



Influence of biochar produced from different pyrolysis temperature on nutrient retention and leaching

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ABSTRACT

Biochar application has been received much attention because biochar can improve the fertilizer utilization efficiency of soil. However, the effect of biochar produced at different temperature on the nutrient retention and leaching remains poorly understood. In this study, we observed the nutrients leaching from a sandy loam soil amended with biochar produced at different temperature. The properties of biochars produced from wheat straw at four contrasting pyrolysis temperatures (250, 350, 450, and 550°C) showed that increasing pyrolysis temperature increased pH value and specific surface area but reduced the electrical conductivity and cation exchange capacity. With the temperature increased, the nitrogen loss was significant decreased ($p > 0.05$) from 109.6 mg to 53.3 mg in biochar amended soil. However, dissolved organic carbon (DOC), available P, Na and K were significant increased ($p > 0.05$). These results demonstrate that the pyrolytic temperature has a great influence on biochar properties, which in turn affect the leaching of the available nutrients.

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Introduction

Excessive application of fertilizers to arable land has caused various ecological problems (Yu et al. 2007), such as nutrient leaching (nitrogen, phosphorus or dissolved organic carbon), which is regarded as the primary source of surface and groundwater contamination and has become a worldwide environmental concern (Ding et al. 2010; Yao et al. 2012). Leaching not only poses a threat to the surface and groundwater, but also causes the low nutrient-use efficiency in different field crops, which results in the increase of the fertilizers usage and costs for the farmers (Cheng et al. 2008). Therefore, it is crucial to develop effective technologies to keep applying nutrients in the topsoil and consequently increase its utilization efficiency (Ding et al. 2010). In general, either minimizing the use of fertilizer (Gentile et al. 2009) or amending the adsorption quality of soil (Lehmann et al. 2003) is regarded as a solution to reduce nutrient leaching. However, minimizing the use of fertilizer may decrease the crop productivity (Quiroga-Garza et al. 2001). Recently, biochar application was introduced as an alternative option to overcome this problem (Lehmann 2007).

Biochar is a charcoal, pyrolyzed from a wide range of carbon-rich biomass materials, such as crop and wood residues, animal manures and a range of industrial wastes (paper sludge and bio-solids) (Sohi et al. 2010); and once added into soil, it can store the soil carbon for a long period, improve the soil structure and increase the crop yield (Lehmann et al. 2006). Also, recent publications have highlighted that biochar application has the potential to improve the fertilizer utilization efficiency of soil by reducing nutrient leaching (Ding et al. 2010; Yao et al. 2012) or by directly

supplying nutrients to plants (Lehmann et al. 2003; Laird et al. 2010; Major et al. 2010). Owing to its large specific surface area (SSA), cation exchange capacity (CEC) and high pH value, biochar is considered as a good sorbent, which can adsorb nutrients and retain them in soil (Yao et al. 2012; Mukherjee and Zimmerman 2013). However, these benefits of biochar are directly related to their physicochemical properties, which mainly depend on the biochar feedstock and variations in the parameters, such as temperature, used in their production process (Spokas and Reicosky 2009; Singh et al. 2010; Zimmerman et al. 2011). The previous studies demonstrated that the change in pyrolytic temperature led to great variation in biochar properties which influence the sorption of biochar for pesticides (Zhang et al. 2011; Cheng et al. 2016; Chen et al. 2009) and the emission of CO₂ and N₂O from the soil amended with biochar (Wang et al. 2013; Yuan et al. 2014). These studies clarify that the pyrolytic temperature has a direct influence on the benefits introduced by biochar amendment. However, the data relating to influence of pyrolytic temperature on nutrient leaching are still limited. Therefore, the aim of this study was to investigate the influence of the pyrolytic temperature on the physicochemical properties of biochar derived from wheat straw, as well as to evaluate the amount of nutrient leaching from a sandy clay loam soil amended with biochars produced at different temperatures.

Materials and methods

Studied soil

Soil was collected at the Henfaes Research Centre from the Ah horizon (0–15 cm, sandy loam) of a freely draining, grassland soil (Eutric Cambisol), which receives regular fertilization (120 kg N, 60 kg K and 10 kg P annually). This site is used for both grassland and arable production and is characterized by a mean annual temperature of 11°C (range –5 to 25°C) and mean annual rainfall of 1060 mm (temperate climate regime).

The sampled soil was sieved to pass 5 mm sieve for removing plant residues and stones and then dried at 20°C prior to use. The major properties of the soil are shown in Table 1, and additional properties are given in Jones et al. (2011), (2012) and Farrar et al. (2012).

Biochar production

Wheat straw was collected from Henfaes Research Centre, Wales, North Wales (53°14' N, 4°10' W). After the wheat straw was dried in an oven at 80°C for 24 hours, it was cut into 10 cm chips, loaded into a beaker, and covered with a Duran crystallizing dish. Next, the beaker was placed in a muffle furnace for pyrolysis. The rate of heating was 20°C min⁻¹, and the holding time was 1 h. Four peak pyrolytic temperatures were used (250, 350, 450, and 550°C), and the corresponding biochars were named B₂₅₀, B₃₅₀, B₄₅₀, and B₅₅₀, respectively.

Table 1. Soil and wheat characteristics.

	Soil	Straw
pH	6.4 ± 0.0	6.4 ± 0.2
EC (μs cm ⁻¹)	40.9 ± 0.9	1026 ± 47
Total C (g kg ⁻¹)	21.6 ± 1.9	422.5 ± 0.7
Total N (g kg ⁻¹)	2.6 ± 0.1	5.5 ± 0.1
DOC (mg C kg ⁻¹)	99.1 ± 1.9	1666 ± 129
P (mg P kg ⁻¹)	3.92 ± 0.2	67.8 ± 1.7
K (mg K kg ⁻¹)	77.1 ± 13.1	7816 ± 35
Ca (mg Ca kg ⁻¹)	734.6 ± 9.5	4524 ± 273
Na (mg Na kg ⁻¹)	30.4 ± 2.2	150.3 ± 2.0
NO ₃ ⁻ -N (mg N kg ⁻¹)	10.0 ± 0.4	0.7 ± 0.1
NH ₄ ⁺ -N (mg N kg ⁻¹)	4.7 ± 0.4	14.8 ± 0.9

Values represent means ± SEM (n = 4).

Biochar yield

Biochar yield was calculated according to the amount of feedstock and biochar:

$$\text{Yield} = M_b/M_f \times \% \quad (1)$$

Where M_b is the amount of biochar and M_f is the amount of feedstock.

Biochar analysis

The ash content of wheat straw and biochar was measured after the samples were heated at 575°C in a muffle furnace for 3 h (Monti et al. 2008). pH value and electrical conductivity (EC) (1:20 w/v in distilled water) were determined using standard probes for pH and EC. Water holding capacity (WHC) was measured using the international standard method ISO16378. Briefly, about 2.0 g biochar or straw was saturated in the distilled water for 4 h, and then placed on the moist sand for 2 h, afterward, samples were heated in the oven (105°C) for 24 h, and the residues were weighed for calculating WHC. Cations exchange capacity (CEC) of the biochars or straw was measured using a modified NH_4 -acetate compulsory displacement method (Gaskin et al. 2008). Briefly, 0.2 g biochar or 0.5 g straw was soaked with 20 mL deionized water, shaken, and centrifuged, followed by the decantation of the supernatant. This process was repeated five times to remove interference soluble salts. Afterward, 20 mL of Na-acetate (1M, pH 7) was added to the sample prior to centrifugation at 2500 rpm for 10 min and the following decantation of the supernatant. This process was again repeated five times to ensure the exchange site was saturated with Na ions. Afterward, the sample was washed with 20 mL ethanol and centrifuged and the supernatant was again decanted. By repeating this process five times, the excess Na ions were removed. Finally, Na ions were displaced with NH_4 -acetate (pH 7) and measured by a flame photometer (Model 410; Sherwood Scientific Ltd, Cambridge, UK). Specific surface area (SSA) of biochar or straw was measured on a surface area analyzer (Autosorbi/monosorb, Quantachrome, USA) with nitrogen absorption at 77 K using the Brunauer–Emmett–teller (BET) method.

Leaching experiment

The experiment had five main treatments: 1) un-amended soil (Control); 2) B_{250} amended soil; 3) B_{350} amended soil; 4) B_{450} amended soil and 5) B_{550} amended soil. Biochar was added into soil at the soil-to-biochar ratio of 10:1. All treatments were performed in quadruplicate. Each treatment pot [12.8 x 12.8 x 11.0 cm (w, l, h)] was watered with the distilled water that was gradually added until the leachate appeared, and incubated in a constant temperature room (10°C and 80% relative humidity). Based on the rainfall data from the field area, an average of 35 mL of distilled water was added into each soil pot per day. The incubation observation period was divided into two parts; before and after fertilizer application. During the first part (four weeks), the leachate was collected at day 1, 3, 5, 7, 10, 14, 17, 21, 28. After collecting the sample at day 28, the fertilizer which was made by dissolving ammonium nitrate (NH_4NO_3) and potassium phosphate dibasic anhydrous (K_2HPO_4 and KH_2PO_4) with the concentration of 80 mg kg^{-1} , 30 mg kg^{-1} and 45 mg kg^{-1} for N, P and K respectively was added and the leachate was collected at day 29, 31, 33, 35, 38, 42, 45, 49, 56. All leachate samples were analyzed at once.

Leachate analyses

Dissolved organic carbon (DOC) and dissolved nitrogen (DN) in the leachate were analyzed via the multi N/C total organic carbon measurement instrument (Analytik Jena, model 2100/2100 S). Dissolved organic nitrogen (DON) was calculated according to the results of DN, NH_4^+ -N and NO_3^- -N. Available NO_3^- -N and NH_4^+ -N were determined with the colorimetric methods of

Mulvaney (1996) and Miranda et al. (2001). The available P in the leachate were measured with the method of Murphy and Riley (1962) and the Na, K and Ca in the leachate were analyzed with a flame photometer (Model 410). These indicators in soil and biochar/straw were also analyzed with above methods after extracted with 0.5 M K_2SO_4 or 0.5 M Acetic acid.

Statistical analysis

Statistical procedures were carried out with the software package SPSS 19.0 for Windows (SPSS Inc., Chicago, IL, USA). All measurements were reported as mean values with standard error mean. The one-way analysis of variance (ANOVA) followed by the Least Significance Difference (LSD) test was used to test for significant differences between treatments, with a significant cut off value of 95%.

Results

Biochar characterization

With the increase pyrolytic temperature, pH value of the biochar increased from 5.4 to 9.7 (Table 2) and the biochar yield decreased from 47.4 to 30.8% (Table 2). SSA of biochar increased from 2.7 to 10.5 $m^2 g^{-1}$ with the increase temperature, whereas CEC and EC decreased from 68.7 to 22.0 $cmol kg^{-1}$ and from 3.4 to 1.3 $ms cm^{-1}$ (Table 2).

The carbon composition of biochar increased significantly from 555.7 to 691.8 $g kg^{-1}$ with the increase pyrolytic temperature from 250 to 550°C (Table 2). The amount of the cations K, P and Ca increased with the increase temperature, whereas Na and NH_4^+ -N concentrations showed no trend in variation with the changing temperature (Table 2).

Nitrogen leaching

Over the duration of the experiment, the accumulate NO_3^- -N in the leachate from the control treatment was 74.04 mg which was significant higher ($p > 0.05$) than those in the leachate from the soil amended with biochar (Figure 1(a)). Among soil receiving biochar treatment, the NO_3^- -N leaching significantly decreased ($p > 0.05$) with the increase pyrolytic temperature (Figure 1(a)). The accumulate NH_4^+ -N in the leachate from the control treatment was 11.08 mg, which was significant higher ($p > 0.05$) than those in the biochar amended soil (Figure 1(b)). However, the accumulate NH_4^+ -N in leachate was increased with the increase pyrolytic temperatures among biochar amended soil (Figure 1(b)). In

Table 2. Physical and chemical properties of biochar pyrolyzed at 250 °C (B₂₅₀), 350 °C (B₃₅₀), 450 °C (B₄₅₀) and 550 °C (B₅₅₀).

	B ₂₅₀	B ₃₅₀	B ₄₅₀	B ₅₅₀
Yield (%)	47.4 ± 0.8a	37.7 ± 0.4b	33.6 ± 0.3c	30.8 ± 0.3d
pH	5.4 ± 0.1d	8.8 ± 0.1c	9.2 ± 0.1b	9.7 ± 0.2a
EC ($ms cm^{-1}$)	3.4 ± 0.1a	1.8 ± 0.2b	1.4 ± 0.0c	1.2 ± 0.1d
SSA ($m^2 g^{-1}$)	2.7 ± 0.0d	5.2 ± 0.0b	4.6 ± 0.0c	10.5 ± 0.0a
CEC ($cmol/kg$)	68.7 ± 0.5a	58.6 ± 1.7b	40.5 ± 1.2c	22.0 ± 1.3d
Total C ($g kg^{-1}$)	555.7 ± 3.2d	584.0 ± 4.0c	666.5 ± 7.6b	691.8 ± 4.2a
Total N ($g kg^{-1}$)	9.8 ± 0.4b	10.3 ± 0.2a	10.6 ± 0.4a	10.2 ± 0.2a
DOC ($g C kg^{-1}$)	1.4 ± 0.1b	2.0 ± 0.1a	1.0 ± 0.0c	0.6 ± 0.1d
P ($g P kg^{-1}$)	0.1 ± 0.0c	0.3 ± 0.0a	0.2 ± 0.0b	0.1 ± 0.0c
K ($g K kg^{-1}$)	15.1 ± 0.7b	21.2 ± 1.5a	20.2 ± 0.9a	21.0 ± 0.9a
Ca ($g Ca kg^{-1}$)	8.9 ± 0.3d	12.8 ± 0.1b	11.4 ± 0.9c	14.6 ± 0.6a
Na ($mg Na kg^{-1}$)	365.8 ± 16.7b	402.7 ± 12.5a	347.8 ± 34.5b	262.8 ± 5.0c
NO_3^- -N ($mg N kg^{-1}$)	0.00	0.00	0.00	0.00
NH_4^+ -N ($mg N kg^{-1}$)	5.48 ± 0.4b	5.38 ± 0.7b	3.67 ± 0.6a	5.04 ± 1.2ab

EC denotes electrical conductivity; SSA denotes specific surface area; CEC denotes cation exchange capacity and TOC denotes total organic carbon. All values represent means ± SEM ($n = 4$, except for the carbonization rate which was calculated 10 times). Different letters (a, b, c and d) represent significant differences between treatments at the $P < 0.05$ level.

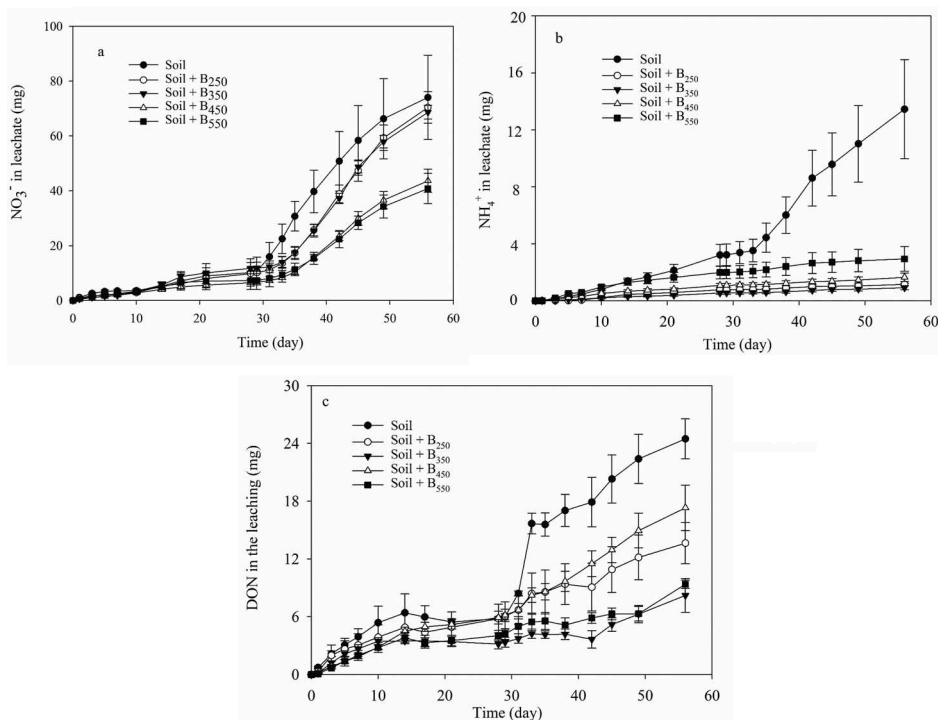


Figure 1. Nitrogen and dissolved organic carbon in the leachate collected: (a) NO_3^- -N; (b) NH_4^+ -N; (c) DON. The mean of four replicates \pm SEM are presented.

contrast, a significant decrease ($p > 0.05$) in DON leaching was found for soil containing biochar, and the extent of the decrease was not uniform (Figure 1(d)).

Dissolved organic carbon leaching

Compared to untreated soil treatment, more DOC was lost in soil containing biochar B₂₅₀ or B₃₅₀, but no significant difference ($P > 0.05$) was observed for soil containing biochar B₄₅₀ or B₅₅₀ (Figure 2(a)). Furthermore, DOC loss decreased with the increase pyrolytic temperature. However, DOC loss to DOC total (%) were the similar except of the treatment B₂₅₀.

Nutrients leaching

Leaching of the cumulative nutrient elements K, Na, P and Ca are influenced differently through biochar amendment (Figure 3). In the Figure 3(a,e), the accumulate loss K and K loss to K total (%) both showed biochar amendment increased K loss. In the Figure 3(b,f), the accumulate loss Na showed biochar amendment increased the loss of Na, however, Na loss to Na total demonstrated that only in the treatment B₅₅₀ more Na was lost than in the un-amended soil (Figure 3(f)). As for P, the accumulate loss showed biochar amendment increased the loss of P (Figure 3(d)), but P loss to P total (%) showed more P loss only appeared in the treatment B₂₅₀ and B₅₅₀ (Figure 3(g)). In the Figure 3(d,h), less Ca loss ($P > 0.05$) were observed in biochar amendment soil. And among in biochar amendment soil, the loss Ca increased with the decrease of pyrolysis temperature. However, there is a stranger phenomenon that most of Ca loss in the unamend soil was happened after the fertilizer adding.

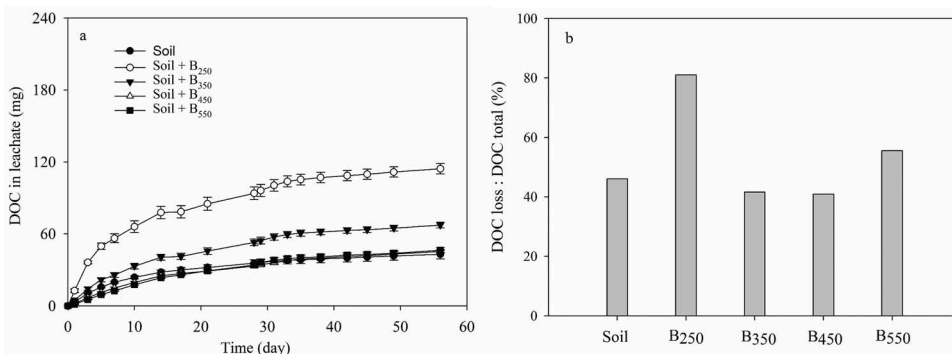


Figure 2. DOC in the leachate collected from different treatments: (a) DOC in the leachate (the mean of four replicates \pm SEM is presented); (b) ratio DOC loss/DOC total.

Discussion

Effect of pyrolysis temperature on biochar characteristics

The pyrolysis process affects the composition and structure of the biochar (Al-Wabel et al. 2013; Méndez et al. 2013; Yuan et al. 2014) also observed in this study, With the increase pyrolytic temperature, more volatile components were lost, resulting in the decrease biochar yield (Novak et al. 2009). Lehmann and Joseph (2009) considered that it is common for thermally pyrolysis biochars to be alkaline, and most biochar pH results were consistent with this point, except of B₂₅₀, which probably still contained some organic acid produced during the pyrolysis process. In this study, the increase pyrolytic temperature lead to the increase SSA and the decrease CEC that is consistent with the results of several previous studies (Al-Wabel et al. 2013; Méndez et al. 2013; Yuan et al. 2014).

Effect of biochar on nitrogen leaching

The data in our experiment support the hypothesis that biochar application decreases N loss from the leaching. However, this effect extent is depending on the biochar properties. In this study, the SSA and WHC increased with the increase pyrolytic temperature indicated the biochar sorption capacity increases with the increase pyrolytic temperature. This viewpoint was confirmed in the experiment that After the biochar amendment, a significant decrease ($P > 0.05$) in the NO_3^- -N leaching after the biochar amendment. Previous studies have also shown biochar amendment decrease NO_3^- -N leaching because of the change in the soil anion retention capacity and nitrification (Dempster et al. 2012a; Knowles et al. 2011). Furthermore, the addition of biochar to the soil is known to decrease N mineralization and nitrification (Dempster et al. 2012b) that may play another important role in leaching of NO_3^- -N during the experiments. The NH_4^+ -N leaching were significantly lower ($P > 0.05$) in the biochar amended soil. This is supported by previous studies that demonstrated that biochar amendments can decrease NH_4^+ -N leaching (Dempster et al. 2012a; Lehmann et al. 2003; Ding et al. 2010), and that attributed this decreasing to the increase nutrient and water retention capacities of the soil (Lehmann et al. 2003). However, we found the increase NH_4^+ -N leaching with the increase pyrolytic temperature among the biochar amended treatments. We considered that the decrease in CEC of biochar with the increase pyrolytic temperatures is a reason for the change in NH_4^+ -N leaching. Although DON cannot directly be used by microbial, after transformation in freshwater by UV photolysis, DON still contributes significantly to eutrophication, therefore the N losses in the form of DON is considered to be a threat to the surface and the ground water (Murphy et al. 2000). In this study, biochar amendments decreased DON leaching which is inconsistent with the report of Dempster et al. (2012b). Even though most DON carries a

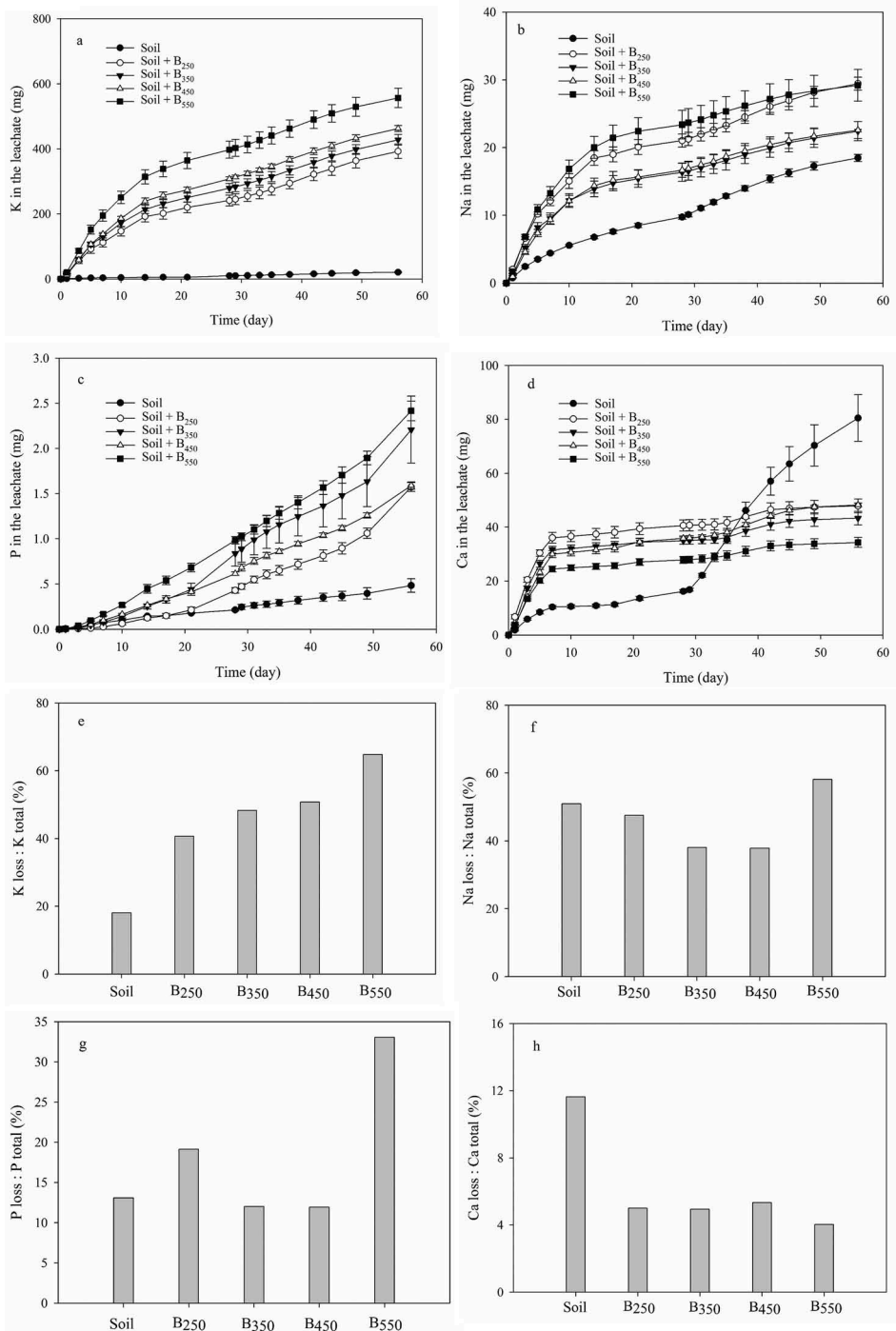


Figure 3. The nutrient elements (P, Ca, Na and K) in the leachate collected from different treatments: (a) K; (b) Na; (c) P; (d) Ca (the mean of four replicates \pm SEM is presented); (e) ratio K loss/K total; (f) ratio Na loss/Na total; (g) ratio P loss/P total; (h) ratio Ca loss/Ca total.

net negative charge, the discrepancy was still observed between the leaching of DON and NO_3^- -N, indicating different leaching mechanisms. Overall, biochar application decreases the loss of nitrogen in the leaching.

Effect of biochar on DOC leaching

Biochar application has been proposed worldwide as an effective measure to increase soil carbon sequestration (Steinbeiss et al. 2009; Whitman and Lehmann 2009). Once used as an amendment into a soil, biochar can directly supply the nutrient as fertilizer and indirectly increase nutrient use efficiency (Peng et al. 2011). In our experiments, the amount of DOC added to the soil decreased (Table 2) with the increase pyrolytic temperatures which is similar to the cumulative DOC leaching (Figure 2), indicating that more DOC is lost due to the addition of DOC. On the other hand, the SSA and the micro-porosity increased with the increase pyrolytic temperature (Table 2) indicating that adsorption of DOC by biochar increase with the increase pyrolytic temperatures. The discrepancy between the losses of DOC in pure soil and in the soil amended with different biochars demonstrates that at least some DOC was released from biochar. Therefore, the data suggests that a combination of release and adsorption of DOC by biochar controls the leaching mechanism of DOC from the soils.

Effect of biochar on nutrient leaching

Plenty evidences, support the fact that biochar can be used for soil amendment and to improve the retention of fertilizers and crop productivity which are attributable to the ability of biochar (Beesley et al. 2011; Lehmann et al. 2011). In our experiment, the cumulative loss of nutrient elements (K, P, Na; except Ca) in the leachate from the biochar amended soil was much higher compared to the unamend soil (Figure 3). This was the result of adding more nutrient elements (K, P, Na) into the soil through the application of biochar because these nutrient elements were at least partly mobile. In the Figure 3(e), we found the ratio of loss to total K in the unamend soil was significantly lower ($P > 0.05$) than in the biochar amendment soil indicated that in the biochar amendment soil, the increasing loss K was not only from biochar, it also accelerates the loss of K in soil. As for the Na and P, although the accumulate loss showed more loss in the biochar amendment soil, however, the ratio of loss to total demonstrated the increase Na and P in the biochar amendment soil just because of the Na and P in biochar. In addition, the comparison of the ratio of total Na, P and DOC indicated that the loss of Na and P may be due to the loss of DOC (Figure 2(b), Figure 3(f,g)). It is remarkable, that the application of fertilizer accelerated the Ca leaching in all treatments, indicating that an antagonistic effect may have taken place between Ca and N, P K.

This study shows that the pyrolysis temperature has a great influence on the physicochemical characteristics of biochar that is directly related to soil nutrient leaching and retention. As sandy clay loam soil is fertile and able to retain a part of the nutrients, the high-temperature biochars are recommended to be used, because they have an enhanced ability to reduce nitrogen leaching (Figure 1) and to increase the fertilizer-use efficiency. The use of low-temperature biochar is suggested for poor soils, especially hardened and impervious soils, because biochar could directly offer more fertilizer (Table 2) and can change the conditions to improve the fertilizer-use efficiency. In brief, biochar application is a potential method to reduce nutrient leaching and enhance fertilizer use efficiency, which will mitigate the risk of eutrophication, although the extent is depending on the biochar feedstock type, the soil, and the pyrolysis conditions. However, this suggestion is based on the data from the incubation experiments, and more evidence is needed from further experiments under different conditions or from field data.

Conclusion

In this study, we found that the increased pyrolytic temperatures caused an increase of biochar pH and specific surface area and an decrease of electrical conductivity, cation exchange capacity and biochar yield. The effects of biochar on nutrient leaching and retention in sandy clay loam soil vary with the biochar properties, which are affected by pyrolytic temperature. Enhancing pyrolytic

temperatures reduce nutrient leaching and improve the fertilizer use efficiency. Taken into account the discrepancy between the simulation tests carried out under indoor conditions and processes occurring under actual field conditions, further experiments need to perform focusing on the influences of feedstock and pyrolysis conditions on biochar properties before biochar used in a specific farm test.

Disclosure statement

No potential conflict of interest was reported by the authors.

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