment in K content of soil from 39.3 to 48.5 mg kg^{-1} was reported following the application of *Conocarpus* spp. wood waste biochar at the rate of 10 mg kg^{-1} (El-Naggar et al. 2015). Regarding factors controlling the amount of increment in soil exchangeable K^{+}, the

Table 8 Regression model for CEC and exchangeable Ca^{2+} including soil parameters and biochar addition rate at 12th week of incubation for three soils, which have higher exchangeable Ca^{2+} than added biochar; regression coefficients are displayed

Soil properties	Intercept value	Biochar rate (%)	Original Exch. Ca^{2+} (mmol kg^{1})	Clay (%)	
Exch. Ca^{2+} (mmol kg^{-1})	164.33***	− 3.61***	1.14***	− 7.09***	$R^2 = 0.993$
CEC ($mmol_{(+)}$ kg^{-1})	− 78.62***	− 1.98***	0.850***	3.39***	$R^2 = 0.998$

n = 45

Exch., exchangeable

***Significant at $p < 0.001$

**Significant at $p < 0.01$

Pearson correlation (Table 5) revealed the negative contribution to soil initial exchangeable cations and clay fraction on the increase of soil exchangeable K^+ after biochar application. The low effectiveness of biochar to increase soil exchangeable K^+ in soils with high proportions of clay could be due to the fixation or trapping of K^+ between the layers of clay minerals. The high rate of K fixation in soils with relatively high activities of K is in agreement with finding of Matthews and Sherrell (1960). On the other hand, following the addition of biochar with K^+, higher increments of K^+ in soils with relatively lower original K^+ compared with the increment in soils with higher original K^+ content can be expected.

Although no effect of biochar was observed on exchangeable Mg^{2+} content in most soils (Table S3—ESM), the multivariate analysis of variance (Table 4) did indicate a significant effect of biochar application rate on exchangeable Mg^{2+} content. However, the higher variability in soil exchangeable Mg^{2+} content arises due to soil type and period of soil incubation. Here, the results indicated an effect of biochar on soil exchangeable Mg^{2+} content. The multivariate analysis of variance considers the overall effect by taking the average of all soils and summing it. Focusing on individual soils, the increment of exchangeable Mg^{2+} was significant in only two soils with very low original exchangeable Mg^{2+} contents. This suggests that Mg was released from biochar when in soils with relatively low available Mg content. These findings accord with the report of Wu et al. (2011). Similarly, the application of peanut hull biochar increased soil Mg content (Gaskin et al. 2010). The release of Mg in acidic soils from biochar was also reported (Xu et al. 2013). Other studies have shown insignificant change in soil Mg content following the addition of biochar produced from a mixture of hardwood (primarily oak, *Quercus* spp. and hickory, *Carya* spp.) (Laird et al. 2010). Even if the substantial increment in soil exchangeable Mg^{2+} was significant only in two soils, the percentage of change relative to the control was significantly correlated with soil initial exchangeable Mg^{2+} content and the clay fraction of soils (Table 5). This implies that the initial exchangeable Mg^{2+} and clay fraction comprise the main limiting factors for biochar-induced change in soil exchangeable Mg^{2+} content. This principle is identical with exchangeable K^+ content in soils. The amount of Mg^{2+} added from biochar (containing certain amounts of Mg) will be high in soils with relatively lower original exchangeable Mg^{2+} than in soils with higher original exchangeable Mg^{2+} content. In addition, the low increment of exchangeable Mg^{2+} in soils with high amounts of clay could be due to the trapping of Mg^{2+} between the layers of clay minerals.

5 Conclusions

The main findings of this study investigating a wide range of soils with different properties treated with elevated rates of high-temperature pyrolysis biochar (700 °C) can be summarized as follows: (i) Greater biochar addition yields a greater rise in pH and 8% biochar addition is the most effective rate. The increment is higher in soils that have relatively low original pH, CEC, exchangeable Ca^{2+} content, and clay percentage. (ii) The addition of the same type of high-temperature produced biochar to different types of soils can result in both a decrease and an increase of soil CEC and soil exchangeable Ca^{2+} content, where the effect differs according to specific soil properties. The percentage of biochar-induced changes in both CEC and exchangeable Ca^{2+} is high in soils with low initial pH, CEC, exchangeable Ca^{2+} and Mg^{2+}, and a low percentage of clay. (iii) The addition of biochar increases exchangeable K^+ content in a range of soils, where the size of increment is higher in soils with lower original contents of soil exchangeable K^+ and Mg^{2+}, and lower percentage of clay.

Our findings clearly demonstrate that knowledge of biochar properties as well as soil properties is useful for predicting the efficiency of biochar application to alter soil properties. Among soil properties, soil exchangeable Ca^{2+} content is the salient factor controlling the magnitude of biochar-induced changes to soil CEC and exchangeable Ca^{2+} content.

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4.3. The Role of Biochar and Soil Properties in Determining the Available Content of Al, Cu, Zn, Mn, and Cd in Soil

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The Role of Biochar and Soil Properties in Determining the Available Content of Al, Cu, Zn, Mn, and Cd in Soil

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Abstract: The purpose of the study was to understand the mechanisms of biochar-induced changes in the available content of aluminum (Al), cadmium (Cd), zinc (Zn), copper (Cu), and manganese (Mn) in a wide range of soils. Five soils from different regions of the Czech Republic were incubated for 12 weeks with four rates of biochar (0.5%, 2%, 4%, and 8% *w*/*w*). The available concentrations of Al, Cd, Zn, Cu, and Mn were determined on the 7th and 84th day of incubation. There was a significant decline in the available content of Al, Zn, Cu, Mn, and Cd except in the available content of Al in one soil, which is characterized by very low Al content, higher cation exchange capacity (CEC), and neutral pH = 7.0. The decline in the mobile contents of Al, Zn, Cu, Mn, and Cd was significant in all cases of 8% biochar rate. The decline in the content of Al, Zn, Cu, Mn, and Cd was mainly due to the increment in soil pH and increment in CEC, decline in dissolved organic carbon (DOC), and the release of exchangeable Ca^{2+} and K^{+} from biochar. The application of high amounts of biochar to soil could increase the available content of some metals like Al. On the other hand, biochar could efficiently reduce the mobility of Al, Zn, Cu, Mn, and Cd in soil, while the decline is mainly caused by biochar-induced changes in soil pH, CEC, DOC, and exchangeable Ca^{2+} and K^{+} content of treated soils.

Keywords: biochar; metals; immobilizations; mechanisms; soil properties

1. Introduction

Soil acidification connected with increased mobility of metals like Al, Cu, Zn, Mn. and Cd can result in higher environmental risk of these elements, especially via potential leaching to surface and/or groundwater, or via higher bio accessibility of these elements [1]. For instance, acidification of soil from pH 5.6 to pH 4.5 and pH 3.0 by simulated acid rain substantially increased the mobile proportions of Cu, Pb (lead), Cd, and Zn [2]. Shifts in the distribution of elements due to the soil acidification were documented [3]. Effect of soil acidification and the subsequent mobilization of Cd and Zn is well documented [4]. Besides Cd and Zn, the enhanced mobility of elements such as Cu, Fe, Mn, and Al is often discussed within the potential detrimental impact of soil acidification on soil parameters [5,6]. Higher uptake of elements such as Cd and Zn by plants growing in the acidified soil can cause toxic effects to plants [7]. The rise in the mobile content of Al (reaching the phytotoxic levels of this element in soil solution) was reported by Singh et al. [8] when the soil was acidified to a pH level of less than 5. According to these authors, the toxicity of Al in acidic soils represents a worldwide problem resulting in reduced crop yields.

Various materials have been tested to mitigate the long-term acidification of soils, such as calcium silicate (i.e., wollastonite), clay minerals (zeolite, montmorillonite, illite, and sepiolite), lime, hydroxyapatite, and biochar [9–13]. The ability of biochar to remediate both organic and inorganic contaminants is reported [14–19]. For example, the application of both bamboo and rice straw biochar was effective in decreasing extractability of Cu, Cd, and Zn [20]. In this context, biochar showed better Cd immobilization efficiency compared to liming, especially in the soils with low buffering capacity [9]. Wang et al. [21] also observed better Cd immobilization of wheat straw biochar compared to other organic matter sources (vermicompost) due to the higher stability of Cd complexes. In addition to this, Lu et al. [22] highlighted the effectivity of poultry litter and eucalyptus biochar (3% rate) to reduce the mobility of Cd in acidic soil. However, Mukwaturi and Lin [23] reported the reductive dissolution of Fe and Mn from the organic matter content of soil, resulting in the increased mobile proportions of these elements in soil. According to the findings of Alozie et al. [24] biochar in combination with low molecular weight organic acids could potentially enhance the reductive dissolution of iron and manganese oxides in the soil, leading to enhanced release of Fe and Mn originally bound to these oxides. The main mechanisms for the adsorption of metal by biochar are thought to be complexation, cation exchange, precipitation, and electrostatic interactions [25]. The functional groups, which are responsible for the sorption of metals are carboxylic, amino, and hydroxyl groups [25]. Addition of biochar could increase soil pH and CEC and result in the increase of negative surface charges on both soil and biochar, which in turn enhances the sorption of As, Cr, Cd, Pb, and Hg [15,25]. Hence, the role of biochar-induced changes of soil pH, CEC, DOC, and exchangeable Ca^{2+} and K^+ in determining the available content of Al, Cu, Zn, Mn, and Cd has been poorly studied. The main objectives of the study were to: i) investigate the interaction of biochar-induced changes in soil pH, CEC, DOC, and exchangeable Ca^{2+} and K^+ with the immobility of Al, Zn, Cu, Mn, and Cd and ii) assess the potential of biochar to alter mobility of Al, Zn, Cu, Mn, and Cd in a set of soils varying from acidic to neutral pH. We hypothesized that the change in soil properties (pH, CEC, exchangeable Ca^{2+}, K^+, and DOC) would be responsible for biochar-induced changes in the available content of Al, Zn, Cu, Mn, and Cd.

2. Material and Methods

2.1. Soil Sampling and Biochar Production

Five soils have been selected with a wide range of properties (pH, CEC, nutrient content and textural classes) were collected from five different agricultural sites in the Czech Republic. The selection of soils with a wide range of properties was manly intended to enable the investigation of biochar-induced change in soil properties on the immobilization and/or mobilization of Al, Zn, Cu, Mn, and Cd. Each soil was collected from the top layer (0–20 cm), air-dried, and passed through a 2 mm sieve prior to use. Biochar was produced from willow tree chips at 700 °C by fast pyrolysis in a fluidized bed reactor then milled to pass through a 2 mm sieve. The above-mentioned temperature of biochar production was selected to obtain stable biochar after exploitation of the highest possible energy. The localization and specific properties of soils and biochar are shown in Table 1. More detailed characterization of soils and biochar used in this study is presented in Hailegnaw et al. [26,27].

2.2. Experimental Design

Incubation experiment was set up using 500 mL plastic pots for 12 weeks in controlled environmental conditions at room temperature (25 ± 2 °C). The experiment was designed with 5 treatments: Control (soil + no biochar), soil + 0.5% biochar, soil + 2% biochar, soil + 4% biochar, and soil + 8% biochar (*w*/*w* ratio). Four rates of biochar (0.5%, 2%, 4%, and 8% were selected to simulate field application rates of biochar of 0.5% and 2% and the slightly higher rates of 4% and 8% to determine the biochar effect. Individual pots of soil–biochar mixture were weighed and thoroughly mixed separately, then each pot was filled at the beginning of incubation to ensure homogeneity and pots were regularly irrigated every third day to reach 60% of maximum water holding capacity. Soil maximum water holding capacity was determined by filling Mitscherlich columns with air-dried soil of known weight and moisture content. Subsequently, the columns were soaked in water for two hours to ensure saturation of soil in the column, then the water in the soil was drained for 12 h. The maximum water holding capacity was calculated gravimetrically as the amount of water retained by the known amount of soil (dry weight) in the Mitscherlich columns. Samples of incubated soil and/or soil-biochar mixture were sampled on the 7th day (week 1) and 84th day (week 12) of incubation.

Table 1. Selected physiochemical properties of incubated soils and biochar.

Properties	Kbely	Lhota	Humpolec	Žamberk	Lukavec	Biochar
Localization	50°08′01.9″ N	49°42′00.0″ N	49°33′00.0″ N	50°08′39.6″ N	49°33′00.0″ N	-
	14°33′56.3″ E	13°59′00.0″ E	15°21′00.0″ E	16°30′50.0″ E	14°58′00.0″ E	-
Soil type	Chernozem	Fluvisol	Cambisol	Cambisol	Cambisol	-
pH	7.01	5.91	4.50	4.80	5.30	9.50
CEC (mmol kg^{-1})	217 ± 0.30	130 ± 4.70	90.3 ± 2.00	74.9 ± 3.70	48.5 ± 6.00	102 ± 5.20
Total C (%)	4.28 ± 0.09	2.67 ± 0.04	1.60 ± 0.09	1.98 ± 0.09	1.48 ± 0.13	87.5 ± 0.20
DOC (mg kg^{-1})	120 ± 1.70	76.3 ± 2.40	11.7 ± 0.60	63.6 ± 2.00	63.4 ± 2.10	281 ± 8.67
CO_3^{2-} (%)	2.17 ± 0.01	0.21 ± 0.00	0.20 ± 0.00	0.18 ± 0.00	0.20 ± 0.01	0.19 ± 0.01
Al (mg kg^{-1}) †	27,205 ± 1470	25,008 ± 1327	29,275 ± 83.0	20,178 ± 863	35,811 ± 607	988 ± 10.0
Cu (mg kg^{-1}) †	46.0 ± 3.90	24.0 ± 4.32	49.0 ± 2.05	102 ± 0.61	18.0 ± 0.40	7.00 ± 1.60
Zn (mg kg^{-1}) †	138 ± 0.45	240 ± 43.0	156 ± 12.0	61.0 ± 12.9	80.0 ± 0.60	15.0 ± 2.40
Mn (mg kg^{-1}) †	417 ± 0.0	1077 ± 600	427 ± 13.1	792 ± 53.0	735 ± 9.30	893 ± 15.0
Cd (mg kg^{-1}) †	0.12 ± 1.65	0.26 ± 0.89	1.34 ± 0.58	0.18 ± 0.03	0.15 ± 0.001	0.12 ± 0.01
Al (mg kg^{-1}) §	0.81 ± 0.33	1.19 ± 0.04	5.97 ± 0.28	3.04 ± 0.31	5.04 ± 0.98	38.9 ± 0.85
Cu (mg kg^{-1}) §	0.25 ± 0.14	0.11 ± 0.00	0.16 ± 0.01	0.07 ± 0.00	0.09 ± 0.01	0.04 ± 0.00
Zn (mg kg^{-1}) §	n.d	1.83 ± 0.03	0.85 ± 0.21	0.24 ± 0.00	0.21 ± 0.04	0.26 ± 0.02
Mn (mg kg^{-1}) §	1.84 ± 0.27	14.7 ± 0.38	67.4 ± 0.59	67.6 ± 0.78	29.3 ± 2.12	0.12 ± 0.017
Cd (mg kg^{-1}) §	0.07 ± 0.04	0.14 ± 0.01	0.04 ± 0.00	0.03 ± 0.00	0.03 ± 0.00	n.d
Sand (%)	14.9	39.6	30.2	26.1	27.9	-
Silt (%)	60.2	45.5	48.4	59.9	61.2	-
Clay (%)	24.9	14.9	21.4	14.1	11.6	-
Textural Class	Silt Loam	Loam	Loam	Silt Loam	Silt Loam	-

†: Pseudo total content, §: 0.01 M $CaCl_2$ extractable content, n.d: not detectable (detection limit of inductively-coupled plasma–optical emission spectrometer (ICP-OES) = 0.01 mg kg^{-1} Cd, 0.02 mg kg^{-1} Al), CEC: cation exchange capacity, DOC: dissolved organic carbon.

2.3. Chemical Analysis

The pH of soil and biochar was determined after extraction with 0.01 M $CaCl_2$ ($w/v = 1/5$) ISO 10390 [28] by Argus pH meter (Sentron) with transistor CupFET probe. The concentration of available Al, Zn, Cu, Mn, and Cd in soil samples was determined by inductively-coupled plasma–optical emission spectrometer (ICP–OES, Agilent 720, Agilent Technologies Inc., Santa Clara, CA, USA) after extraction for 2 h with 0.01 M $CaCl_2$ ($w/v = 1/10$). Determination of CEC was done according to [29]. Soil samples of 2.5 g were added in a 50 mL Nalgene tube and agitated with 30 mL of 0.1 M $BaCl_2$ for 1 h and the supernatant was collected after centrifugation. The saturation was done three times, with the supernatant added to a 100 mL flask for the determination of exchangeable cations (Ca^{2+}, K^+, and Mg^{2+}) by ICP–OES. After the three-step saturation of soil sample with 0.1 M $BaCl_2$ solution, the exchanged Ba^{2+} was released by agitating the centrifuged pellet with 30 mL of 0.02 M $MgSO_4$ solution for 2 h. After the 2-h agitation, the solution was centrifuged and the remaining Mg^{2+} in the supernatant was determined for the estimation of CEC. The total proportion of carbon was determined by a CHNS Vario MACRO cube (Elemental Analyzer system GmbH, Hanau, Germany) analyzer. DOC was measured after extraction of soils for 2 h with 0.01 M $CaCl_2$ ($w/v = 1{:}10$), and measured using the Skalar San Plus System continuous flow segmented analyzer (Skalar, Netherlands) according to the method used by Jászberényi and Sarkadi [30]. The pseudo total content of elements (Al, Zn, Cu, Mn, and Cd) in soils was determined by ICP–OES after microwave-assisted aqua regia extraction [31]. Aliquots (~0.5 g) of air-dried soil samples were placed in a digestion vessel with 10 mL of qua regia (i.e., nitric and hydrochloric acid mixture in the ratio $\varphi_r = 1{:}3$) and heated in an Ethos 1 (MLS, Germany) microwave-assisted wet digestion system for 45 min at 210 °C. After cooling, the digest was transferred into a 50 mL Teflon vessel and evaporated to dryness at 160 °C. Then the remaining digest was transferred to a 25 mL glass tube, filled with deionized water, and concentration of elements was determined by inductively-coupled plasma–optical emission spectrometer (ICP-OES).

2.4. Data Processing

One-way analysis of variance (ANOVA) was used to determine the effect of biochar application on soil-available Al, Zn, Cu, Mn, and Cd under Tukey's significance difference test at $p < 0.05$. Multivariate analysis of variance (MANOVA) was done to determine the effect of factors (soil type, biochar, and their interaction effect).

Decline or increase in percentage of soil-available Al, Zn, Cu, Mn, and Cd in biochar-amended soils was calculated according to Equation (1).

$$X\ (\%) = \left(\frac{C_0 - C_n}{C_0}\right) \times 100 \tag{1}$$

where X denotes change in percentage of available Al, Cu, Zn, Mn, and Cd; C_0 is the concentration in the control (mmol kg^{-1}); and C_n is the concentration in the biochar-amended treatments (mmol kg^{-1}). Correlation analysis was used for the assessment of relationships between variables, where Pearson's correlation of $p < 0.05$ was used as the criterion for significance. All the statistical analyses were performed using SPSS 17.0 software.

3. Results

3.1. Availability of Al

The application of 8% biochar significantly ($p = 0.05$) increased the available content of Al in Kbely soil (Figure 1). In the remaining four soils 8% biochar significantly ($p = 0.05$) decreased the available content of Al. In the three acidic soils, namely, Humpolec (pH = 4.5), Žamberk (pH = 4.8), and Lukavec (pH = 5.3), the significant decline started from the application of 2% biochar rate, while only 8% caused a significant decline in Lhota soil (pH = 5.91). The amount of available Al content decline was in the range of 6% and 86% at 0.5% and 8% biochar application rate, respectively. The available content of Al was negatively correlated (r > −0.67) with soil pH, CEC, and exchangeable Ca^{2+} and K^+ except for a positive correlation (r > 0.9) with pH and exchangeable K^+ in Kbely soil (Table 2). Moreover, based on the result reported in Table 3, the available content of Al was positively correlated with the percentage of change in the DOC in all soils. As is indicated by the multivariate analysis of variance (Table 4), the soil was the source of the highest variation ($F = 117$, $p = 0.00$), followed by the biochar ($F = 14.3$, $p = 0.00$), and finally, the interaction between soil and biochar ($F = 9.21$, $p = 0.00$).

Table 2. Pearson correlation coefficient of available Al content with soil pH, CEC, and exchangeable Ca^{2+} and K^+ after addition of four levels of biochar (0.5%, 2%, 4%, and 8%) at the 12th week of incubation.

	Al ($n = 5$)				
	Kbely	**Lhota**	**Humpolec**	**Žamberk**	**Lukavec**
pH	0.98 **	−0.97 **	−0.96 **	−0.95 **	−0.94 **
CEC	−0.094 **	−0.94 **	−0.89 *	−0.96 **	−0.93 *
Exchangeable Ca^{2+}	−0.93 *	−0.82 *	−0.86 *	−0.93 *	−0.95 **
Exchangeable K^+	0.91 *	−0.98 **	−0.67	−0.75	−0.85 *

** Correlation is significant at $p = 0.01$, * correlation is significant at $p = 0.05$.

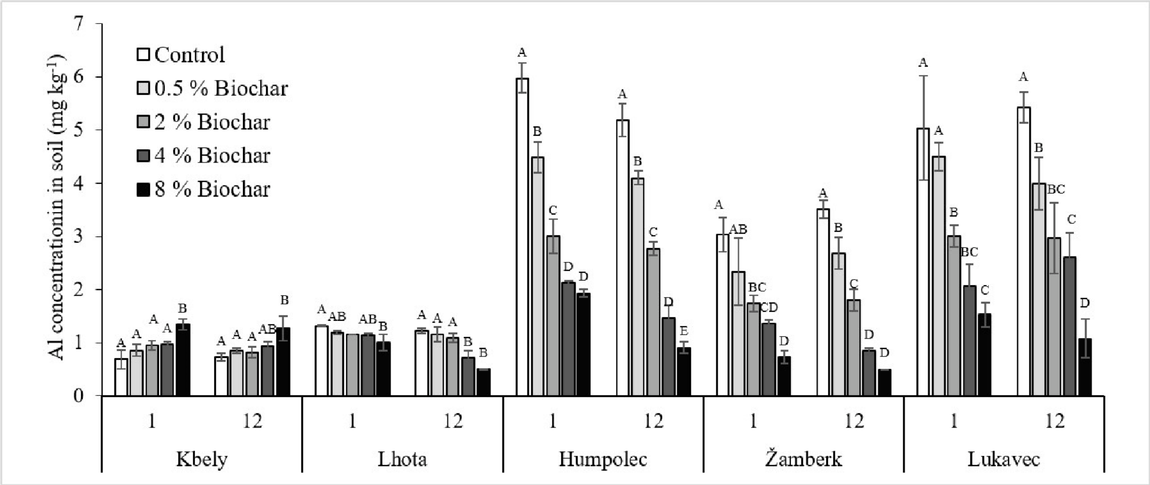

Figure 1. Effect of biochar addition on soil-available content of Al (mg kg^{-1}). On the horizontal axis, 1 and 12 stand for 1st and 12th week of incubation period or sample collection time, respectively. Different capital case letters represent significance difference (p < 0.05) of treatments within same sample collection time of same soil.

Table 3. Pearson correlation coefficient of percentage change in the available content of Al, Cu, Zn, Cd, and Mn (content in the control subtracted from biochar treatments) in individual soils with the percentage of change in DOC.

	Kbely	**Lhota**	**Humpolec**	**Žamberk**	**Lukavec**
Al (n = 4)	0.96 **	0.82 **	0.97 **	0.98 **	0.94 **
Zn (n = 4)	-	0.98 **	0.96 **	0.94 **	0.99 **
Cu (n = 4)	0.95 **	0.97 **	0.97 **	0.93 **	0.98 **
Mn (n = 4)	−0.30	0.94 **	0.98 **	0.98 **	0.92 **
Cd (n = 4)	0.85 **	0.96 **	0.82 **	0.94 **	0.99 **

** Significant at p = 0.01; correlation was not done in the case of Kbely due to the available content of Zn being below the detection limit of ICP used for the measurement (below 0.02 mg kg $^{-1}$).

Table 4. Multivariate analysis of variance in the change of soil Al, Cu, Zn, Cd, and Mn content (content in the control subtracted from biochar treatments) with interaction and single effect of factors.

		Soil	**Biochar**	**Soil * Biochar**
Al	*F*	117	14.3	9.21
	df	4	3	12
	p	*0.00*	*0.00*	*0.00*
Cu	*F*	8.41	18.0	0.36
	df	4	3	12
	p	*0.00*	*0.00*	*0.96*
Zn	*F*	3.39	604	2.77
	df	3	3	9
	p	*0.041*	*0.00*	*0.036*
Cd	*F*	46.6	135	2.75
	df	4	3	12
	p	*0.00*	*0.00*	*0.02*
Mn	*F*	56.9	134	4.95
	df	4	3	12
	p	*0.00*	*0.00*	*0.00*

The italicized values indicate the significance level at n = 20. DF: degree of freedom, *F: F* test, and *p: p* value, *; interaction effect.

3.2. *Availability of Cu*

The addition of biochar decreased the available content of Cu in all soils up to 58%, irrespective of soil types (Figure 2). The application of biochar at low rates (0.5% and 2%) showed a significant decline only in some cases, whereas 4% and 8% biochar rates significantly decreased the available content of Cu in all five soils. Available Cu content after biochar addition had a significant negative correlation with soil pH, CEC, and exchangeable Ca^{2+} and K^+ in most cases except in Lhota soil insignificant correlation and Kbely soil, which had a strong positive correlation ($p = 0.05$) with CEC and exchangeable Ca^{2+} (Table 5). Additionally, there was a positive correlation between the available content of Cu and the percentage of change in the DOC (Table 3). Based on the multivariate analysis of variance (Table 4), biochar was the highest source of variation ($F = 18.0$, $p = 0.00$), followed by soil ($F = 8.41$, $p = 0.00$). The available content of Cu was negatively correlated ($r > -0.62$) with soil pH, CEC, and exchangeable Ca^{2+} and K^+ except for a positive correlation ($r > 0.99$) with CEC and exchangeable Ca^{2+} in Kbely soil (Table 5).

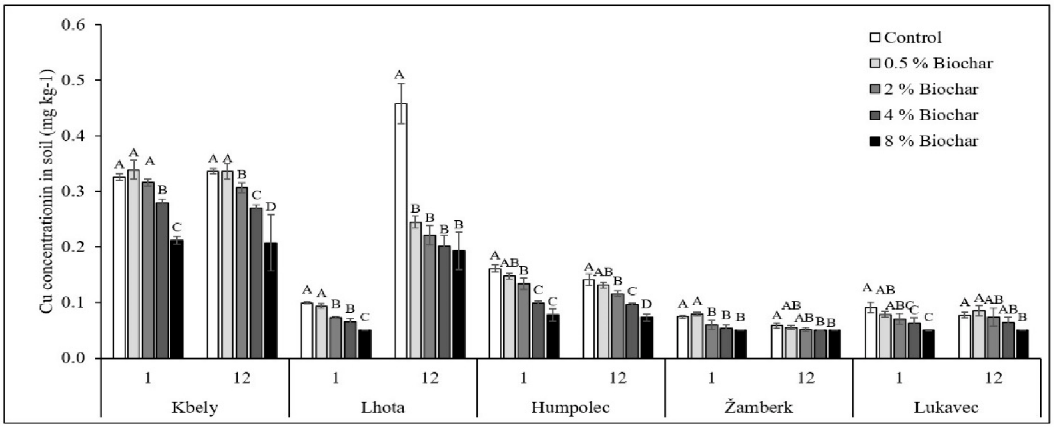

Figure 2. Effect of biochar addition on soil-available content of Cu (mg kg^{-1}). On the horizontal axis, 1 and 12 stand for 1st and 12th week of incubation period or sample collection time, respectively. Different capital case letters represent significance difference ($p < 0.05$) of treatments within same sample collection time of same soil.

Table 5. Pearson correlation coefficient of available Cu content with soil pH, CEC, and exchangeable Ca^{2+} and K^+ after addition of four levels of biochar (0.5%, 2%, 4% and 8%) at the 12th week of incubation.

	Cu ($n = 5$)				
	Kbely	**Lhota**	**Humpolec**	**Žamberk**	**Lukavec**
pH	−0.95 **	−0.66	−0.99 **	−0.87 *	−0.97 **
CEC	0.99 **	−0.68	−0.97 **	−0.978 **	−0.94 **
Exchangeable Ca^{2+}	0.99 **	−0.23	−0.95 **	−0.87 *	−0.96 **
Exchangeable K^+	−0.99 **	−0.66	−0.83*	−0.62	−0.94 **

** Correlation is significant at $p = 0.01$, * correlation is significant at $p = 0.05$.

3.3. *Availability of Zn*

Available content of Zn declined in four soils with biochar addition except Kbely soil (Figure 3). In the four soils, the decline ranged between 18% and 97% at 0.5% and 8% of biochar application rate, respectively. The addition of 0.5% biochar was enough to induce a significant decline in Lhota, Humpolec, Žamberk, and Lukavec soils. The fifth soil, Kbely, had an available content of Zn below the detection limit of ICP-OES used in this study (below 0.02 mg kg^{-1}). Based on the multivariate analysis of variance (Table 4), biochar was the source of the highest variation ($F = 604$, $p = 0.00$) then soil ($F = 3.39$, $p = 0.041$) and the interaction between soil and biochar ($F = 2.77$, $p = 0.036$). The available content of Zn was negatively correlated (r > −0.62) with soil pH, CEC, and exchangeable Ca^{2+} and K^+ in all soils except Kbely (Table 6). There was also a positive correlation between the available content of Zn and the percentage of change in the DOC in all soils except Kbely (Table 3).

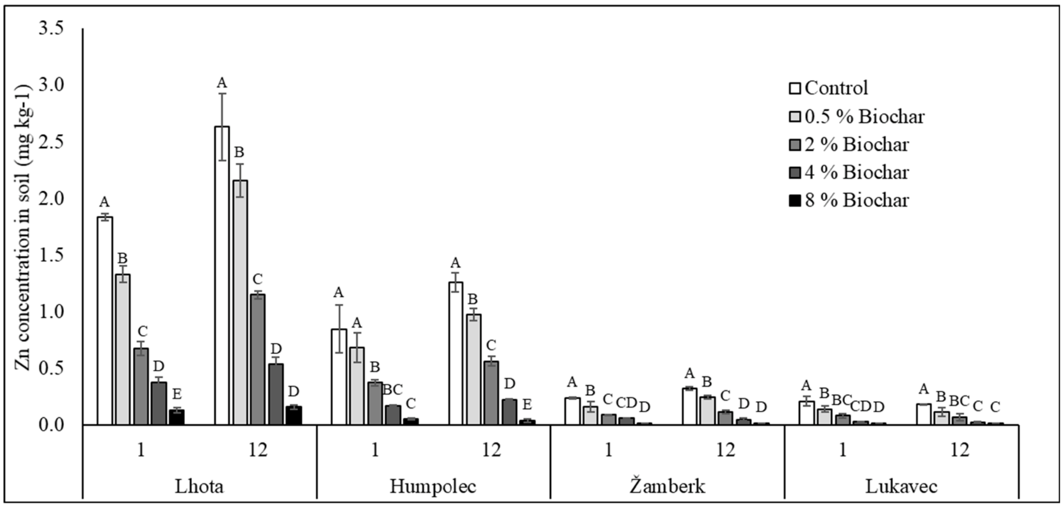

Figure 3. Effect of biochar addition on soil-available content of Zn (mg kg^{-1}). On the horizontal axis, 1 and 12 stand for 1st and 12th week of incubation period or sample collection time, respectively. Kbely soil is not presented due to the available content of Zn is below detection limit of ICP used for the measurement (below 0.02 mg kg^{-1}). Different capital case letters represent significance difference ($p < 0.05$) of treatments within same sample collection time of same soil.

Table 6. Pearson correlation coefficient of available Zn content with soil pH, CEC, and exchangeable Ca^{2+} and K^+ after addition of four levels of biochar (0.5%, 2%, 4%, and 8%) at the 12th week of incubation.

	Zn (n = 5)				
	Kbely	**Lhota**	**Humpolec**	**Žamberk**	**Lukavec**
pH	-	−0.95 **	−0.97 **	−0.92 *	−0.86 *
CEC	-	−0.91 *	−0.89 *	−0.96 **	−0.79
Exchangeable Ca^{2+}	-	−0.7	−0.87 *	−0.92 *	−0.87 *
Exchangeable K^+	-	−0.94 **	−0.68	−0.71	−0.68

** Correlation is significant at $p = 0.01$, * correlation is significant at $p = 0.05$; correlation was not done in the case of Kbely due to the available content of Zn is below detection limit of ICP used for the measurement (below 0.02 mg kg^{-1}).

3.4. Availability of Mn

Effect of biochar on soil-available Mn was similar to that of available Cu. However, the decline in Kbely was significant ($p = 0.05$) only during the first week of incubation at the 8% biochar rate (Figure 4). In the remaining four soils, the content of available Mn was significantly decreased starting at 2% of biochar application rate with the decline up to 79% relative to the control. The trend in soil-available Mn content after biochar addition of these four soils was negatively correlated with soil pH, CEC, and exchangeable Ca^{2+} and K^+ content except for Kbely soil (Table 7). Based on the multivariate analysis (Table 4), the biochar was the source of the highest variation ($F = 135$, $p = 0.00$), followed by soil ($F = 46.6$, $p = 0.00$), and the interaction between soil and biochar ($F = 2.75$, $p = 0.02$). The available content of Mn was negatively correlated (r > −0.8) with soil pH, CEC, and exchangeable Ca^{2+} and K^+ except a positive correlation with CEC and exchangeable Ca^{2+} in Kbely soil (Table 7). Additionally, there was a positive correlation between the available content of Mn and the percentage of change in the DOC of all soils except Kbely (Table 3).

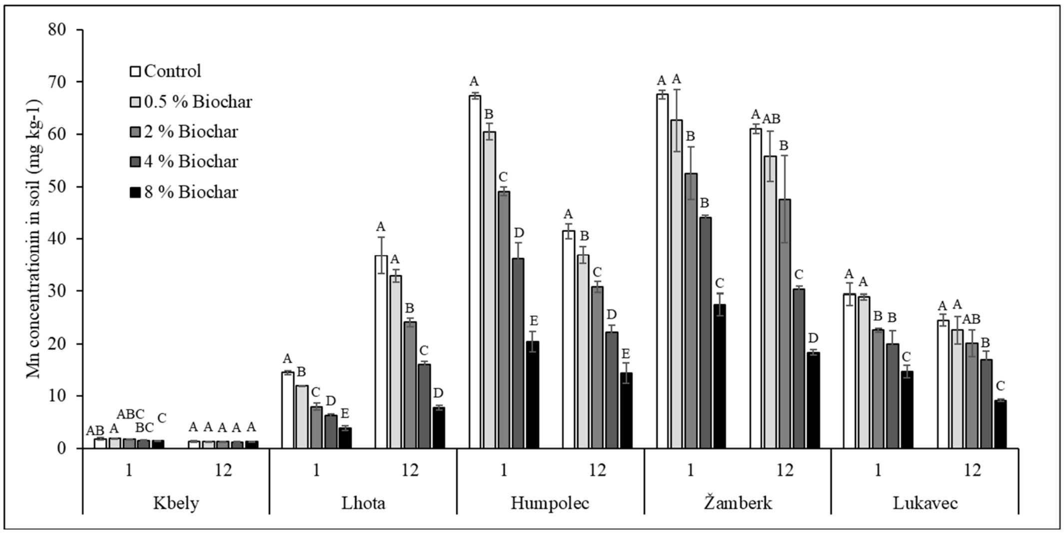

Figure 4. Effect of biochar addition on soil-available content of Mn (mg kg^{-1}). On the horizontal axis, 1 and 12 stand for 1st and 12th week of incubation period or sample collection time, respectively. Different capital case letters represent significance difference ($p < 0.05$) of treatments within same sample collection time of same soil.

Table 7. Pearson correlation coefficient of available Mn content with soil pH, CEC, and exchangeable Ca^{2+} and K^{+} after addition of four levels of biochar (0.5%, 2%, 4%, and 8%) at the 12th week of incubation.

	Mn ($n = 5$)				
	Kbely	**Lhota**	**Humpolec**	**Žamberk**	**Lukavec**
pH	−0.56	−0.99 **	−0.99 **	−0.99 **	−0.99 **
CEC	0.31	−0.96 **	−0.96 **	−0.87 *	−0.99 **
Exchangeable Ca^{2+}	0.34	−0.80	−0.93 *	−0.98 **	−0.99 **
Exchangeable K^{+}	−0.28	−0.98 **	−0.80	−0.89 *	−0.96 **

** Correlation is significant at $p = 0.01$, * correlation is significant at $p = 0.05$.

3.5. Availability of Cd

The Cd content of all soil decreased due to biochar addition (Figure 5). The amount of Cd decline was in the range between 0.1% and 81% at the 0.5% and 8% biochar application rate, respectively. The application of 0.5% biochar did not induce a significant decline in many cases but the 2% biochar rate induced a significant ($p = 0.05$) available Cd content decline in the four acidic soils (Lhota, Humpolec, Žamberk and Lukavec), whereas 4% and 8% biochar rate induced a significant decline of Cd in all soils at both incubation periods. Based on the multivariate analysis (Table 4), biochar was the source of the highest variation ($F = 134$, $p = 0.00$), soil ($F = 56.9$, $p = 0.00$) and the interaction between soil and biochar ($F = 4.95$, $p = 0.02$). The available content of Cd was correlated in negative way (r > −0.5) with soil pH, CEC, and exchangeable Ca^{2+} and K^{+} except for a positive correlation (r > 0.8) with CEC and exchangeable Ca^{2+} in Kbely soil (Table 8). Additionally, there was a positive correlation between the available content of Cd and the percentage of change in the DOC in all soils except Kbely (Table 3).

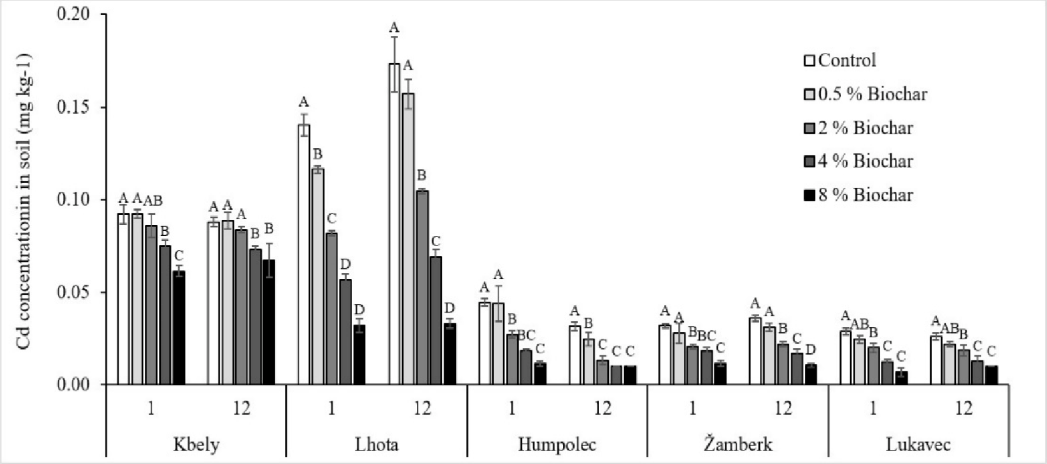

Figure 5. Effect of biochar addition on soil-available content of Cd (mg kg^{-1}). On the horizontal axis, 1 and 12 stand for 1st and 12th week of incubation period or sample collection time, respectively. Different capital case letters represent significance difference (p < 0.05) of treatments within same sample collection time of same soil.

Table 8. Pearson correlation coefficient of available Cd content with soil pH, CEC, and exchangeable Ca^{2+} and K^+ after addition of four levels of biochar (0.5%, 2%, 4%, and 8%) at the 12th week of incubation.

	Cd (n = 5)				
	Kbely	**Lhota**	**Humpolec**	**Žamberk**	**Lukavec**
pH	−0.96 **	−0.98 **	−0.88 *	−0.96 **	−0.95 **
CEC	0.89 *	−0.95 **	−0.75	−0.93 *	−0.89 *
Exchangeable Ca^{2+}	0.92 *	−0.80	−0.74	−0.96 **	−0.96 **
Exchangeable K^+	−0.89 *	−0.97 **	−0.51	−0.80	−0.82 *

** Correlation is significant at p = 0.01, * correlation is significant at p = 0.05.

4. Discussion

4.1. Availability of Al

The addition of biochar significantly decreased the available content of Al in four soils. The result is consistent with the finding of Yuan and Xu [32], who reported decline in the exchangeable content of Al by 33.4% and 55% after the application of canola and peanut straw biochar produced at 350 °C, respectively. An increment of soil pH up to 1.2 was also evident in the four soils with a significant Al content decline [26]. The increment in the pH of soils could play two vital roles. Firstly, as the pH increases, the freely-available Al could decrease by the precipitation of Al^{3+} to the insoluble Al oxides/hydroxides [33]. Thus the increment in pH of soil converts the aluminum species to the monomer of $Al(OH)^{2+}$ and $Al(OH)_2{}^+$, which are easily adsorbed by biochar through ion exchange with –COOH or phenolic –OH groups [34]. The complexation of Al with the organic hydroxyl and carboxyl functional groups of biochar through ion exchange was confirmed by Qian and Chen [35]. The complexation of Al with the organic functional groups of biochar is attributed to the hydrolysis of Al and the esterification reaction of carboxylate groups [36]. Similarly, Jansen et al. [37] reported the formation of insoluble Al–DOC precipitate complexes at a higher pH by the formation of stable ring structures on the functional groups of DOC and decline in the available content of both Al and DOC. This is evident from Table 3, which shows that the percentage of declined available Al content of biochar treatments relative to control was significantly correlated with the percentage of decline in DOC (r > 0.8, p = 0.01). Secondly, the increment in the pH of soils could result in the dissociation of organic matter, which add more deprotonated acidic functional groups (increased CEC), and this further contributes to the binding of metals like Al on the surface of organic matter. The complexation of humic substance-originated carboxylic and phenolic groups with Al^{3+} is also an important mechanism for the retention of Al by soils [38]. Other possible reasons explaining the decline could be the exchange of exchangeable Al with exchangeable Ca^{2+} and K^+ content of biochar. The full report of biochar effect on the pH, exchangeable Ca^{2+}, K^+, and CEC of these soils is contained in our previously-published paper [26]. The release of base cations (Ca^{2+}, Mg^{2+}, and K^+) and their replacement by exchangeable Al^{3+} at the surface of biochar has been widely studied [32]. On the contrary, the content of available Al increased in Kbely soil up to 0.54 mg kg^{-1} at 8% of biochar addition rate. The increment was significant ($p = 0.05$) at 8% of biochar addition and it ranged from 10% up to 94% at the 0.5% and 8% of biochar rate, respectively. However, the increment of available Al content in Kbely soil was by far lower than the toxic level of Al as the base cations (Ca, K, Mg)/Al molar ratio at 8% of biochar addition was 105. The possible toxicity of Al could be reached when sum of cations (Ca, K, Mg) to Al ratio is lower than 1 [39]. The exceptional case of Kbely is due to soil-specific properties. This is supported by our multivariate analysis of variance (Table 4), which revealed the higher main effect attributed from soil ($F = 117$, $p < 0.001$) rather than biochar ($F = 14.3$, $p < 0.001$) and the interaction effect soil with biochar ($F = 9.21$, $p < 0.001$). Kbely soil is characterized by neutral pH, higher exchangeable Ca^{2+}, higher CEC, and higher DOC as compared to other soils (Table 1). The neutral pH (7.01) of Kbely soil, which is much higher than other soils and the further increment by biochar resulted in mobility of Al. This is indicated by a positive significant ($r = 0.98$, $p = 0.01$) correlation between pH and available content of Al in Kbely soil after the addition of biochar (Table 2). The stability of Al up to the pH value near 6.5 and the increment in the mobility of Al above this pH point is reported by the study of Driscoll and Schecher [40]. The addition of biochar in Kbely soil decreased soil CEC and content of exchangeable Ca^{2+} [26]. Therefore, the increment in the available content of Al in Kbely soil could be also due to the release of Al to soil solution from biochar and the replacement by exchangeable Ca^{2+}. Our biochar was characterized by much higher content of available Al content than all used soils in this incubation (Table 1).

4.2. Availability of Cu

The addition of biochar significantly decreased the available content of Cu in all soils. The first reason for the biochar caused decline in the available content of Cu was the increment of soil pH. The biochar-induced decline in the available content of Cu was significantly and negatively correlated with the change in soil pH (Table 5). Meaning that, the biochar-induced increment in the pH of soil resulted in the decline of available Cu content. The increment of pH could facilitate the adsorption of hydrolyzed $CuOH^+$ species by biochar [41]. Additionally, the increment of CEC because of the oxygen-containing organic functional groups of soil and biochar (–COOH and –OH) could contribute to the decline in the available content of Cu through ionic exchange. The carboxyl groups originated from the organic fraction of biochar have the potential to immobilize Cu in soil [42]. In our study, the relative percentage of declined DOC as a result of biochar addition is significantly and positively correlated ($r > 0.9$, $p = 0.05$) with percentage of declined Cu content (Table 3), meaning that the greater amount of decline in DOC induced by biochar addition matched with the greater decline in the available content of Cu. This could clearly indicate the direct link between the decline in the available Cu content and the decline in soil DOC content. The mechanism behind this could be the complexation of Cu with DOC through the ion exchange on oxygen-containing functional groups of DOC on both soil and biochar. Similar trends of available Cu and DOC content have been reported [43]. The adsorption of Cu could be also facilitated by biochar-induced decline in DOC [44] and facilitated the binding of organic matter with Cu [20]. An increment in the adsorption of Cu up to 28.2% due to the organic matter loading of biochar has been reported [45]. Based on their findings, the loading of humic acid (HA) up to <100 mg of carbon per L on the surface of biochar increased the negative surface functional groups of biochar and resulted in higher Cu adsorption [45]. From Table 5, it can be also concluded that there is an involvement of biochar-induced CEC increment in the decline of available Cu content in all soils except Kbely (characterized by the highest CEC level among the set of soils). The increment in the CEC of soils could increase the negatively-charged surface functional groups of both soil and biochar, thus facilitating the adsorption of Cu. Our biochar also had higher aromatic character as the production temperature was high (700 °C) with and H/C atomic ratio of 0.11. The increment in the production temperature of biochar could result in the decline of H/C ratio, leading to an increase in the aromaticity of biochar and thus causing the immobilization of Cu [46]. The multivariate analysis of variance (Table 4) revealed the highest effect was from biochar ($F = 18$, $p < 0.01$) rather than soil ($F = 8.4$, $p < 0.01$) or their interaction effect (F = 0.3, $p = 0.96$). This could indicate the efficiency of biochar in decreasing the availability of Cu irrespective of soils, with the effect size varying with soil properties discussed above.

4.3. Availability of Zn

The addition of biochar decreased the available content of Zn in all soils except Kbely. Similarly, the findings of Yang et al. [19] presented a decrease in the available Zn from 62.2% to 52.9% at 5% of fine and coarse textured straw biochar, respectively. Removal of Zn in pore water up to 66% by 5% rice straw biochar was reported by [20]. In another study, application of sugarcane-derived biochar (700 °C) at the rate of 5% reduced the available content of Zn by 54% [17]. In our study, the availability of Zn after the addition of biochar negatively correlated with soil pH, CEC, and exchangeable Ca^{2+} and K^+, and was significant ($p = 0.05$) in most cases for all soils except Kbely (Table 6). The highest effect of biochar ($F = 604$, $p < 0.01$), followed by soil (F = 3.39, $p = 0.041$) and their interaction effect ($F = 3.39$, $p = 0.036$) on the induced changes, has been confirmed by the multivariate analysis of variance (Table 4). This is evidence of the clear contribution of biochar-induced pH and CEC increment in the decline in the available content of Zn. The high linkage of mobile Zn with soil pH and the enhanced immobilization of Zn with the increment in pH have been widely discussed by He et al. [47]. This is due to the increment in the pH-dependent negative charges of soil, the dominance of hydrolyzed Zn forms and the co-precipitation with Fe oxides [48]. Additionally, the formation of hemimorphite ($Zn_4(H_2O)(Si_2O_7)(OH)_2$) and hydrozincite ($Zn_5(CO_3)_2(OH)_6$) was reported as a possible mechanism for the immobilization of Zn^{2+} by biochar [49]. However, due to the very low content of CO_3^{2-} in the biochar used in this study (Table 1), we did not expect the formation of hydrozincite. However, the alkalinity of soil after the addition of biochar could favor the formation of colloid $Zn(OH)_2$, then dissolved silicates could be adsorbed on the colloids of $Zn(OH)_2$ and this could result in the co-precipitates structure forming amorphous hemimorphite. When we come to the exceptional Kbely soil, the low content of Zn could be highly linked to the high content of carbonate in Kbely soil as compared to other soils (Table 1). The mobility of Zn in soils with high carbonate content is low due the formation of $ZnCO_3$ [50].

4.4. Availability of Mn

The decline in the available content of Mn was significantly correlated with the increment in soil pH. This association indicates one of the reasons for the decline in the available content of Mn is due to the low mobility of Mn at the higher pH induced by biochar [51]. Additionally, the increment of soil pH could contribute to the decline in the available content of Mn by enhancing the binding Mn with DOC-originated oxygen containing functional groups from both biochar and soil. Biochar-induced pH increment and binding of Mn with OH group are responsible for the decline in the mobility of Mn [51]. The potential for Mn^{2+} complexation with organic solid increases at a higher pH [52]. Furthermore, the exchange of Mn from soil exchange sites with exchangeable Ca^{2+} and K^+ originated from biochar could contribute to the decline. The multivariate analysis of variance (Table 4) has shown high variation in biochar treatments ($F = 134$, $p < 0.01$) rather than soil ($F = 56.9$, $p < 0.01$) and their interaction effect ($F = 4.95$, $p < 0.00$). This could again confirm the ability of biochar to reduce the availability of Mn irrespective of soils.

4.5. Availability of Cd

The application of biochar was able to induce a significant decline in the available content of Cd. Yang et al. [19] reported a significant decline of Cd in naturally-contaminated soil at 5% rice straw biochar application. Similarly, the application of 10% biochar produced at 500 °C from residues of orchards was able to reduce the available content of Cd by the factor of 10 compared to control without biochar [53]. From the multivariate analysis of variance (Table 4), we observed a higher effect of biochar (F =135, $p < 0.01$) rather than soil type (F =135, $p < 0.01$) and their interaction effect (F =135, $p < 0.01$), thus confirming that the key factor in the decline of Cd content is biochar rather than soil type, with soil properties determining the amount of decline. The decline in the available content of Cd in all tested soils was negatively correlated with the trend in soil pH, CEC, and exchangeable Ca^{2+}, K^{+} content of all soils except Kbely, whereas CEC and exchangeable Ca^{2+} were positively correlated (Table 8). An increment in the pH of soils could generally reduce the mobility of Cd. This is in agreement with the finding of Beesley and Marmiroli [54], where the increment of soil pH was the main reason for the decline in the available content of Cd in biochar-applied soil. The increment in soil pH after biochar application to soil was again reported to reduce mobility of Cd in soils [20]. The increment of exchangeable Ca^{2+} and K^{+} could indicate the exchange of cations for the decline in the available content of Cd. The increment in CEC of soils after biochar addition is always related to the abundance of more surface negative charges, thus facilitating the adsorption of Cd. This is supported by other studies [55,56]. For example, based on the finding of Zhang et al. [56], the release of the sum of K, Ca, Na, and Mg was equal to the amount of adsorbed Cd by biochar. Furthermore, the decline in the available content of Cd could be linked to the decline in DOC induced by biochar due to the complex formation with oxygenated functional groups of DOC from both soil and biochar. The complexation of Cd with –COOH and –OH functional groups through ion exchange is thought to be the main reason for metal removal by the biochar [57]. This is also supported by the positive correlation of DOC decline with the decline in the available content of Cd in biochar treatments (Table 3).

5. Conclusions

In this study, we incubated five soils with a wide range of physicochemical properties from different regions of the Czech Republic for 12 weeks. The available content of Al increased in one soil having low original available content of Al, high pH, and high cation exchange capacity compared to other soils and the increment was significant only at 8% of biochar application rate, while a decline in the remaining four soils was prevalent. The increment in the available content of Al is mainly attributed to the increment in the pH of soil above 6.5, the exchange of Al with exchangeable Ca^{2+} portion of biochar, and decline in the CEC of Kbely soil. The available content of Cu and Cd was decreased by biochar in all soils. Application of 0.5% biochar was not able to induce significant decline as well as 2% biochar in some cases but 4% and 8% of biochar significantly reduced the available content of Cu and Cd in all five soils at both incubation periods. Biochar decreased the available content of Zn and Mn in all soils except Kbely. This is due to the low available content of Zn and Mn in Kbely soil, which could be linked to the high content of carbonate in this soil. In the remaining four soils, 4% and 8% biochar rates induced a significant decline of available Zn and Mn content at both incubation periods. The immobilization of all studied elements was potentially related to the increment in the pH and cation exchange capacity of soils by biochar, the exchange with exchangeable Ca^{2+} and K^{+}, and the decline in the dissolved organic carbon content of soils.

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Conflicts of Interest: The authors declare that there is no conflict of interest.

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4.4. The interaction effect of biochar with stabilised and un-stabilised ammonium sulphate on the 1 maize growth performance, nutrient use efficiency and chemistry of soil solution

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Co-application of high temperature biochar with 3,4-dimethylpyrazol e-phosphate treated ammonium sulphate improves nitrogen use efficiency in maize

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This study aimed on the increasing nitrogen use efficiency (NUE) of maize via the use of high temperature produced biochar (700 °C). Maize was grown to maturity on two contrasting soils (acidic Cambisol and neutral Chernozem) in pots with a treatment of biochar co-applied with ammonium sulphate stabilised by a nitrification inhibitor (3,4-dimethylpyrazole-phosphate, DMPP) or un-stabilised. The combination of biochar with ammonium sulphate containing DMPP increased maize biomass yield up to 14%, N uptake up to 34% and NUE up to 13.7% compared to the sole application of ammonium sulphate containing DMPP. However, the combination of biochar with un-stabilised ammonium sulphate (without DMPP) had a soil-specific influence and increased maize biomass only by 3.8%, N uptake by 27% and NUE by 11% only in acidic Cambisol. Further, the biochar was able to increase the uptake of phosphorus (P) and potassium (K) in both stabilised and un-stabilised treatments of ammonium sulphate. Generally, this study demonstrated a superior effect from the combined application of biochar with ammonium sulphate containing DMPP, which improved NUE, uptake of P, K and increased maize biomass yield. Such a combination may lead to higher efficiency of fertilisation practices and reduce the amount of N fertiliser to be applied.

Nitrogen (N) is usually the most growth-limiting nutrient of crops, so crop production is highly dependent on the N soil supply capacity[1]. From N sources, plants can take up N mainly in the form of ammonium ($N{-}NH_4^+$) and nitrate ($N{-}NO_3^-$). However, their availability in soils is limited and accounts for only 2% of the total soil N content. Due to the growing demand in crop production, the use of inorganic N fertilisers has dramatically increased over the past 50 years[2], resulting in crop yields enhanced by 30–50%[3]. However, overall nitrogen use efficiency (NUE) of applied fertilisers by cereals is typically ranging from 30 to 50%[4].

Such low NUE leads to environmental issues[5] and fertilisers are applied in an excessive amount to cope with the low NUE. This excessive use of inorganic fertilisers causes numerous problems related to soil chemistry, root growth, losses of nitrogen and may result in soil degradation. Low NUE is mainly caused by the decline in the availability of nitrate and ammonium at the later stages of crop growth due to the losses of these species through volatilisation, denitrification and leaching[6]. Recently, N fertilisers containing nitrification inhibitors are in use to reduce the fast oxidation of NH_4^+ and its subsequent leaching to reduce the N losses from soil[7–9]. Biochar (BC) is among the materials often cited as the effective soil additive being able to induce N sorption and reduce losses[10–12]. Moreover, BC application has been recommended for the restoration of degraded and acidified soils due to the excessive use of N fertilisers[13]. BC is also known to increase soil pH[14], increase the soil content of base cations (Ca^{2+}, Mg^{2+} and K^+) and increase the cation exchange capacity (CEC) of soils[15–18]. The reduction of both NH_3 volatilisation and NO_3^- leaching due to the adsorption effect of BC has also been reported[18–21]. This effect of BC arises from the alkaline components of BC, including ash and carbonates of Ca^{2+}, Mg^{2+} and K^+[22,23], unique physical properties (high porosity and surface area) and chemical properties (negatively and positively charged surface)[24]. Ammonium sulphate can be more efficiently combined with biochar than other N forms of fertilizers to improve NUE. Urea-N is available to plants after the hydrolysis, increasing soil pH[25], so its co-application

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Properties	Suchdol	Žamberk	Biochar
Localization	50°07′40″N, 14°22′35″E	50°08′40″N, 16°30′50″E	–
Soil type	Chernozem	Cambisol	–
pH§	6.90	4.80	9.50
CEC (mmol kg^{-1})	249.3 ± 4.0	74.9 ± 3.7	102 ± 5.2
Total N (%)	0.16 ± 0.00	0.20 ± 0.00	0.40 ± 0.02
Organic carbon (%)	1.61 ± 0.1	1.60 ± 0.0	–
C/N ratio	13.2 ± 0.16	9.96 ± 0.16	219.98 ± 12.9
DOC (mg kg^{-1})§	13.4 ± 4.3	63.6 ± 2.0	–
N–NH$_4^+$ (mg kg^{-1})§	5.7 ± 0.8	23.5 ± 3.2	–
Available P (mg kg^{-1})§	6.23 ± 0.17	2.36 ± 0.07	n.d
Available K (mg kg^{-1})§	65 ± 0.21	31.7 ± 0.59	2278 ± 66
Available Mg (mg kg^{-1})§	77 ± 0.86	21.1 ± 0.2	192 ± 11
Available S (mg kg^{-1})§	25.4 ± 1.81	17.2 ± 0.1	32 ± 1.6
P (mg kg^{-1})$^{¥}$	955 ± 12.5	530 ± 12.0	496 ± 0.22
K (mg kg^{-1})$^{¥}$	6680 ± 113	3816 ± 158	2670 ± 225
Ca (mg kg^{-1})$^{¥}$	9987 ± 64.8	1607 ± 32.8	6676 ± 586
Mg (mg kg^{-1})$^{¥}$	4940 ± 12.9	2332 ± 68.0	1176 ± 71.9
S (mg kg^{-1})$^{¥}$	227 ± 13.9	150 ± 5.4	127 ± 11.6
Exch.Ca^{2+} (mmol kg^{-1})	253 ± 3.7	72 ± 0.6	176 ± 13.5
Exch. K$^+$ (mmol kg^{-1})	4.6 ± 0.1	1.6 ± 0.1	50.4 ± 0.3
Exch. Mg^{2+} (mmol kg^{-1})	11.8 ± 0.3	2.7 ± 0.1	23.2 ± 7.3
Sand (%)	13.16	26.08	–
Silt (%)	60.05	59.82	–
Clay (%)	26.77	14.08	–
Textural class	Silt clay Loam	Silt Loam	–

Table 1. Selected physiochemical properties of soils and biochar (Hailegnaw et al., 2019b). §0.01 mol L^{-1} CaCl$_2$ extract, n.d: not detected (0.05 mg kg^{-1}), Exch.: exchangeable. $^{¥}$Pseudo-total content.

No ammonium sulphate (NoAS)	Un-stabilized ammonium sulphate (USAS)	Stabilized ammonium sulphate with DMPP (SAS)
Control (no biochar)	No biochar + 1.0345 g N from USAS	No biochar + 1.0345 g N from SAS
1% biochar	1% biochar + 1.0345 g N from USAS	1% biochar + 1.0345 g N from SAS
2% biochar	2% biochar + 1.0345 g N from USAS	2% biochar + 1.0345 g N from SAS

Table 2. The experimental design set up.

with biochar could further increase soil pH[15,26–28] making nutrients like phosphorous less available. Fertilizers containing both ammonia and nitrate forms are less effective to regulate N soil transformation[25].

Hence, we hypothesised that soil application of biochar in the combination with ammonium sulphate (AS) stabilised with 3,4-dimethylpyrazole-phosphate (DMPP) could increase the nitrogen use efficiency (NUE) and yield of maize biomass. Further, this study aimed to elucidate the mechanisms and chemical changes caused by the co-application of these materials.

Material and methods

Soil and biochar sources and characteristics. Two soils with desired properties were selected based on our previously published work[20,29], where an identical biochar (wood chips pyrolysed at 700 °C) was used. The relatively higher biochar production temperature (700 °C) was preferred due to the need for producing relatively stable biochar with relatively lower ammonium and a higher nitrate sorption capacity. Out of the ten soils used in the previous studies, two contrasting soils were chosen: (1) Chernozem (silt clay loam; locality Suchdol, Czech Republic) a soil characterised by a neutral pH and a decline in the concentration of exchangeable Ca and cation exchange capacity (CEC) after the application of BC and (2) Cambisol (silt loam; locality Žamberk, Czech Republic) soil was selected for its acidic pH and an increase in the concentration of exchangeable Ca and CEC after BC application. Detailed characteristics of the soils and BC are presented in Table 1.

Pot experiment. The pot experiment was set up using 5 kg (dry weight) soil in 6-L pots in a precipitation-controlled vegetation hall. Nine treatments were set up (Table 2) to achieve the aim of the study in a completely randomised design for each soil. Each treatment was prepared in four replicates.

The nitrogen fertilisation rate represented 207 mg N kg^{-1} of soil and corresponded roughly with the N application rate of 600 kg N ha^{-1} in field conditions. In this study, stabilised ammonium sulphate (SAS) was bought from COMPO EXPERT GmbH (Germany) with the product trade name NovaTec Solub 21 having (0.205% of 3,4-dimethylpyrazole-phosphate (DMPP) and 21% N). The corresponding un-stabilised ammonium sulphate (USAS) treatment was fertilised using ammonium sulphate ($(NH_4)_2SO_4$; 21% N) from the AGRO CS Group (Říkov, Czech Republic). Fertilisers were applied in the form of powder and were thoroughly mixed with soil. After preparing all the treatments, five maize seeds were sown per pot and thinned to three plants per pot two weeks after sowing. Each pot was regularly irrigated to 60% of the soil maximum water holding capacity. Soil solution was collected over the vegetation period using Rhizon MOM suction cups as described by Refs.[30,31]. Maize aboveground biomass was harvested 115 days after sowing, oven-dried (65 °C) and ground to a fine powder before analyses. After the harvest, soil samples were collected and analysed for the available content of mineral N.

Soil analyses. The measurements of soil and biochar pH were done using an Argus pH meter (Sentron, Netherland) with a transistor CupFET probe after the extraction of samples with 0.01 M $CaCl_2$ (w/v = 1/5). The available content of nutrients in both soil and biochar were determined by the use of inductive coupled plasma-optical emission spectrometry (ICP-OES; Agilent 720, Agilent Technologies Inc., Santa Clara, CA) after the extraction of samples with 0.01 M $CaCl_2$ in 1:10 (w/v) for 2 h[32]. The available content of inorganic N (nitrate and ammonium nitrogen) were measured by the Skalar San Plus System continuous flow segmented analyser (Skalar, Netherlands) after extraction of samples with 0.01 M $CaCl_2$ (w/v = 1/10) for 2 h[33]. The total content of C and N were determined by the use of a CHNS elemental analyser (Vario MACRO cube system GmbH, Hanau, Germany). The total organic carbon (TOC) was determined according to Sims et al.[34], i.e. spectrophotometrically following the oxidation of organic matter (OM) with $K_2Cr_2O_7$. Determination of cation exchange capacity was done according to Gillman et al.[35] by a three-step saturation of samples (1 h for each agitation) with 0.1 M $BaCl_2$ solution and collecting the extracts for determination of exchangeable cations (Ca^{2+}, K^+ and Mg^{2+}) by ICP-OES. The pellet remaining after extraction was used for subsequent release of Ba^{2+}, where it was agitated with 0.02 M $MgSO_4$ for two hours, and then CEC was calculated based on the amount of Mg^{2+} retained by the soil or biochar. The pseudo-total contents of elements (P, Ca, K, Mg and S) in both soils and biochar were determined by ICP–OES after microwave assisted *aqua regia* extraction[36].

Plant analysis. The concentration of nutrients in maize biomass was determined after the digestion of plant samples with concentrated HNO_3 (65% v/v; Analytika) and H_2O_2 (30% v/v; Analytika) in an Ethos 1 microwave-assisted wet-digestion system (MLS, Leutkirch, Germany), and P, S, Mg and Ca concentrations in the digests were determined by ICP-OES. The concentrations of K were determined using flame atomic absorption spectrometry (F-AAS; Varian AA285FS, Varian, Australia). The total concentrations of N in maize tissue were determined by the Kjeldahl method (Vapodest 50 s, Gerhardt, Germany).

Statistical analysis. All statistical analyses were performed using SPSS 17.0 software. The effect of biochar was determined by one-way analysis of variance (ANOVA) at $p < 0.05$ followed by the Tukey test to assess the effect of the individual treatments. The interactions of the variables (e.g. biochar application, fertiliser application and soil) on maize biomass and yield component were analysed by a multivariate analysis of variance, MANOVA. The repeated measure analysis of variance rANOVA was implemented to describe the within-subject effect of sampling time and between-subject effect of soil, biochar, fertiliser and their interaction on the pH and nutrient content of soil solution. The uptake of nutrients (mg per pot) by maize was calculated as Eq. (1).

$$Nutrient\ uptake = Maize\ dry\ matter\ yield \times shoot\ nutrient\ concentration \tag{1}$$

where maize dry matter yield was in g per pot and shoot nutrient concentration was in mg g^{-1}.

Nitrogen use efficiency (NUE) and sulphur use efficiency (SUE) was calculated according to Eq. (2).

$$NUE(\%) = \left[(N_{FT} - N_{CT})/N_{ap}\right] \times 100 \tag{2}$$

where N_{FT} is the N or S uptake in fertilised treatment, N_{CT} is the N or S uptake in corresponding control, non-fertilised treatment, and N_{ap} is the amount of N or S applied in a pot in the form of ammonium sulphate.

Results

Biomass yield. The biomass yield in the SAS and USAS treatments was up to 5 times higher than in the NoAS treatments. The effect of biochar on maize biomass was not significant in the case of NoAS and USAS treatments (Fig. 1). However, in the SAS, the application of 2% biochar significantly increased maize biomass by 10 and 8% in the Chernozem and Cambisol soils, respectively. In the Chernozem with the 2% application, the biochar with SAS showed significantly higher biomass than USAS treatment (Fig. 1). Moreover, the biomass yield of maize was higher in the Cambisol in the 1% BC and 2% BC treatments of USAS and the 1% BC treatments of SAS than in the corresponding treatments of the Chernozem. The main factor influencing the maize biomass yield was the application of fertiliser (F = 5391, $p > 0.001$), followed by type of soil (F = 131, $p > 0.001$) and the application of biochar (F = 11.9, $p > 0.001$), see supporting information (SI S1). The interaction effect of biochar and fertiliser was also a source of significant (F = 5.39, $p = 0.001$) effect.

The uptake of nutrients by maize. *Nitrogen.* The application of biochar in NoAS and USAS treatments of the Chernozem was not able to induce any significant effect, while in the SAS treatments, the application of 2% biochar induced a significant ($p = 0.05$) increment of N uptake of 26% (Fig. 2). On the acidic Cambisol, the

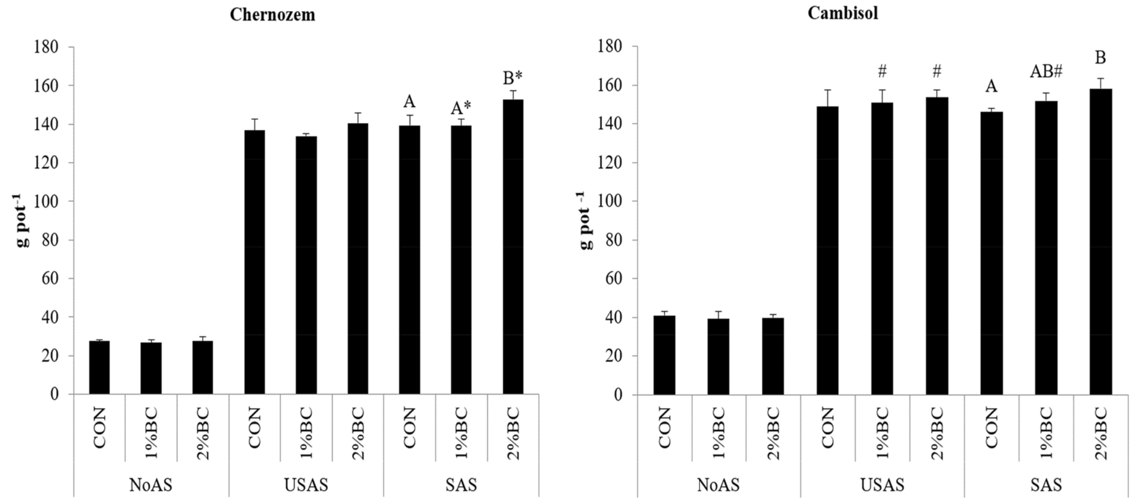

Figure 1. The yield of maize aboveground biomass at full maturity. USAS (un-stabilized ammonium sulphate) and SAS (stabilized ammonium sulphate with DMPP). Different upper-case letters indicate a significant difference between variants within the same treatments of the same soil. *Represents a significant difference along biochar treatments of SAS and USAS (pair wised t-test between 1% BC of USAS and 1% BC of SAS and between 2% BC of USAS and 2% BC of SAS). #Represents significant difference of pair wise t-test along different soils of similar treatments (CON of USAS Chernozem with CON of USAS Cambsiol and likewise). *NoAS* No ammonium sulphate, *CON* control, *1% BC* 1% biochar, *2%BC* 2% Biochar.

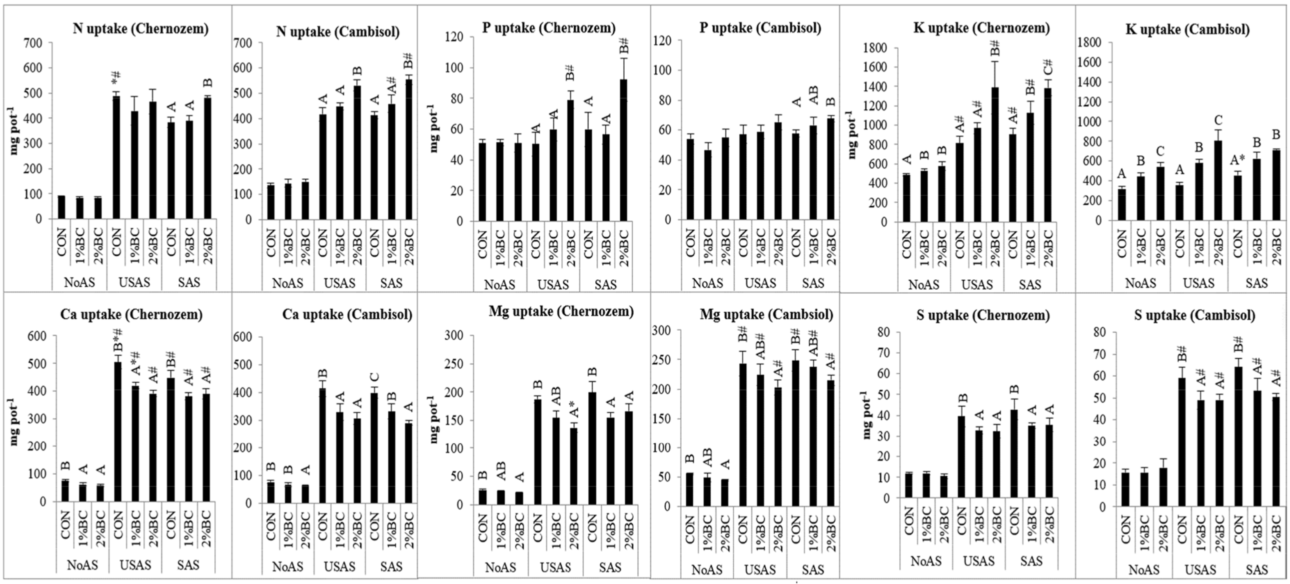

Figure 2. The uptake nutrients (N, P, K, Ca, Mg and S) by aboveground biomass of maize as affected by biochar, USAS (un-stabilized ammonium sulphate) and SAS (stabilized ammonium sulphate with DMPP). Different upper-case letters indicate a significant difference between variants within the same treatments of the same soil. *Represents a significant difference along biochar treatments of SAS and USAS (pair wised t-test between 1% BC of USAS and 1% BC of SAS and between 2% BC of USAS and 2% BC of SAS). #Represents significant difference of pair wise t-test along different soils of similar treatments (CON of USAS Chernozem with CON of USAS Cambisol and likewise). *NoAS* No ammonium sulphate, *CON* control, *1% BC* 1% biochar, *2%BC* 2% biochar.

application of 2% BC induced a significant increment of N uptake in both the USAS and SAS treatments by 27 and 34%, respectively. In the Chernozem, the uptake of N in control treatment of USAS was higher than the control treatment of SAS. In the Cambisol, the uptake of N was significantly higher at the 1 and 2% BC treatments of SAS than the corresponding treatment of the Chernozem soil. The multivariate analysis of variance of the between-subject effects (SI S1) revealed that the highest effect was fertiliser ($F = 1592$, $p < 0.001$), then soil ($F = 48.4$, $p < 0.001$) and biochar ($F = 40.7$, $p < 0.001$) on the uptake of nitrogen. More interestingly, there was also a significant interaction effect for fertiliser and biochar ($F = 13.4$, $p < 0.001$), soil, biochar and fertiliser ($F = 3.40$,

		NUE (%)		**SUE (%)**	
		Chernozem	**Cambisol**	**Chernozem**	**Cambisol**
USAS	1% biochar	−5.84	3.11	−0.59	−0.88
	2% biochar	−2.23	10.9	−0.63	−0.87
SAS	1% biochar	0.59	4.48	−0.69	−0.97
	2% biochar	9.47	13.7	−0.66	−1.22

Table 3. The effect of biochar on the use efficiency of nitrogen (NUE) and sulphur (SUE). Nutrient use efficiency in percentage calculated per added amount of N and S from fertilizer.

$p < 0.015$) and an interaction between soil and biochar (F = 12.1, $p < 0.001$) (SI S1). The application of 2% BC increased the NUE by 9.5% in the Chernozem with the SAS treatment and by 11 and 13.7% for the USAS and SAS treatments of the acidic Cambisol, respectively (Table 3).

Phosphorus. In both soils, the application of biochar without fertiliser was not able to induce any significant changes in P uptake (Fig. 2). However, the application of 2% biochar with both USAS and SAS was able to induce significant ($p < 0.05$) increments of P uptake by 58 and 54%, respectively on the neutral Chernozem and significant ($p < 0.05$) increments of 14 and 18% in the USAS and SAS treatments of the acidic Cambisol, respectively. The uptake of P for the 2% BC treatments of USAS and SAS was significantly higher for the Chernozem soil than for the corresponding treatments of Cambisol. The application of fertiliser had the highest effect (F = 32.8, $p < 0.001$) on the uptake of P (SI S1). It was followed by the effect of biochar (F = 31.8, $p < 0.001$) and the interaction effect of soil with biochar (F = 8.29, $p < 0.001$), then the fertiliser with biochar (F = 6.81, $p < 0.001$). The interaction between soil, fertiliser and biochar also had a significant (F = 5.27, $p < 0.001$) effect.

Potassium. Soil type induced the highest effect (F = 333, $p < 0.001$) on the uptake of K, then fertiliser (F = 140, $p < 0.001$), biochar (F = 96.8, $p < 0.001$), the interaction of soil with fertiliser (F = 46.1, $p < 0.001$), fertiliser with biochar (F = 8.98, $p < 0.001$) and the interaction effect of soil, fertiliser and biochar (F = 2.55, $p < 0.001$) (SI S1). The application of biochar induced an increment of K uptake in all treatments of both soils. In particular, the application of 2% biochar induced a significant ($p < 0.05$) increment of K uptake in all treatments (NoAS, SAS and USAS) of both soils (Fig. 2), while a 1% application induced a significant increment in all treatments of Cambisol and SAS and USAS treatment of the Chernozem. The increment was higher in the case of the acidic Cambisol as compared to the neutral Chernozem. The uptake of K in the Chernozem soil CON, as well as the 1 and 2% BC of both USAS and SAS was significantly higher than corresponding treatments of the Cambisol soil (Fig. 2). The increment of K uptake in Chernozem was by 19, 70 and 53%. Meanwhile in the Cambisol, it was by 71, 127 and 57% at the 2% BC application rate in the NoAS, USAS and SAS, respectively.

Calcium. The highest impact on the uptake of Ca was obtained from the application of fertiliser (F = 2588, $p < 0.001$) then soil type (F = 148, $p < 0.001$), biochar (F = 104, $p < 0.001$), the interaction of soil with fertiliser (F = 44.9, $p < 0.001$) and fertiliser with biochar (F = 17.4, $p < 0.001$) (SI S1). The application of biochar decreased the uptake of Ca in all treatments (NoAS, SAS and USAS) of both soils (Fig. 2). In the case of the Chernozem, the application of both 1 and 2% biochar significantly ($p < 0.05$) reduced the uptake of Ca in all treatments (NoAS, SAS and USAS) (Fig. 2). The declines with the 2% of biochar rate were by 22, 22 and 13% for the NoAS, USAS and SAS, treatments, respectively. In the case of the acidic Cambisol, the decline was significant ($p < 0.05$) at both the 1 and 2% application of biochar for the SAS and USAS, while it was significant only at the 2% biochar application rate at NoAS treatments. The declines for the 2% BC rate were 17, 26 and 27% for the NoAS, USAS and SAS, respectively. The uptakes of Ca in the Chernozem soil CON as well as the 1 and 2% BC of both the USAS and SAS were significantly higher than corresponding treatments of the Cambisol soil (Fig. 2).

Magnesium. The highest effect on the uptake of Mg was obtained from the application of fertiliser (F = 1524, $p < 0.001$), then soil (F = 332, $p < 0.001$) and biochar (F = 38.2, $p < 0.001$), the interaction of soil with fertiliser (F = 19.2, $p < 0.001$) and fertiliser with biochar (F = 6.18, $p < 0.001$) (SI S1). As that of Ca, the uptake of Mg declined with the application of biochar in all treatments (NoAS, SAS and USAS) of both soils (Fig. 2). The application of 2% biochar induced a significant ($p = 0.05$) decline in all treatments of both soils, while only 1% caused a decline in the SAS and USAS of Chernozem soil. The declines in Chernozem soil at the 2% biochar rate were 17, 27 and 17% for NoAS, USAS and SAS, respectively; while in the Cambisol, the declines were 19, 17 and 13 for the NoAS, USAS and SAS, respectively. Inversely, the uptakes of Mg in the Cambisol soil CON as well as 1 and 2% BC for both USAS and SAS were significantly higher than the corresponding treatments for Chernozem soil (Fig. 2).

Sulphur. The highest effect on the uptake of S was from fertiliser (F = 708, $p < 0.001$) then soil (F = 296, $p < 0.001$) and the interaction of soil with biochar (F = 30.2, $p < 0.001$), biochar (F = 26.7, $p < 0.001$) and the interaction of fertiliser with biochar (F = 7.44, $p < 0.001$) (SI S1). The application of biochar without fertiliser was not able to induce any significant change in either soil, while both 1 and 2% biochar induced a significant decline in the SAS and USAS treatments of both soils (Fig. 2). The declines of S uptake in the Chernozem soil at 2% biochar

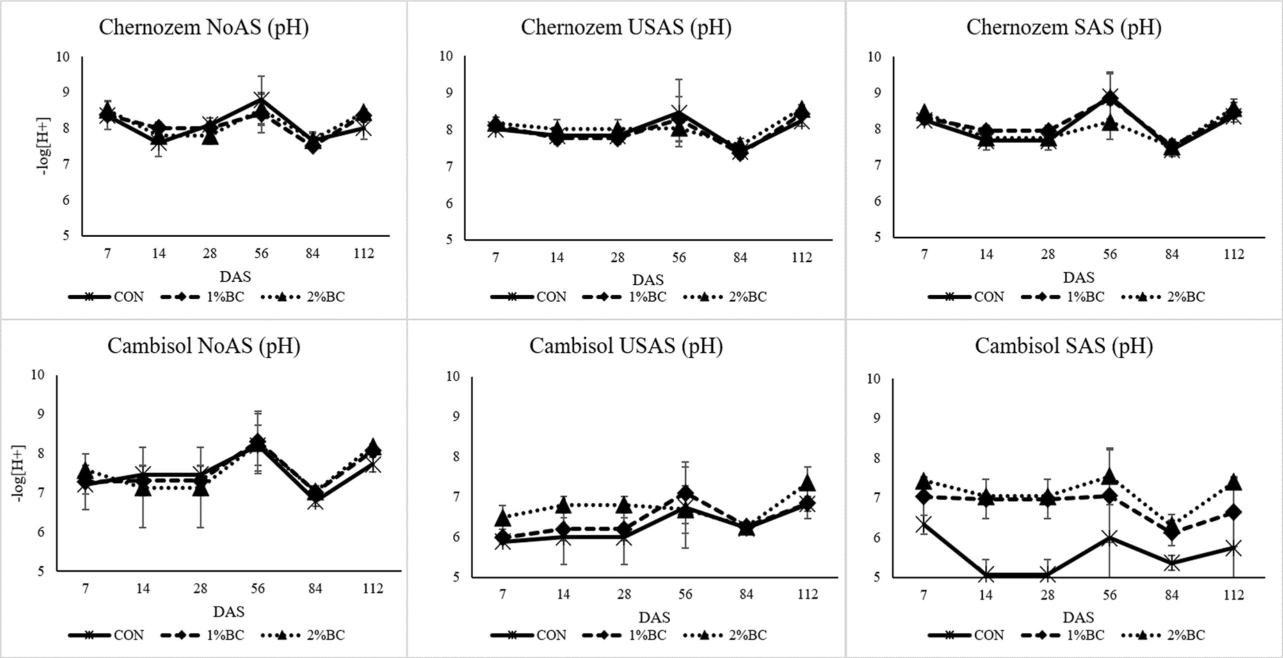

Figure 3. The effect of biochar, USAS (un-stabilized ammonium sulphate) and SAS (stabilized ammonium sulphate with DMPP) on the pH of soil solution, *NoAS* No ammonium sulphate, *CON* control, *1%BC* 1% biochar, *2%BC* 2% biochar, *DAS* day after sowing.

application were by 18 and 17% in USAS and SAS, respectively and by 17 and 22% for USAS and SAS in the Cambisol, respectively. The S use efficiency from the applied fertiliser declined with the application of biochar in both the SAS and USAS treatments (Table 3). The decline was up to 0.63, 0.66 with 2% biochar in the USAS and SAS treatments of the Chernozem and up to 0.87, 1.22% in the USAS and SAS treatments of Cambisol, respectively. All USAS and SAS treatments in Chernozem soil had significantly higher uptakes of S than their respective treatments in Cambisol.

pH and composition of soil solution.

pH. All the investigated factors soil, biochar, fertiliser, sampling period, the interaction of soil with biochar and the interaction of biochar with fertiliser had a significant effect on the pH of the soil solution. Based on the rANOVA, the source of highest variation was soil type with ($F = 201$, $p < 0.001$), then time of sampling ($F = 20.2$, $p < 0.001$) (SI S2). The effect of biochar on the pH of the soil solution was minimal in the case of the Chernozem soil, while in the case of the acidic Cambisol, co-application of biochar with AS significantly increased the pH of the soil solution at least by the seventh DAS (Fig. 3). At the seventh DAS, the highest increment in pH was in the SAS treatments of the acidic Cambisol, which was up to 1.11 units with the 2% biochar application.

Nitrate and ammonium. An increment of NO_3^- N concentration was detected in the control treatment of USAS in the Chernozem and all USAS treatments of the Cambisol between 7 and 14 DAS, while in the remaining treatments, the concentration of NO_3^- N was rather decreasing over time (Fig. 4). The rANOVA for the effect of factors on the concentration of NO_3^-–N in the soil solution is presented in SI S2. Based on the rANOVA (SI S2) soil type, biochar, fertiliser, sampling period and the interaction of biochar with fertiliser had a significant effect on the concentration NO_3^-–N in soil solution. The highest effect was attributed to the sampling period ($F = 230$, $p < 0.00$). The concentration of NH_4^+–N in soil solution was significantly affected by soil, biochar, fertiliser, the period of sampling and the interaction of soil with biochar (SI S2). At the seventh DAS, higher concentrations of NH_4^+–N were detected in the soil solution of SAS compared to USAS. Lower concentrations of NH_4^+–N in soil solution were found in variants treated by biochar application by at least the seventh DAS (Fig. 5). After harvesting the maize, the soils were analysed for the available fractions of mineral N (SI S3). The effect of biochar on both NO_3^- N and NH_4^+–N was very negligible in the Chernozem soil except a significant decline in the NO_3^- N content of the NoAS treatment. In the case of the Cambisol, the application of 2% biochar significantly decreased the content of soil NH_4^+ and increased the content of NO_3^- in the USAS and SAS treatments.

Phosphorus and sulphur. The concentration of P was significantly higher in the Chernozem soil as compared to the Cambisol (Fig. 6). Only the main factors soil, fertiliser and time of sampling induced a significant effect on the concentration of soil solution P (SI S2). The highest effect was attributed from time of sampling with $F = 193$, $p < 0.001$. In all treatments, the concentration of P had a decreasing trend over time and a slightly lower concentration was detected in biochar-treated soils, especially at seven DAS. The application of AS fertiliser increased the concentration of S in soil solution. The effect of biochar on the concentration of S was not very noticeable

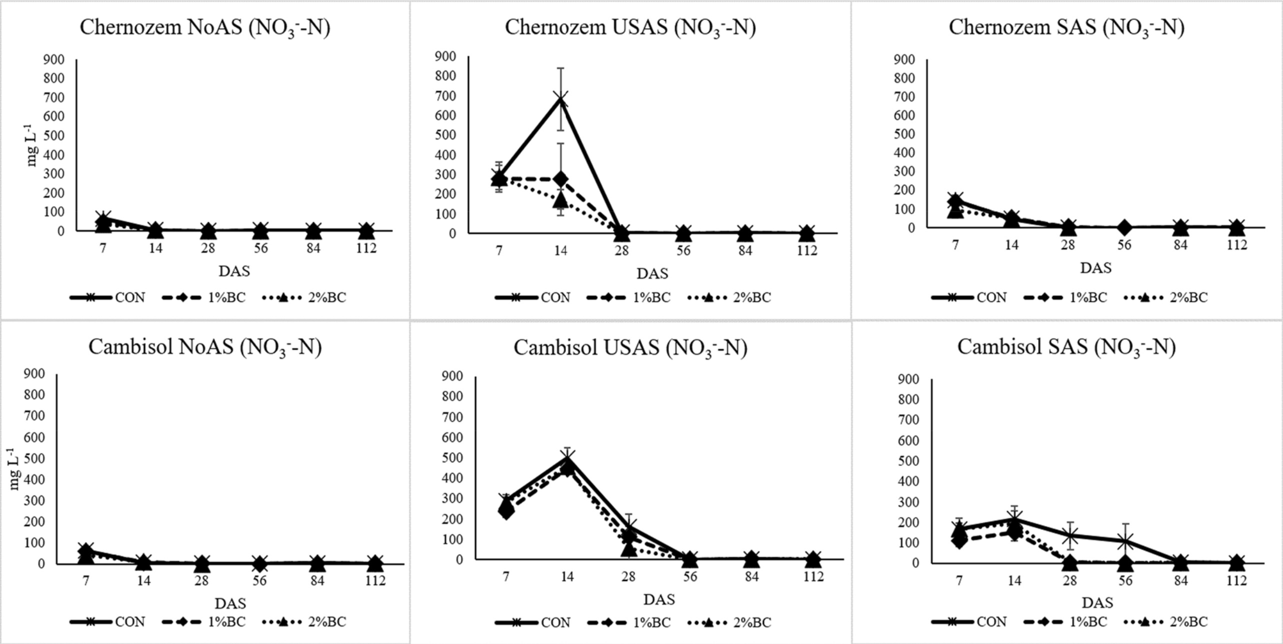

Figure 4. The effect of biochar, USAS (un-stabilized ammonium sulphate) and SAS (stabilized ammonium sulphate with DMPP) on the concentration of NO_3^-–N (mg L^{-1}) in soil solution. *NoAS* No ammonium sulphate, *CON* control, *1%BC* 1% biochar, *2%BC* 2% biochar, *DAS* day after sowing.

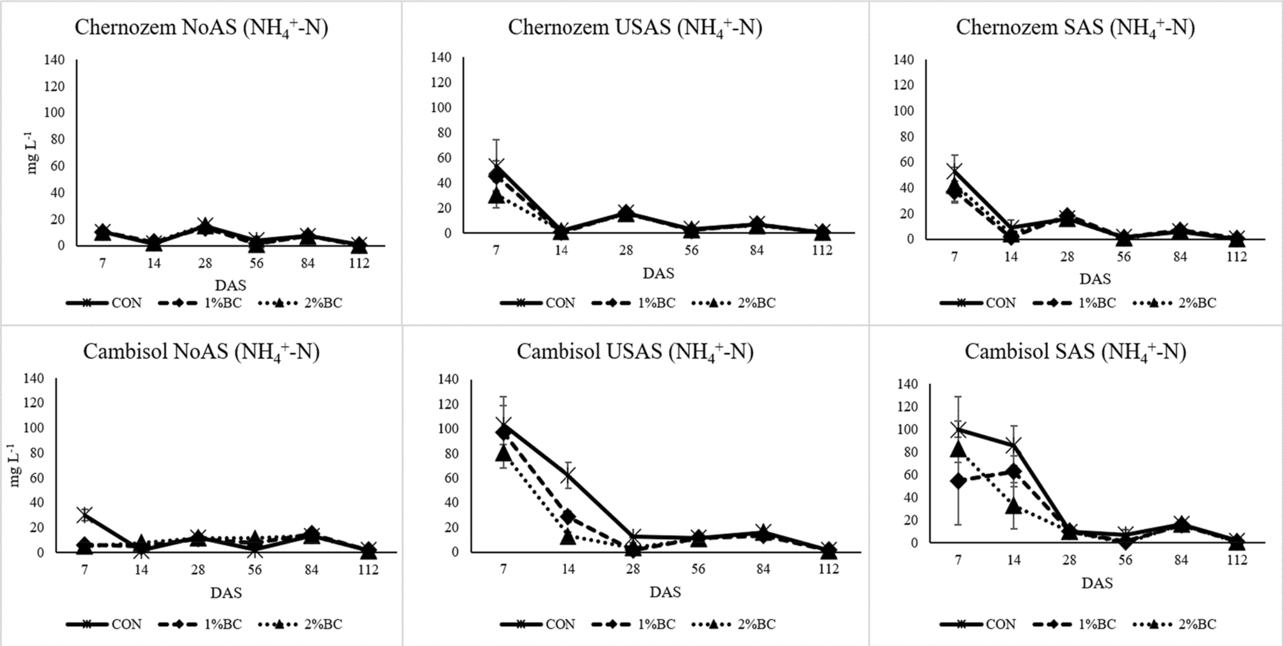

Figure 5. The effect biochar, USAS (un-stabilized ammonium sulphate) and SAS (stabilized ammonium sulphate with DMPP) on the concentration of NH_4^+–N (mg L^{-1}) in soil solution. *NoAS* No ammonium sulphate, *CON* control, *1%BC* 1% biochar, *2%BC* 2% biochar, *DAS* day after sowing.

except for a slight decline in SAS and USAS treatments by the seventh DAS (SI S4). All the investigated factors except the interaction of soil with biochar had a significant effect on the concentration S in soil solution (SI S2). The greatest effect was from the application of fertiliser ($F = 250$, $p < 0.001$).

Potassium, calcium and magnesium. All the factors investigated, except the interaction of biochar with fertiliser, had a significant effect on the concentration of K in soil solution, with the highest effect arising from the period of sampling $F = 744$, $p < 0.001$ (SI S2). A higher concentration of K was in the Cambisol than in the

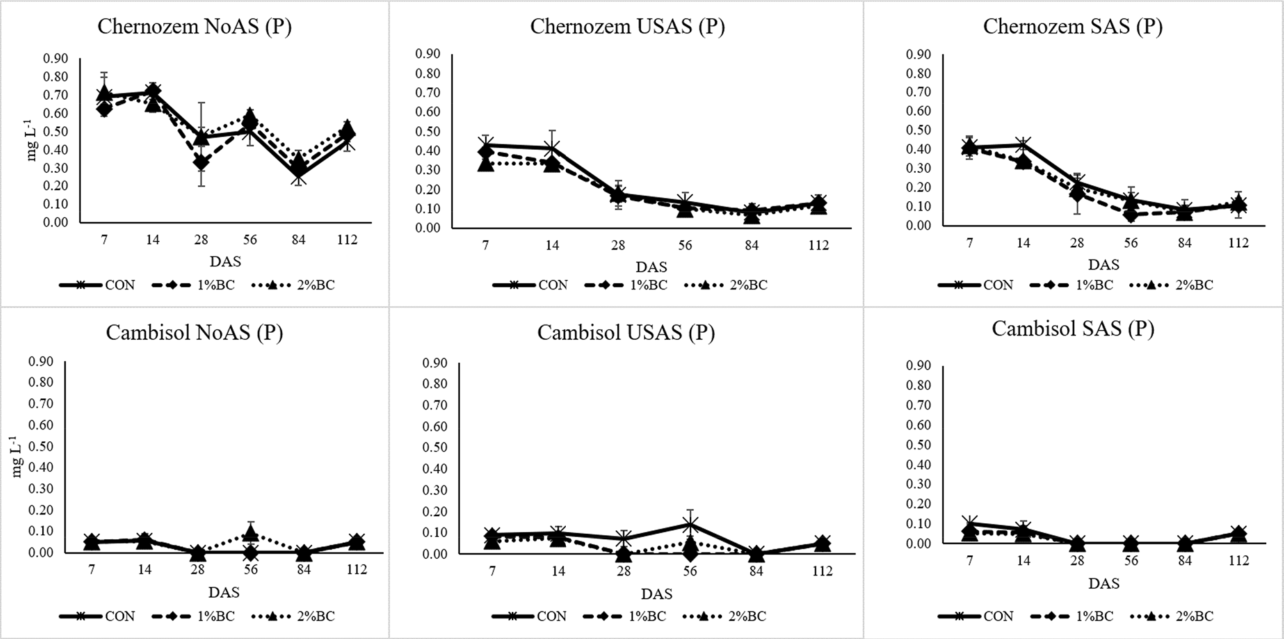

Figure 6. The effect of biochar, USAS (un-stabilized ammonium sulphate) and SAS (stabilized ammonium sulphate with DMPP) on the concentration of P (mg L^{-1}) in soil solution. *NoAS* No ammonium sulphate, *CON* control, *1%BC* 1% biochar, *2%BC* 2% biochar, *DAS* day after sowing.

Chernozem soil. Application of AS fertilisers increased the concentration of K in soil solution, especially at DAS 7, and decreased over time. Furthermore, the application of BC resulted in higher K concentrations in soil solution, but this effect was detectable only at the early stage of the experiment (SI S5). Similarly, the application of AS fertiliser significantly increased the concentration of Ca and Mg in the soil solution of both soils, by at least the 7th day of sampling. Among the investigated factors, biochar, fertiliser, time of sampling and the interaction of biochar with fertiliser had a significant effect on the concentration of Ca (SI S2). The highest effect was from the time of sampling with $F = 442$, $p < 0.001$. The concentration of Ca showed a decline over time except for a significant increment in control treatment of USAS Ca from 959 mg L^{-1} (7 DAS) to 1555 mg L^{-1} (14 DAS) in the Chernozem (SI S6). In the case of Mg, only the main factors soil, fertiliser and time of sampling induced a significant effect on the concentration of soil solution Mg (SI S2). The highest effect was from the application of fertiliser with $F = 267$, $p < 0.001$. Again, the concentration of Mg showed a decline over time except for a significant increment in the control treatment of USAS from 43 mg L^{-1} (7 DAS) to 65 mg L^{-1} (14 DAS) (SI S7).

Discussion

Mechanisms of NUE improvement. The highest maize aboveground biomass was achieved by the combination of 2% BC and stabilised ammonium sulphate (SAS) identically on both soils (Fig. 1). Moreover, the application of BC was effective to increase maize biomass only in combination with SAS. Based on the between-subject effects analysis of variance (SI S1), the factor with the highest influence on the uptake of N and maize biomass was the fertiliser, which is due to the N supplied. The significant increment of maize biomass at the co-application of biochar and DMPP treated ammonium sulphate was mainly due to the increment of N uptake and improved NUE as the highest increments of N uptake (34%) and NUE (13.7%) were in the treatment of SAS combined with 2% BC. The increment of maize biomass, improved uptake of N and NUE when the biochar was co-applied with the SAS indicates the positive association effect of biochar with DMPP. One of the mechanistic reasons for the improved yield and NUE in these treatments could be due to further delay of the nitrification by biochar. Therefore, biochar could further extend, or delay the nitrification inhibition induced by DMPP and slows the release of nitrate for the later stage of maize growth[37]. This output is in complete disagreement with the findings of Sheikhi et al.[38], Fuertes-Mendizábal et al.[39], and Keiblinger et al.[40], where authors presented the negative interaction of DMPP with biochar.

Other important finding is that the biochar-induced increment of NUE was higher in the acidic Cambisol fertilized by DMPP treated ammonium sulphate. This could indicate the better interaction of biochar with DMPP treated ammonium sulphate in the acidic soils as compared to neutral or alkaline soils. The first reason for the better joint effect of biochar with DMPP treated ammonium sulphate in the acidic Cambisol could be due to the acidic pH (4.8) and higher sand content of the Cambisol (26.1%) than the Chernozem (13.2%). The short delay of NH_4^+ oxidation by DMPP in soil with a higher proportion of clay is expected due to the sorption of DMPP by clay minerals and their reduced effect[41], while the opposite is true in soils with a high proportion of sand and further prolongation by biochar is expected. Secondly, the nitrification inhibitory effect of DMPP is much higher in acidic soil as compared to alkaline soils[42], which is again further prolonged by the application of biochar. This was noticeable for the USAS and SAS treatments of Cambisol at 7 and 14 DAS (Fig. 5). This all leads to a low rate of NH_4^+ oxidation to NO_3^- and the subsequent slow release for the later stage of maize growth. Moreover, even if we expect some excess nitrification in this soil, the nitrate loss due to leaching could be very low as adsorption of nitrate by biochar at the acidic pH of the Cambisol is higher than the neutral pH of the Chernozem soil. This is because of the more favoured adsorption of NO_3^-–N in the acidic soil conditions[24]. This statement agreed with the NO_3^-–N and NH_4^+–N contents in the 0.01 M $CaCl_2$ extraction of soil samples collected after the harvest of maize (SI S3). There was a significantly higher concentration of NO_3^-–N in the Cambisol with 2% biochar with SAS and USAS treatments after the harvest of maize than in the controls (no biochar), whereas there was a significant decline in the content of NH_4^+–N. This was not true in the case of the neutral Chernozem soil, which indicates that NH_4^+ was being slowly nitrified in the biochar treatments of acidic Cambisol, especially in the SAS and USAS treatments accompanied by NO_3^-–N availability even after the harvest of the maize, which is beneficial for the next cropping season.

The uptake and use efficiency of sulphur. The uptake of S was higher in the SAS and USAS treatments of the Cambisol than that of the Chernozem. This is in agreement with the high content of available S in the Cambisol soil solution of the USAS and SAS treatments. The application of biochar induced a decline in the uptake of S in the SAS and USAS treatments. The application of biochar in the fertilised treatments reduced sulphur use efficiency up to 1.22%, meaning that there were always lower uptakes of S in the biochar treatments of SAS and USAS than in the controls in both soils. This is mainly due to the low availability of S in the soil solution of biochar treatments (SI S4). The decline in the availability of S from biochar in treatments of SAS and USAS could be due to the precipitation of Ca released from biochar with sulphate and the adsorption by biochar. This is because the same trend was shown for the Ca uptake, which declined with the biochar application and nevertheless gave a higher Ca depletion in the soil solution of biochar treatment of USAS and SAS. The decline of Ca and S in soil solution was significantly ($p = 0.05$) correlated ($r = 0.95$) in the Chernozem soil and ($r = 0.89$) in Cambisol. This phenomenon could indicate that the co-precipitation of Ca and S resulted in the decline of both Ca and S in the biochar treatments of USAS and SAS. The increment in S adsorption and the formation of S-Ca precipitate in the Ca-rich condition is evident[43]. Biochar could also decrease the availability of S due to the sorption of SO_4^{2-} by electrostatic interaction with the charged surface of biochar[44]. The decline in the content of sulphate by biochar application has been reported due to the formation of weakly soluble $CaSO_4$[45].

The content of S in the treatment without fertiliser was lower compared to ammonium sulphate treatments (SAS and USAS). This is mainly due to the release of sulphate from applied ammonium sulphate and the improved uptake of S in the soils having higher contents of N. The decrease of sulphur uptake in low N available conditions has been described by Clarkson et al.[46]. Again, the multivariate analysis (SI S1) confirmed a higher effect of fertiliser ($F = 708$, $p < 0.001$) compared to soil type. There was also a significant interaction effect of biochar and fertiliser ($F = 7.44$, $p < 0.001$) revealing the highest effect of biochar to reduce the uptake of S is in fertilised treatments, while it had insignificant effects in NoAS treatments.

The uptake of phosphorus. The uptake of P was generally higher in the Chernozem soil than in the Cambisol due to the higher availability and total content of P in Chernozem soil (Table 1) and a subsequent significant higher concentration of P in the soil solution (Fig. 6). The single application of biochar without N fertiliser was not able to induce significant changes in P uptake. However, biochar was able to increase the P uptake in the USAS and SAS treatments of both soils without a detectable increment of P in soil solution. This is likely not due to the release of P from biochar, as the applied biochar does not have available P for plant uptake (Table 1). In similar studies, the application of biochar at the rate of 10 t ha^{-1} was able to increase maize P uptake[47]. The main reason for the increment of P uptake could be the biochar-induced weakening/inhibition of phosphate anions ($H_2PO_4^-$, HPO_4^{2-} or PO_4^{3-}) adsorption by the Al/Fe (hydr)oxides of soils[48]. The adsorption of soil HPO_4^{2-} or PO_4^{3-} by Fe (hydr)oxides is expected to be lower at the relatively higher pH induced by biochar. This is due to the repulsion of negatively charged HPO_4^{2-} and/or PO_4^{3-} by the negatively charged surface sites of the ferrihydrite and as a result of OH^- ion competition on the negatively charged sorption sites at the higher soil pH induced by biochar[49]. The increment of soil pH due to the release of Ca^{2+}, Mg^{2+} and K^+ from biochar could effectively reduce the solubility of reactive Al^{3+} oxides, and this could reduce the sorption of P in acidic soil[50]. The biochar-induced increment of soil pH is evident and significant especially in the SAS and USAS treatments of acidic Cambisol at least at the seventh DAS (Fig. 3). Biochar could increase soil pH by releasing exchangeable base cations (Ca^{2+}, K^+ and Mg^{2+}) and their subsequent replacement by the exchangeable Al^{3+} and H^+ on the exchangeable sites of biochar as well as the binding of surplus H^+ ion to the negatively charged (carboxylic, hydroxyl and phenolic) surface functional groups of biochar[15,51]. Thus, the better expression of pH increment in the SAS and USAS treatments of acidic Cambisol than the neutral Chernozem is simply due to the greater effectiveness of biochar to increase soil pH in soils having low pH, CEC and exchangeable Ca^{2+}.

The uptake of potassium, calcium and magnesium. Based on the multivariate analysis of variance (SI S1), the highest factor affecting the uptake of K was soil due to the higher uptake of K in the Chernozem soil with the higher content of both total and available K content than the Cambisol (Table 1) and their release to the soil solution. The second highest factor influencing the uptake was the application of ammonium sulphate. The reason for the higher uptake of K in the ammonium sulphate treatments is the higher availability of K induced by the displacement of exchangeable K^+ to the soil solution by NH_4^+ from the applied ammonium sulphate (SI S3). Based on the study of Wang et al.[52], the application of AS increased the content of water-soluble K up to 160%, while the exchangeable content of K^+ declined by up to 19%, supporting the release of K^+ into the soil solution due to the displacement from the exchangeable site of soils by NH_4^+. The third significant effect was from the application of biochar. The application of 2% biochar was able to induce a significant increment of K uptake in all treatments of both soils. The improvement of K uptake in the biochar-amended treatments of our soil is expected due to much higher $CaCl_2$ (0.01 M) and extractable contents of K (2278 mg kg^{-1}) from the biochar used in this study compared to the Chernozem (65 mg kg^{-1}) and Cambisol (32 mg kg^{-1}) soils. Biochar could serve as a potential source of K, and this results in the subsequent increment of K uptake[53]. The release and improvement of K uptake by crops after biochar application have been previously reported[54,55]. Similarly, the improvement of K availability and the subsequent increment of K uptake by maize was reported after the application of 2% vineyard pruning biochar[56].

The effect of biochar on the uptake of Ca and Mg was opposite to the uptake of K. The application of biochar decreased the uptake of both Ca and Mg. The decline in the uptake of both elements with biochar application is due to the antagonistic effect of K uptake. This agrees with all treatments; declines in the Ca and Mg concentrations were noticeable in all treatments where there was an increment of K uptake. The increment of K availability by biochar application could induce a reduction of Ca and Mg uptake due to the blockage of non-specific Ca and Mg transporters by the uptake of K. Therefore, the competition of K for transporters and preferential uptake of K in the K rich soil solution induces a reduction of Ca and Mg uptake[57]. The study of Horie et al.[58] confirmed that the class II high-affinity potassium transporter (HKT) was involved in the transport of K, Ca and Mg, and hence preferentially transporting K over the divalent cations (Ca^{2+} and Mg^{2+}), leading to the suppression of Mg and Ca uptake in K-rich environment. The highest effect of fertiliser (SI S1) on the uptake of Ca and Mg is linked to the higher maize biomass in the fertilised treatments, which was 5 times higher than the control and increment of Ca and Mg in soil solution (SI S6 and S7). The increment of available Ca and Mg content in fertilised treatment of soil solution is again caused by the displacement of exchangeable Ca^{2+} and Mg^{2+} from the exchangeable site of soils by NH_4^+[59]. The effect of NH_4^+ on the displacement of Ca^{2+} and Mg^{2+} from the exchangeable site of soil can be observed from the increased concentration of Ca and Mg in the USAS and SAS treatments compared to control in both soils (SI S6 and S7). Similarly, the oxidation of NH_4^+ to nitrate is known to release $2H^+$ ion[60]. Thus, the temporary increment of Ca and Mg in USAS and SAS treatments of both soil could be also associated with the replacement Ca^{2+} and Mg^{2+} by the H^+ ion released from the nitrification result of $(NH_4)_2SO_4$. Further biochar induced a decline of Ca content in the soil solution of the neutral Chernozem and an increment in the acidic Cambisol. Biochar is principally capable of increasing available Ca content in soils having lower original Ca content than the biochar used, while biochar could induce a decline of Ca content when added to soils having higher Ca contents than the biochar applied[15]. The neutral Chernozem had a much higher content of exchangeable Ca^{2+} (253 mmol kg^{-1}) than the acidic Cambisol (72 mmol kg^{-1}) and biochar (176 mmol kg^{-1}) (Table 1). Thus, when this type of biochar was added to the neutral Chernozem, we would expect a decline of Ca content, while incrementing in the acidic Cambisol.

Mechanisms of biochar interaction with ammonium sulphate treated by DMPP. As discussed above, the positive impact of high temperature produced biochar co-application with DMPP treated ammonium sulphate fertilizer on the NUE and biomass of maize is mainly attributed due to the weak adsorption of NH_4^+ by the high temperature produced biochar (700 °C) used in this study. Therefore, the weakly adsorbed NH_4^+ could slowly nitrify and become available for the plant uptake at the later crop growing stages. This directly goes with the intended use of DMPP, which slows the nitrification of NH_4^+. Some previously published works of other studies seem quite opposing to our finding in some ways, which is attributed only to the higher production temperature of biochar (700 °C) used in this study. For example, the adsorption of DMPP by lower temperature produced biochar was reported for the biochars pyrolyzed at 450 °C[38], 500 °C[39], 400 °C and 525 °C[40]. In those studies, the presence of low NH_4^+ concentration in the treatments containing DMPP with biochar seems holding back the intended use of DMPP to limit the process of nitrification. However, the low availability of NH_4^+ in soils where low temperature produced biochar was applied is expected due to the strong sorption of NH_4^+ by easily available negatively charged oxygen containing functional groups of low temperature produced biochar[23,61]. Further, the lower temperature produced biochar can adsorb DMPP. Fuertes-Mendizábal et al.[39] reported the adsorption of DMPP driven by the oxygen containing functional groups, more specifically carboxyl groups, of the lower temperature produced biochar (500 °C) used in their study. This is in the agreement with the finding of Keiblinger et al.[40], reported a greater adsorption of DMPP by the biochar produced at 400 °C than the biochar produced from the same feedstock at the higher temperature (525 °C). The occurrence of the phenomena (adsorption of NH_4^+ and DMPP by biochar) is expected to be very low in our study due to the loss of oxygen containing functional groups proportional with the rise in production temperature. The clear decline of oxygen containing functional groups with the rise in temperature is evident[62]. Therefore, the use of high temperature produced biochar is a choice for the overall better performance of biochar-DMPP combination.

Conclusion

The interaction effect of biochar with ammonium sulphate containing DMPP (NovaTec Solub 21) on the biomass and yield component of maize was studied on two soils with contrasting properties. The outcome revealed the effectiveness of biochar co-application with ammonium sulphate containing DMPP to induce a significant increment of maize biomass as well as the uptake of N, P and K.

Co-application of biochar with ammonium sulphate containing DMPP was able to increase maize biomass by 10%, nitrogen use efficiency by 13.7%, the uptake of P by 54%, and the uptake of K by 57% compared to a single application of ammonium sulphate containing DMPP. The interaction of biochar with ammonium sulphate containing DMPP was more effective to increase maize biomass, N uptake and K uptake in the acidic Cambisol, while P uptake increased in the neutral Chernozem. The application of biochar also induced a decline in the uptake of Ca and Mg because of the antagonistic effect of K. Additionally, biochar induced a decline of S uptake when co-applied with ammonium sulphate. In the case of un-stabilized ammonium sulphate, biochar was not able to induce a significant change in maize biomass, while there was an increment in N uptake only in the acidic Cambisol, an increment in the uptake of K in both soils and a decline in the uptake of Ca, Mg and S. Furthermore, the effect of biochar was also pronounced in the soil solution by increasing the concentrations of K, Mg in the soil solution of both soils, while there was an increment of Ca in the acidic Cambisol and a decline in the neutral Chernozem.

Generally, the interaction effect of biochar on the maize biomass, NUE and uptake of N was much higher when combined with ammonium sulphate containing DMPP than its co-application with un-stabilized ammonium sulphate and a single application of both stabilised and un-stabilized ammonium sulphate. Hereafter, we conclude that the application of high temperature produced biochar with ammonium sulphate containing DMPP could increase crop yield and improve nitrogen use efficiency due to a greater extent by the reduction of nitrogen losses.

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Author contributions

N.S.H carried out the experiment and wrote the manuscript, N.S.H., F.M, and P.T. participated in the conceptualization of the experimental design and reviewing the manuscript, J.S., and M.K. reviewed the manuscript, P.T. supervised the overall experiment. All authors have read and agreed to the revised version of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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5. Comprehensive Discussion

5.1. Effect of biochar on soil pH and cation exchange capacity

The results from our 12 weeks incubation experiment clearly demonstrated the possible use of biochar to ameliorate acidity of soils. The observed increment in soil pH was up to 1.2 unit, the amount of increment varying from soil to soil. The amount of pH increment was always in positive relation with biochar addition rate. This finding is in agreement with the finding of very recent studies (Aamer et al., 2020; Jiang et al., 2020; Cooper et al., 2020; Ghorbani et al., 2019; Manolikaki and Diamadopoulos, 2017). Based on the report of Ghorbani et al. (2019), biochar was able to increase soil pH up to 0.69 unit. The type of soil used, and biochar rate determined the level of pH increment. Generally, biochar was more effective to increase soil pH, when soils have lower original pH, lower CEC, lower exchangeable Ca^{2+}, lower clay fraction and higher sand content. This generalization agrees with the correlation analysis, where the change rate of the soil pH after biochar addition was positively and significantly correlated with sand content ($r = 0.75$, $p = 0.001$), whereas negatively correlated with original soil pH ($r = - 0.76$, $p = 0.001$), CEC ($r = 0.82$, $p = 0.001$), exchangeable Ca^{2+} ($r = - 0.83$, $p = 0.001$), and content of clay fractions ($r = - 0.72$, $p = 0.001$). The higher the rate of biochar application resulted in higher capacity to induce soil pH increase; furthermore, there was higher pH increment in acidic soils as compared to neutral soils. This is in agreement with the findings of Ghorbani et al (2019), where they identified greater absolute increment of soil pH in soils with lower pH as compared to soils with higher original pH. The release of base cations, the replacement of soil exchangeable Al^{3+} and H^+ by the exchangeable Ca^{2+} and K^+ (Li et al., 2018), the binding of H^+ by the negatively charged functional groups of biochar (phenolic, carboxylic, and hydroxyl) are the major mechanisms for soil pH improvement following biochar addition to soil (Gul et al., 2015). Furthermore, decarboxylation of organic anions after the addition of biochar, which consumes surplus H^+ could also increase soil pH (Barekzai and Mengel, 1993). When we come to soil CEC, biochar was able to increase CEC in seven soils, which has lower original exchangeable Ca^{2+} content than biochar and significantly reduced CEC in three soils having higher original exchangeable Ca^{2+} content than biochar. From this result, we clearly understood that the main factor determining magnitude of biochar effect on soil CEC is the original exchangeable Ca^{2+} content of soils in comparison to the exchangeable Ca^{2+} content of the applied biochar. The ability of biochar to increase CEC is confirmed by other studies (Cooper et al., 2020; Mahmoud et al., 2020). The biochar mediated increment of soil CEC could arise from the negatively charged surface, surface charge density and higher surface area of biochar (Li et al., 2018). Moreover, the considerable content of exchangeable cations (Ca^{2+}, K^+ and Mg^{2+}) in biochar also contribute for the increment of soil CEC (Sohi et al., 2010).

5.2.Effect of biochar on soil dissolved organic carbon content

Biochar significantly decreased DOC content in ten experimental soils, the decline ranged up to 88% at the 8% of biochar application rate. More conclusively, the increment in the production temperature of biochar is expected to reduce the content of DOC in the biochar (Liu et al., 2019). The high temperature biochar used in this study (700 °C) is also expected to have high micropore surface area due to the opening of biomass surface due to the degradation of biomass volatile matter (Bagreev et al., 2001) and this facilitate surface adsorption of soil DOC by biochar. In addition to the production temperature, the biochar that is milled to 2 mm could expose more micropores to the adsorption of more DOC by biochar (Kasozi et al., 2010). The role of physical modification (milling) of biochar to the sorption properties of biochar was confirmed (Fahmi et al., 2018). For example, based on their findings the finest biochar (<50 μm) had better adsorption capacity than both medium (0.25–0.5 mm) and coarse textured (>2 mm) biochar. Thus, the highest production temperature of biochar could potentially reduce biochar originated DOC and the physical modification of biochar by milling and/or washing with water could enable biochar to adsorb more soil originated DOC and further contribute for the effective carbon sequestration. The biochar originated DOC also expected to decline once added to the soil due to the formation of complex between the functional groups (carboxylic, phenolic and hydroxyl) of biochar DOC with soil trace elements forming stable ring structures hereafter reducing DOC.

5.3.Effect of biochar on soil nutrients

5.3.1. Soil nitrate nitrogen and ammonium nitrogen

The output of our study clearly demonstrated the ability of high temperature produced (700 °C) biochar to reduce the leaching of nitrate from soil. The content of soil nitrate reduced in all ten investigated soils following the application of biochar. The decline was higher at the higher rate of biochar application. For example, the addition of 8% biochar was able to decrease soil original nitrate content up to 81%. The results assure the possible use of high temperature produced biochar to prevent nitrate loss from soils. These results are in agreement with the findings of many other studies (Martos et al., 2020; Jiang et al., 2020; Qin et al., 2020; Horák et al., 2020; Aghoghovwia et al. (2020); Sika and Hardie 2014; Xu et al. 2016). The adsorption capacity of biochar used in the study was confirmed by separate adsorption experiment. This experiment estimated maximum $N - NO_3^-$ adsorption capacity of biochar as 11.3 mg of $N - NO_3^-$ per g of biochar according to the Langmuir model. The nitrate adsorption capacity of biochar used in this study is clearly higher than ammonium adsorption. This is due to the elevated biochar production temperature (700 °C) resulting in the release or degradations of O-carrying negatively charged functional groups ($-COO^-$, -COH and -OH), which are responsible for the sorption of ammonium. In the case of ammonium, even if, the maximum $N - NH_4^+$ adsorption capacity of biochar from pure NH_4NO_3 solution is estimated up to 6.6 mg of $N - NH_4^+$ per g of biochar, this adsorption of ammonium was not in agreement with the change of $N - NH_4^+$ in soils. This is mainly due to the very low content of ammonium in soil solution and difference in soil chemistry. The major factors controlling the amount of nitrate decline in soils after the addition of biochar was soil organic carbon content, total nitrogen and carbon content, CEC and the relative ratio of silt+clay and sand. The higher the content of soil organic carbon, total nitrogen and carbon, CEC and the percentage of silt+clay fraction resulted in the lower amount of nitrate decline while the higher the content of sand fraction resulted in the higher decline of nitrate. The details are summarized on Fig 6. The higher nitrate sorption capacity of high temperature biochar (800 °C) than lower temperature produced biochar (400 and 600 °C) is also reported by Kameyama et al. (2012). The mechanisms behind all those soil factors in controlling biochar induced nitrate reduction role is well described in the article under chapter 4.1 of this dissertation work. Thus, the overall finding suggests the possible use of high temperature produced biochar for the control of nitrate loss and therefore increase crop production by improving nitrogen use efficiency.

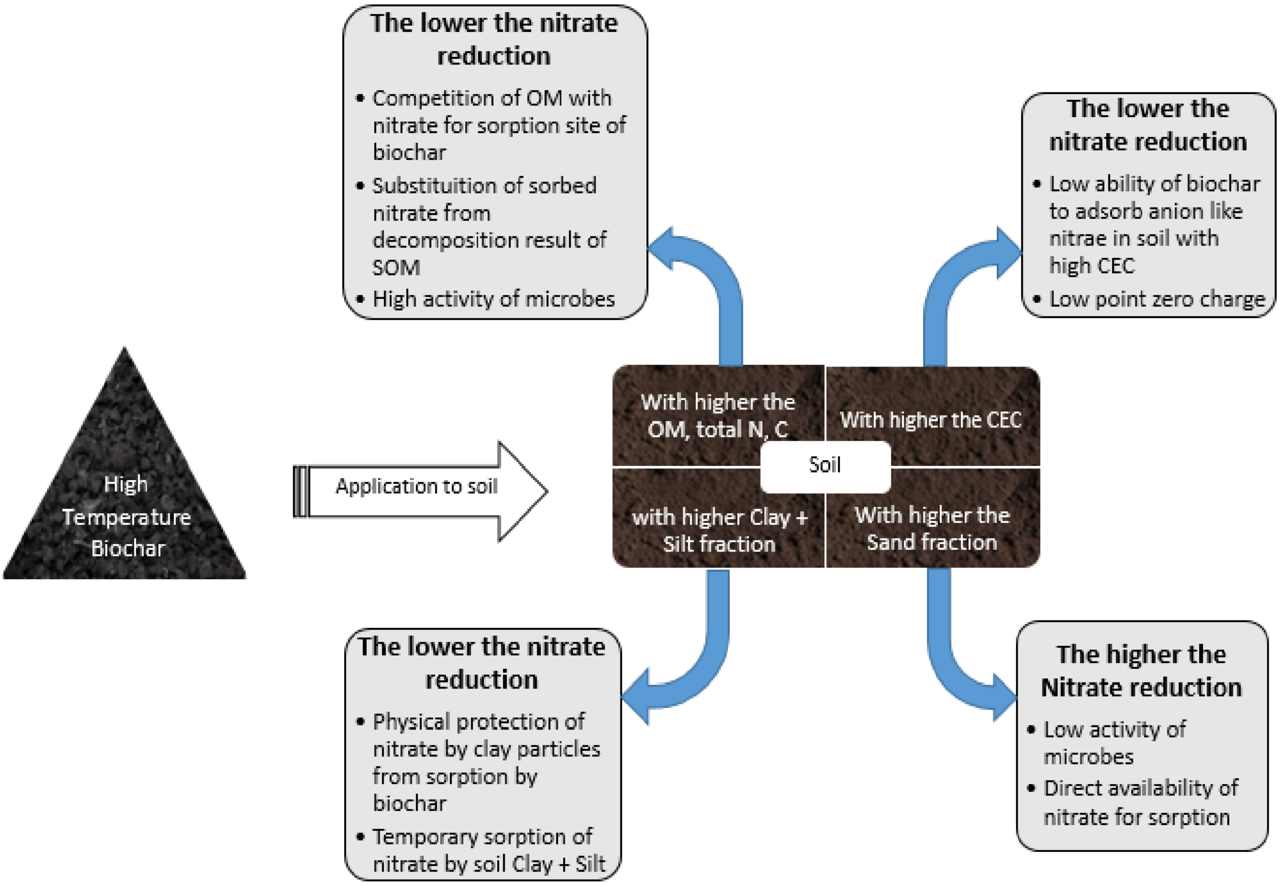

Figure 6. The effect of high temperature produced biochar on soil inorganic N.

5.3.2. Exchangeable cations

The effect of biochar on the exchangeable Ca^{2+} content of soils were quit similar with that of soil CEC. The application of biochar increased exchangeable Ca^{2+} content in seven soils, which have lower original exchangeable Ca^{2+} than the content in the biochar. However, a decline in the exchangeable Ca^{2+} content was evident in three soils with highe original exchangeable Ca^{2+} content than the content in biochar. The increment of exchangeable Ca^{2+} in soils after the addition of biochar to soils could be expected due to considerably higher content of Ca in the biochar (Cornelissen et al., 2018; Al-Wabel et al., 2018). Biochar was able increase soil exchangeable K^+ content in all ten soils. This is mainly due to the direct release of exchangeable K^+ from biochar, having much higher exchangeable K^+ content than all incubated soils. Soil type and the rate of biochar greatly determined the amount of increment. The highest increment in exchangeable K^+ was at higher biochar addition rate and in soils with the lower original exchangeable K^+ content. The increment of soil exchangeable K^+ after the addition of biochar is in agreement with several studies (El-Naggar et al., 2018; Gaskin et al., 2010; Kongthod et al., 2015), due to the release of K^+ from amended biochar to the soil solution. The effect of biochar on the exchangeable Mg^{2+} content of soils was significant only in two soils with very low original exchangeable Mg^{2+} content. This result could be very indicative that biochar could serve as a source of Mg, only when the original content is very low. The increment of soil Mg content was also reported by the study of Gaskin et al. (2010), where the application of peanut hull and pine chip increased soil Mg content. Generally high temperature biochar can be used as a soil conditioner to increase soil pH, CEC and exchangeable cations (Ca^{2+} and K^+) playing a great role in the improvement of soil properties and subsequent effect on crop yield could be expected.

5.4.Effect of biochar on the availability of potentially risk elements in soil

The application of high temperature biochar decreased available content of Al, Zn, Cu, Mn and Cd in soils. Especially the addition of 8% biochar significantly decreased the available content of elements in all soils except Al in one soil. The biochar induced decline in all the investigated elements was always related to the increment of soil pH, CEC, DOC, and the exchangeable Ca^{2+} and K^+ content. Biochar is able to increase soil pH due to its considerable content of ash and alkaline material (Ca^{2+}, K^+). The increment of soil pH by biochar can result in the increase of Al, Zn, Cu, Mn and Cd adsorption. This is due to the pH dependence of soil adsorption sites such as organic matter, carbonates, and surface of clay minerals and their preferential adsorption properties of hydrolyzed metal species, which increases with pH than free metal ions (McLean and Bledsoe, 1992). For example, the strong pH dependence of biochar induced decline in the extractable content of metals especially Cd and Zn (Jing et al. 2020; Yang et al., 2019) have been confirmed. The reason for the decline of both Zn and Cd was proposed due to the liming potential of added biochar and further facilitated adsorption by biochar. There was exceptional increase of available Al in one soil with very low original available Al content. The main reason for the increment of Al in this soil was due to the neutral original pH, which is further increased by the addition of biochar above 6.5. The main mechanisms responsible for the decline of metals after biochar addition to soils are: - 1) The formation complex with the functional groups (carboxylic, phenolic and hydroxyl) of DOC forming stable ring structures on the functional groups of DOC, 2) Exchange to the exchangeable sites of biochar by the exchangeable Ca^{2+} and K^+ content of biochar, 3) Electrostatic interaction between the positively charged metals and the negatively charged biochar, 4) Precipitation with the carbonate and phosphate content of soils and biochar at the higher pH induced by biochar (Li et al., 2017). Consequently, the above all mechanism could have played the role in the reduction of metals in our study. This is due to the reason that in one way or another some evidence have shown on our study. Firstly, soil DOC declined in all soils indicating the possible complexation of metals with the functional groups (carboxylic, phenolic and hydroxyl) of DOC forming stable ring structures on the functional groups of DOC. Secondly, the exchangeable K^+ content increased in all soils and exchangeable Ca^{2+} in most soils, this supporting the mechanism that the exchangeable K^+ and Ca^{2+} of biochar being replaced by the metals. Thus, the above result supports the possible use of high temperature produced wood biochar to reduce the mobility of metals in soil. Therefore, their toxicity to crops could be greatly reduced improving crop yield, their uptake by plant limited and will have very narrow chance to inter human food chain.

5.5. Effect of biochar co-application with stabilized ammonium sulfate

5.5.1. Maize biomass yield and nitrogen use efficiency

Biochar was able to induce a significant increment of maize biomass when co-applied with stabilized ammonium sulfate, while this effect has not shown in un-stabilized ammonium sulfate treatments. The increment of maize biomass was as much as 10%, when 2 % biochar co-applied with stabilized ammonium sulfate. Increment of maize biomass was in line with the increment of N uptake and improved nitrogen use efficiency (NUE). Thus, the increment of maize biomass was because of improved NUE. The application of biochar with stabilized ammonium sulfate induced up to 34% increase in N uptake and 14% increase in NUE, while up to 27% increment in N uptake and 11% of NUE when combined with un-stabilized ammonium sulfate. The possible use of biochar with N fertilizer as a slow N releasing fertilizer has been recommended (Aghoghovwia et al., 2020). This recommendation is due to the potential of biochar to increase NUE efficiency have been reported in very recent study (Xia et al., 2020; Liao et al., 2020; Ibrahim et al., 2020; Omara et al., 2020). The retention of nitrate by biochar from leaching, ammonia from volatilization increases the NUE, therefore improvement of crop growth yield is expected. Further, the better interaction effect of biochar with the stabilized ammonium sulfate on maize biomass and NUE were evident in the acidic soil (pH = 4.8), low CEC (74.9 mmol kg^{-1}) and higher content of sand fraction (26.1%) than neutral soil (pH = 6.9), higher CEC (249.3 mmol kg^{-1}) and relatively lower sand fraction (13.2%). This was attributed due to the higher efficacy of (3,4-dimethylpyrazole-phosphate) DMPP to reduce the oxidation of NH_4^+ in soils with low pH and low clay content. Soils with higher content of sand fraction is expected to have lower adsorption of DMPP, as a result high efficiency is expected and this is further extended by biochar (Barth et al., 2001; Guardia et al., 2018). The higher yield response of sandy, acidic and low CEC soils to the addition of biochar have been widely discussed in the review work of Ye et al. (2020). The general better co-interaction of biochar with the ammonium fertilizer to increase maize yield in the acidic, low pH and low CEC soil is due to the improved availability of nutrients, which is associated to the increment of soil pH, CEC and release of nutrients specially K, Ca and Mg.

5.5.2. The uptake of nutrients in relation to soil solution

Biochar was effective to increase the uptake of P and K, when combined with both stabilized and un-stabilized ammonium sulfate. The increment of P uptake in the stabilized ammonium sulfate was as much as 54% and up to 58% in the case of un-stabilized ammonium sulfate. The highest efficiency of biochar to increase P uptake was found in soils having relatively higher available P content. Overall, single application of biochar was not able to induce any significant improvement of P uptake, as there was no detectable available P content in the applied biochar. The improvement of P uptake in both ammonium sulfate (stabilized and un-stabilized) could be mainly linked to the biochar induced reduced adsorption of phosphate anions ($H_2PO_4^-$,

HPO_4^{2-} or PO_4^{3-}) by the Al/Fe (hydr)oxides present in soils and due to the increment in the repulsion of phosphate by soil surface (Baquy et al., 2020). Biochar could potentially adsorb the (hydr)oxides of Al/Fe and the subsequent reduction in the adsorption of phosphate could be expected (Jiang et al., 2015). In the case of K, biochar was able to increase uptake significantly with fertilizer as well as without fertilizer. The increment of K uptake was in relation to the increment of available K content in the soil solution. The increase of K in the biochar amended treatments is expected due to the much higher content of available K in the biochar applied than the original soil used. The significant amount of K in biochar and the uptake after subsequent release to the soil solution is in agreement with previous findings (Wang et al., 2018: Syuhada et al., 2016). When we come to the uptake of Ca, Mg and S, biochar induced quiet opposite effect to that of K. The single application of biochar and its co-application with both stabilized and un-stabilized ammonium sulfate significantly decreased the uptake of Ca and Mg. The decline is directly associated to the antagonistic effect of preferential K uptake. Similarly, the application of biochar with stabilized and un-stabilized ammonium sulfate decreased the uptake of S. The decline of the uptake was in relation to the decline of S content in soil solution induced by biochar addition. This could be mainly linked to the precipitation of S with Ca released from biochar and changed to less soluble $CaSO_4$ (Zhao et al., 2019) or direct sorption of SO_4^- by biochar (B. Zhao et al., 2017).

6. Conclusion

The wide benefit of biochar from potentially mitigating global warming, reducing the contamination effect of bio-waste to the improvement of degraded soils could essentially increase the production of biochar in the near future. Consequently, the extensive production of biochar could result in making agricultural field as a random dumping site of biochar. Thus, incautious application of biochar to soil could result in unintended result. Hence, this work aimed to determine the effect of soil properties on the biochar induced changes of soil pH, CEC and exchangeable cations (Ca^{2+}, K^+ and Mg^{2+}), to evaluate the efficiency of biochar in reducing the mobility of metals (Al, Cu, Zn, Mn, and Cd), to investigate the effect of biochar on soil NO_3^-, NH_4^+ and DOC. In addition, the interaction of biochar with nitrification inhibitors were studied. The objectives were achieved through the establishment of mass incubation experiment by including ten soils having wide physio-chemical properties. Furthermore, pot experiment was established for the investigation of biochar interaction with N fertilizer.

In agreement with the articulated hypothesis, effect of biochar on soil pH, CEC and exchangeable cations (Ca^{2+}, K^+ and Mg^{2+}) is clearly dependent on soil specific properties. High temperature biochar increased soil pH in all ten incubated soils. The most prominent factor affecting the amount of pH increment after biochar addition was the original soil pH. Biochar has the ability to induce higher pH increment in soils with lower original pH and lower increment in soil with higher original pH. The effect of biochar on CEC and exchangeable Ca^{2+} of the ten soils were opposing each other and it was mainly dependent on the original exchangeable Ca^{2+} content of soils. Thus, biochar increased both CEC and exchangeable Ca^{2+} content in seven soils having lower original exchangeable Ca^{2+} content, while decreasing both CEC and exchangeable Ca^{2+} content in three soils having higher original exchangeable Ca^{2+} content than the content in the amended biochar. This inferring the ability of biochar to increase soil CEC and the exchangeable Ca^{2+} content of soils depends on the relative content of original exchangeable Ca^{2+} in the soil and biochar. On the other hand, biochar was able to increase soil exchangeable K^+ content of all ten soils regardless of the soil type.

Moreover, application of biochar to soil clearly affected the content of soil NO_3^-, NH_4^+ and DOC. The result revealed the undoubtable role of biochar as a mechanism to reduce N loss was very promising as the application of biochar decreased soil N – NO_3^- content in all ten incubated soils, the decline ranging up to 81% at 8% of biochar application rate, while the effect of on soil N – NH_4^+ content was mostly inconsistent. The capability of biochar to adsorb N – NO_3^- was evident from the side adsorption experiment, where biochar adsorbed up to 11 mg of N – NO_3^- and up to 6 mg of N – NH_4^+ per g of added biochar from NH_4NO_3 solution. Therefore, the possible use of high temperature as a mechanism of reducing N loos is an arguably assured. Similar to that of N – NO_3^- , biochar was able to reduce DOC content of all ten soils regardless of their original properties. The decline of DOC ranging up to 88% at the biochar application rate of 8%. The potential of reducing DOC has increased with the increment of biochar application rate and this again could assure the carbon sequestration potential of high temperature biochar.

Further, biochar reduced the mobility of metals (Al, Cu, Zn, Mn, and Cd) in soils and the efficiency varied per specific soil properties. Among the metals, Al was exception as there was an increment of soluble Al in one soil with very lower original content of Al, neutral soil pH and higher CEC. Moreover, the decline of all the metals have been induced through the biochar induced in the increment of soil pH, CEC, and the exchangeable Ca^{2+} and K^+ content of soils.

Additionally, co-application of biochar with nitrification inhibitors treated ammonium sulfate in soils increased crop yield, the uptake of N and K by maize. The better interaction of biochar with nitrification inhibitors treated ammonium sulfate is more evident to increase maize yield and NUE than biochar co-application with un-treated ammonium sulfate fertilizer. Furthermore, biochar is more efficient to increase maize yield and NUE in poor acidic soil than slightly fertile neutral soil. The better performance of biochar was evident when co-applied in the low fertile acidic soil than the slightly fertile neutral soil. The positive effect of biochar to increase the uptake of K is always parallel with the antagonistic effect on the uptake of Ca and Mg, thus it has to be taken into consideration.

Generally, biochar could be used to increase soil pH, CEC, exchangeable cations (mainly Ca^{2+} and K^+), to reduce the losses of inorganic N from soil, efficiently sequester carbon and to increase the efficiency of nitrification inhibitors. However, thus all advantage of biochar is highly depending on the original properties of soils and biochar application rate.

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