Effect of biochar application method on nitrogen leaching and hydraulic conductivity in a silty clay soil

Shuailin Li, Yongwang Zhang, Weiming Yan, Zhoupeng Shangguan

Abstract

Biochar is anticipated to be an effective option for mitigating nitrogen (N) leaching and improving the hydraulic characteristics of soil, particularly sandy soil. However, little attention has been paid to understanding the effect of biochar on N leaching and hydraulic conductivity (K) in fine-textured soil. Additionally, whether different biochar application methods have different effects on N leaching and K remains unclear. Therefore, our objective in this study is to determine the effects of biochar with different application methods on nitrate/ammonium leaching and K in silty clay soil. The three biochar application patterns were as follows: A, biochar was mixed into 0–10 cm of surface soil; B, biochar was mixed into 10–20 cm of subsurface soil; and C, biochar was mixed evenly into 0–20 cm of plow layer soil. In addition, biochar was added at three rates, namely, 1%, 2% and 4% (mass ratios), and a soil column without biochar addition served as the control (CK). Our results demonstrated that the choice of biochar application method significantly influenced N leaching and soil K and balance between the soil K and N leaching, particularly for nitrate. Additionally, the leaching of N in silty clay soil occurred mainly in nitrate form. Compared with the CK, all 1% biochar treatments increased nitrate leaching (except 1% biochar treatments increased nitrate leaching (except C1%, which showed no differences from the CK) and tended to decrease K. However, all 4% biochar treatments increased nitrate leaching due to a high K. All 2% biochar treatments significantly reduced nitrate leaching by 8.3–17.0%, and 2% significantly increased the saturated hydraulic conductivity (Ka) of soil by 20.9%. Hence, the mixing of biochar at a rate of 2% into the subsurface soil effectively mitigated N leaching and increased K in silty clay soil. These findings could have some implications for the field application of biochar. For instance, the combination of subsurface biochar application with that of fertilizer to roots in orchards or with deep tillage in fields, which would mimic the B2% model, would yield multiple benefits, including lower costs.

1. Introduction

Water stress and nutrient deficits constitute the major constraints to primary production in arid and semiarid environments (Austin, 2011; Zand-Parsa et al., 2006). Nitrogen (N) fertilization is a common practice for achieving higher yields (Long et al., 2010; Malhi et al., 2012), but the performance of this practice still depends on the soil water status (Turner, 2004; Turner and Asseng, 2005; Zhong and Shangguan, 2014). Additionally, nitrate leaching is one of the main pathways through which N is lost from agricultural soils (Pratiwi et al., 2016), which results in not only a huge waste of resources but also serious environmental problems (Xu et al., 2016). Thus, technical solutions to mitigate N leaching and improve water status are needed.

Biochar, a solid, carbon-rich residue of biomass pyrolysis, has been proposed for carbon sequestration (Lehmann and Joseph, 2009; Woolf et al., 2010) and for improving soil productivity (Liu et al., 2016). Moreover, biochar has been heralded as a material that can prevent fertilizer leaching (Sun et al., 2015; Yoo et al., 2014) and increase both the hydraulic conductivity (K) and the water holding capacity of soil (Ajai et al., 2016; Karhu et al., 2011; Obia et al., 2016). The reduction in N leaching by biochar is most likely attributable to an increase in cation exchange capacity (CEC) and the physical retention of dissolved N (Sika and Hardie, 2014; Xu et al., 2016; Yoo et al., 2014). However, the effect of biochar on N leaching depends on the biochar application rate, the biochar type, the soil characteristics and the environmental conditions (Gao et al., 2016; Sorrenti and Toselli, 2016). Furthermore, biochar could affect the soil K (Barnes et al., 2014; Githinji, 2014; Masiello et al., 2015) and thus exert concomitant effects...
on the leaching of N, particularly in the form of soluble nitrate (Xu et al., 2016). Biochar may influence K by altering the soil porosity, pore shape, pore connectivity and tortuosity of the conducting soil pores (Castellini et al., 2015; Kameyama et al., 2012). The effect of biochar on K also varies with the type of biochar, soil texture and level of biochar use (Borchart et al., 2014; Mukherjee and Zimmerman, 2013). For example, Barnes et al. (2014) found that mesquite wood biochar amendment (10%; w/w) decreased the saturated hydraulic conductivity (Ksat) by 92% in sand and 67% in organic soil but increased the Ksat by 328% in clay-rich soil. Kameyama et al. (2012) reported that increases in the Ksat of clay soil were only obtained with higher-concentration bagasse biochar treatments (5–10%; w/w).

To date, little attention has been paid to the biochar-induced changes in both the nutrient leaching and K of fine-textured soil (Castellini et al., 2015), but previous studies have revealed that biochar appears to be effective for improving both the water status and the nutrient retention of sandy soils. For example, Novak et al. (2016) reported that pine chip biochar promoted water infiltration and increased water quality in a compacted subsoil layer of sandy soil. Haider et al. (2017) performed a four-year field experiment and found that wood chip biochar amendments significantly reduced nitrate leaching and improved the moisture content in sandy soil. Nevertheless, it is unclear whether biochar could both mitigate N leaching and increase K in fine-textured soil, and investigating this issue is essential for determining whether biochar can be used to improve soil quality in arid and semi-arid agriculture systems.

Furthermore, recent studies have reported that biochar application methods have significant effects on the hydraulic properties of soil due to the various structures in different soil layers and changes in soil porosity and continuity (Li et al., 2016; Liu et al., 2016). For example, Zhang et al. (2016) indicated that the placement of biochar in the middle layer of a sandy soil column significantly reduced the Ksat and increased the water retention of soil compared with the effects obtained with the uniform mixing of biochar in soil. Additionally, Li et al. (2016) found that the even mixing of 2% (w/w) biochar in the subsoil (10–20 cm) significantly enhanced the wetting front migration rate and the cumulative water infiltration amount in silty clay soil, but the uniform mixing of biochar into plow-layer soil (0–20 cm) significantly decreased the water infiltration amount. Similarly, other application methods in field conditions, such as top dressing or deep banding into the rhizosphere (Lehmann and Joseph, 2009), may also create heterogeneous soil structures that exert different effects on K compared with those obtained with uniform mixing (Liu et al., 2016). However, the effects of biochar application methods on N leaching and K are not well understood. Can we screen some appropriate biochar application methods that can optimize or balance the effects of biochar on N leaching and K in fine-textured soil?

As stated, we made the following hypothesis: (1) the addition of biochar to fine-textured soil may mitigate N leaching and affect K, but the effects depend on the application method, and (2) a high biochar addition rate may increase K and increase the leaching of N, especially as nitrate. The specific objectives of this research were the following: (1) to study the effects of methods of apple branch-based biochar on N leaching and K in silty clay soil, (2) to explore the relationships of N leaching and K under different biochar application methods, and (3) to identify an optimal biochar application method that can mitigate N leaching while increasing K in silty clay soil.

2. Materials and methods

2.1. Soil and biochar materials

This column-based study was conducted in a laboratory set up at the Institute of the State Key Laboratory of Soil Erosion and Dryland Farming on the Loess Plateau, Yangling, China. Bulk soil was collected from the 0- to-20-cm soil layer from Yangling (34°17′57″N, 108°04′06″E), air-dried and ground to pass through a 2-mm sieve. The soil contained 17% clay, 73% silt and 10% sand and was thus considered silty clay according to the U.S. Department of Agriculture (USDA) system. The soil characteristics were as follows: soil pH 7.36, 1.20 g cm⁻³ bulk density, 368.33 μS cm⁻¹ electrical conductivity (EC), 20.60 cmol kg⁻¹ CEC, 3.32 g kg⁻¹ total organic carbon, 0.47 g kg⁻¹ total N, 18.2 mg kg⁻¹ NO₃⁻, 15.90 mg kg⁻¹ NH₄⁺, and 1.27 mg kg⁻¹ Olsen-P.

Biochar derived from apple branches (Malus pumila Mill) was produced by YIXIN Bioenergy Technology Co., Ltd. (Yangling, Shaanxi, China) through slow pyrolysis using a dry distillation method without any input of protective gas (e.g., N₂) into the carbonization system. The furnace temperature was ramped from ambient room temperature to 450 °C at a rate of 30 °C/min and maintained at 450 °C for approximately 8 h. Finally, all biochar samples were crushed and ground to pass through a 2-mm sieve and then mixed thoroughly with soil, and the column was then filled with the soil mixture.

The physiochemical properties of the biochar are presented in Table 1, and the measurement methods have been described by Li et al. (2017). Briefly, the specific surface area of the biochar was tested using the Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1938), and the N adsorption-desorption isotherms at 77 K were measured using an automated gas adsorption analyzer (Micro ASAP2400, Micromeritics, USA) (Hansen et al., 2016). The pH of the biochar was measured in 1:2.5 (w/v) biochar/ Milli-Q water. The EC was determined in 1.5 (w/v; g cm⁻³) biochar-water mixtures. The CEC was determined through passive barium exchange with forced magnesium exchange (Suliman et al., 2016). The elemental C, N, H and O concentrations of the biochar were determined using an elemental analyzer (Flash 2000, Thermo Fisher, USA). The total contents of K, P, Na, Ca, Mg, Fe, Cu, Mn and Zn were measured using an inductively coupled plasma (ICP) optical spectrometer (Vista Axial, VARIAN Medical Systems, USA).

Additionally, scanning electron microscope images were obtained to visually display the variations in the pore surface structure of the biochar (Supplementary Fig. S1). The variability in the functional groups of the biochar was investigated by Fourier transform infrared spectroscopy analysis (Supplementary Fig. S2). The equipment and procedures used for SEM and FTIR were previously detailed by Li et al. (2017).

2.2. Treatments and preparation of the soil columns

The experiment was conducted using three biochar application patterns and three levels of biochar amendments for each pattern. The three biochar application patterns involved the application of biochar to the following soil layers: A, the surface layer of soil (0–10 cm); B, the

<table>
<thead>
<tr>
<th>Specific surface area (m² g⁻¹)</th>
<th>pH</th>
<th>CEC (emu kg⁻¹)</th>
<th>Total C (g kg⁻¹)</th>
<th>Total N (g kg⁻¹)</th>
<th>NO₃⁻ (mg kg⁻¹)</th>
<th>NH₄⁺ (mg kg⁻¹)</th>
<th>H (g kg⁻¹)</th>
<th>O (g kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.22</td>
<td></td>
<td>9.67</td>
<td>32.57</td>
<td>670.15</td>
<td>5.70</td>
<td>0.52</td>
<td>1.86</td>
<td>21.71</td>
</tr>
<tr>
<td>K</td>
<td>P</td>
<td>Na</td>
<td>Ca</td>
<td>Mg</td>
<td>Fe</td>
<td>Cu</td>
<td>Mn</td>
<td>Zn</td>
</tr>
<tr>
<td>6083.4</td>
<td>1802.1</td>
<td>639.2</td>
<td>24185.1</td>
<td>3196.5</td>
<td>5745.8</td>
<td>9.9</td>
<td>91.5</td>
<td>37.3</td>
</tr>
</tbody>
</table>

Note: The units of K, P, Na, Ca, Mg, Fe, Cu, Mn and Zn are mg kg⁻¹.
underlying soil (10–20 cm); and C, the plow layer of soil (0–20 cm) (Fig. 1). The three biochar amendment levels were 1%, 2% and 4% (mass ratios), and a soil column without added biochar was used as a control (CK). Ammonium nitrate (NH₄NO₃) granules were evenly incorporated into the upper 5 cm of all soil columns at a rate of 0.2 g kg⁻¹ to reach a value that was nearly equal to the amount of 120 kg N ha⁻¹ measured in the field. The N addition rate was close to the recommended N fertilizer application rate (101–138 kg N ha⁻¹) for dryland winter wheat on the Loess Plateau (Cao et al., 2017). All the treatments were conducted in triplicate.

In the column experiment, polymethyl methacrylate cylindrical pipes were used for leaching. The columns were 30 cm long with a 7 cm internal diameter. Before the columns were filled with soil, a layer of filter paper and two gauze sealing layers were placed in the bottom of each soil column to prevent the loss of soil particles and impurities, and a thin layer of petroleum jelly was evenly smeared on the column wall to reduce the influence of wall effects on the process of water infiltration. The columns were packed with small taps at intervals of 5 cm and then scratched with a laboratory spatula to ensure natural continuity among the soil layers. A pilot experiment revealed that the bulk densities of the soil and biochar were 1.2 g cm⁻³ and 0.45 g cm⁻³, respectively. Based on changes in the soil bulk density due to biochar amendment, the bulk densities of the CK and the 1%, 2% and 4% biochar-soil layers were set to 1.20, 1.18, 1.16, and 1.12 (g cm⁻³), respectively.

### 2.3. Measurement of soil column leaching and Kₜₑᵢₙ

A vertical one-dimensional constant-head water infiltration method was used to study the leaching and Kₑᵢₙ of soil. The leaching device was composed of a constant-pressure bottle (5-cm internal diameter) with soil columns and beakers. The water head height (H) was a constant 3 cm, and the soil column was placed on the beaker to collect the leachate (Supplementary Fig. S3). The leaching experiment was conducted for 21 consecutive hours (divided into 0–6 h and 6–21 h) under laboratory conditions at room temperature. The average temperature was 22 °C (± 2 °C), and the average relative humidity was 27%. The nitrate/ammonium concentrate of the leachate collected from each column leach stage was measured using a continuous flow analytic system (Autoanalyzer 3, Bran + Luebbe, Germany). After the leaching experiment, the water supply was maintained for 48 h. The volume of the leachate in each column was measured continuously every 30 min until a stable filtrate volume was obtained. This process was repeated six times. The Kₑᵢₙ of soil was calculated according to Eq. (1).

\[ K_{\text{sat}} = \frac{QL}{ATH} \]  

where T is the time elapsed (h), H is the constant water head height (cm), A is the cross-sectional area of the column (cm²), L is the thickness of the soil, and Q is the volume of the leachate at time T (ml).

### 2.4. Statistical analysis

Two-way ANOVAs were used to test for statistical significance at the 95% confidence level, and multiple comparisons were adjusted for Duncan’s multiple range test at a probability level of 0.05. Correlations were analyzed using Pearson tests (two-tailed, p < 0.05). All statistical analyses were performed using SPSS 20.0 software (SPSS Inc., Chicago, IL, USA).

### 3. Results

Using column experiments, we studied the effect of biochar application methods on both N leaching and Kₑᵢₙ under conditions ranging from dry to close to water saturation. Our experimental conditions were representative of field conditions common in the Loess Plateau, concentrating rainfall during the rainy season (Zhong and Shangguan, 2014). Hence, the results could provide some inspirations for biochar field application.

![Fig. 1. Biochar and soil mixing methods. (CK, A, B and C refer to the no-biochar input treatment, the addition of biochar to the surface layer of the soil (0–10 cm), the addition of biochar to the underlying soil (10–20 cm) and the addition of biochar to the plow layer of the soil (0–20 cm), respectively).](image)

![Fig. 2. Nitrate leached during each treatment.](image)
Nitrate leaching

The nitrate masses leached under the different treatments are presented in Fig. 2. The biochar application pattern, the amendment rate and their interaction had significant effects on nitrate leaching at each leaching stage (p < 0.05; Table 2). Compared with the CK, the 2% biochar treatment with the A, B and C application patterns significantly decreased the total nitrate leaching by 12.3%, 8.3% and 17.0%, respectively (p < 0.05; Fig. 2c). Conversely, A1%, B1%, B4% and C4% increased the total nitrate leaching by 13.1%, 6.4%, 26.0% and 5.2%, respectively (p < 0.05; Fig. 2c). The cumulative mass of the leached nitrate during the first 6 h accounted for 94.3% (CK) to 98.2% (C4%) of the total nitrate leached in the entire 21-h eluviation process. Additionally, the nitrate/ammonium leachate amount and the volume of leachate obtained during the 0- to 21-h leaching stage (p > 0.05), and the leachate volumes at each leaching stage were negatively correlated with both the leachate volume (p < 0.05). However, the cumulative mass of nitrate in the leachate obtained in the 6-to-21-h leaching stage significantly increased the amount of nitrate leached during the 6-to-21-h period by 33.6% (p < 0.05; Fig. 3b), but B2% and C4% decreased the amount of ammonium leached by 21.1% and 33.5% (p < 0.05; Fig. 3b), respectively.

3.3. Volume of leachate

The biochar application pattern, addition rate and their interaction had significant effects on the leachate volume (p < 0.05; Table 2). The volumes of leachate obtained during the first 6 h and during the 6-to-21-h interval were consistent under the different treatments. However, the leachate volume obtained with B4% was higher than that obtained with A4% at the first leaching stage but lower than that obtained with A4% at the later leaching stage (Fig. 4a and b).

Overall, compared with the CK, A1% and C1% decreased the leachate volume (p < 0.05), but B1% had no significant effect (p > 0.05, Fig. 4c). A2% and C2% seemed to exert a weak negative effect on the leachate volume, but this effect did not reach significance (p > 0.05). B2% significantly increased the leachate volume by 21.8% (p < 0.05, Fig. 4c), and all 4% biochar treatments significantly increased the leachate volume (p < 0.05, Fig. 4c). Additionally, no significant difference in the leachate volume was found between B2% and B4% (p > 0.05).

3.4. Saturated hydraulic conductivity

The Ksat generally increased with increases in the biochar addition rate under each application pattern, with the exception that B2% exhibited no significant difference from B4% (Fig. 5). The biochar application pattern, amendment rate and their interaction had significant effects on the Ksat (p < 0.05; Table 2). Compared with the CK, all 1% biochar application treatments decreased the Ksat to varying degrees, but only the decrease observed with A1% reached significance (p < 0.05). The A2% and C2% treatments had no significant effects on the Ksat (p > 0.05), but the Ksat obtained with B2% was 20.9%, 30.4% and 20.3% (p < 0.05) higher than that obtained with the CK, A2% and C2% treatments, respectively. Additionally, all 4% biochar treatments significantly increased the Ksat (p < 0.05); specifically, the A4%, B4% and C4% treatments increased the Ksat by 22.1%, 24.8% and 34.8% compared with the CK, respectively.

3.5. Correlations between N leaching and soil K

The correlations among nitrate and ammonium leaching, leachate volume and Ksat are presented in Table 3. Notably, the masses of both nitrate and ammonium leached during the first 6-h stage were positively correlated with the leachate volume (p < 0.05). However, the mass of nitrate in the leachate obtained in the 6-to-21-h leaching stage was negatively correlated with both the leachate volume and Ksat (p < 0.05). In addition, no significant linear correlation was found between the nitrate/ammonium leachate amount and the volume of leachate in the 0-to-21-h leaching stage (p > 0.05), and the leachate volume was significantly correlated with the Ksat at each leaching stage (p < 0.05).

4. Discussion

4.1. Nitrate leaching

The apple branch biochar showed sorption ability for nitrate. In the 6-to-21-h leaching stage, the nitrate leaching amount decreased with increases in the biochar amendment rate, regardless of the application pattern, which is consistent with the results of a previous study (Xu et al., 2016). This reduction in nitrate leaching has been attributed to the nitrate adsorption ability of biochar (Pratiwi et al., 2016), and the

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Table 2
Main and interactive effects of the biochar application pattern and rate on N leaching and hydraulic conductivity.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Time</th>
<th>Pattern</th>
<th>Rate</th>
<th>Pattern × rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>0-6 h</td>
<td>F</td>
<td>P</td>
<td>F × P</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0-6 h</td>
<td>F</td>
<td>P</td>
<td>F × P</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.04</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Leachate</td>
<td>0-6 h</td>
<td>F</td>
<td>P</td>
<td>F × P</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Volume</td>
<td>0-21 h</td>
<td>F</td>
<td>P</td>
<td>F × P</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.04</td>
<td>0.02</td>
<td>0.01</td>
</tr>
</tbody>
</table>

**R²**

- **0-6 h** 43.18 **180.96 16.50 **95
- **0-6 h** 17.44 **74.75 41.46 **92
- **0-6 h** 29.93 **7.23 30.83 **87
- **0-6 h** 53.75 **7.41 76.36 **94
- **0-6 h** 59.82 **439.97 66.10 **98
- **0-21 h** 20.07 **191.28 31.90 **95
- **0-21 h** 38.70 **324.91 50.10 **97
- **Cₖ₅** 11.08 **57.15 3.25 **83

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probable mechanisms are the following: (1) mass solution flows into the biochar particles, where hydrated asymmetric nitrate ions are physically entrapped within the biochar pores (Haider et al., 2016; Kameyama et al., 2012), and (2) bonding occurs between negatively charged nitrate and some functional groups or positively charged cationic salts on the biochar surface (Deenik et al., 2010; Mukherjee et al., 2011). However, some studies have suggested that nitrate sorption is likely to occur due to repulsive forces between the negative surface of biochar and anions (Iqbal et al., 2015). Additionally, the anion exchange capacity may cause nitrate sorption, the amount of nitrate adsorbed by freshly produced biochar is very low (Haider et al., 2016), and hence, the ability of biochar to adsorb nitrate may be limited.

FTIR images of the biochar revealed a prominent band at 1583 cm$^{-1}$ due to oxonium functional groups (Fig. S2), which contribute to the adsorption of nitrate by the biochar (Lawrinenko and Laird, 2015; Pratiwi et al., 2016). However, the relatively low specific surface area of the biochar may further limit its nitrate sorption ability. Previous studies have indicated that nitrate is most likely adsorbed onto high-temperature (above 600 °C) biochars (Yao et al., 2012) because these have a larger surface area due to the formation of greater numbers of micropores (Kloss et al., 2012; Lee et al., 2010; Mukherjee et al., 2011). The specific surface area of the biochar used in this study was 14.22 m$^2$ g$^{-1}$, which is far lower than those of other woody biochars produced at 600 °C (e.g., Douglas fir wood and Douglas fir bark have specific surface areas of 522 and 222 m$^2$ g$^{-1}$, respectively) (Suliman et al., 2016). Therefore, changes in K may dominate nitrate leaching in the presence of large amounts of nitrate. This phenomenon might be the main reason for the positive correlation between the nitrate leached in the first 6 h, which accounted for more than 94% of the total nitrate leached over the 21-h period, and the leachate volume (Table 3).

Furthermore, the mass of both leached nitrate and the leachate volume closely depended on the biochar application method (Table 2). Additionally, consistent with our hypothesis, all 4% biochar treatments had negative effects on mitigating nitrate leaching compared with the CK because the high K was coupled with the biochar’s limited adsorption capacity for nitrate. Interestingly, although the application of biochar at the 1% rate decreased the leachate volume, the amount of leached nitrate was not effectively reduced by any biochar application pattern. This lack of efficacy may be attributable to the buried functional groups in the biochar and the blocking of pore entrances by fine soil particles when more densely packed low-dose biochar is placed in
and diluted the nitrate solution accessible to the underlying biochar-soil column, the upper layer of soil acted as a buffer to result in decreased nitrate leaching and a lower overall double-layer soil interfaces. In the A2% soil column, water was released into the underlying soil (Hillel and Baker, 1988). This short stagnation interface until the energy level increased to a value higher than that of the biochar surface (Hill and Parlange, 1972), which is likely higher than that of the soil (Liang et al., 2006). The increase in the CEC value of the soil caused by the biochar application might have been the main factor responsible for the observed reduction in ammonium leaching, as suggested by previous studies (Lehmann et al., 2003; Sika and Hardie, 2014; Zheng et al., 2013). Additionally, biochar has the potential to reduce ammonium adsorption onto biochar. The CEC of the biochar used in this study was 32.57 cmol kg\(^{-1}\), which is 58% higher than that of the soil (20.60 cmol kg\(^{-1}\)). Thus, the CEC of the biochar-soil mixture was most likely higher than that of the soil (Liang et al., 2006). The increase in the CEC value of the soil caused by the biochar application might have been the main factor responsible for the observed reduction in ammonium leaching, as suggested by previous studies (Lehmann et al., 2003; Sika and Hardie, 2014; Zheng et al., 2013).

In our study, the mitigation of ammonium leaching by biochar was significantly influenced by the biochar application method (Table 2). Additionally, ammonium leaching was positively correlated with the leachate volume in the first 6-h leaching (Table 3), which indicated that changes in K due to the biochar might have affected ammonium leaching similarly to nitrate leaching. In detail, ammonium leaching in the homogeneous C columns was similar to nitrate leaching. The strong chemical adsorption for ammonium and the weak decrease in K in C5% had no effect on ammonium leaching, even though the C5% column had abundant biochar particles. In the heterogeneous A and B columns, the ammonium leaching results were inconsistent with the nitrate leaching results. Ammonium leaching was reduced by A1% but increased by B1% (Fig. 3), and this difference might be attributed to the relatively low ammonium adsorption capacity of biochar at low doses coupled with the lower K obtained with A1%, which was not the case for B1% (Fig. 5). However, the relatively high ammonium adsorption capacity of the biochar-soil mixture obtained with the 2% application rate coupled with the “buffer effect” of the upper layer of soil resulted in a decrease in ammonium leaching obtained with B2%. Nevertheless, B4% had no effect on ammonium leaching, likely because the high soil K limited the ability of the biochar to capture more ammonium in a manner similar to that observed with C4%.

In the heterogeneous A and B columns, the ammonium leaching results were inconsistent with the nitrate leaching results. Ammonium leaching was reduced by A1% but increased by B1% (Fig. 3), and this difference might be attributed to the relatively low ammonium adsorption capacity of biochar at low doses coupled with the lower K obtained with A1%, which was not the case for B1% (Fig. 5). However, the relatively high ammonium adsorption capacity of the biochar-soil mixture obtained with the 2% application rate coupled with the “buffer effect” of the upper layer of soil resulted in a decrease in ammonium leaching obtained with B2%. Nevertheless, B4% had no effect on ammonium leaching, likely because the high soil K limited the ability of the biochar to capture more ammonium in a manner similar to that observed with C4%.

The A2% column presented no protection by “buffer layer” soil, and the negatively charged sites on the biochar surface may be rapidly occupied by ammonium or other cations during the first leaching stage (Pratiwi et al., 2016; Takaya et al., 2016). Additionally, the solution that accumulated above the interface would persistently increase the ammonium concentration (Liu et al., 2016). This phenomenon might explain the increased ammonium leaching observed with the A2%

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**Table 3**

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Variable</th>
<th>Correlation Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-6 h</td>
<td>Nitrate</td>
<td>1 0.578** 0.470** 0.251</td>
</tr>
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<td></td>
<td>Ammonium</td>
<td>1 0.763** 0.542**</td>
</tr>
<tr>
<td></td>
<td>Leachate</td>
<td>0.199 0.849** 0.813**</td>
</tr>
<tr>
<td>6-21 h</td>
<td>Nitrate</td>
<td>1 0.199 0.849** 0.813**</td>
</tr>
<tr>
<td></td>
<td>Ammonium</td>
<td>1 0.292 0.190</td>
</tr>
<tr>
<td></td>
<td>Leachate</td>
<td>1 0.892**</td>
</tr>
<tr>
<td>0-21 h</td>
<td>Nitrate</td>
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<tr>
<td></td>
<td>Ammonium</td>
<td>1 0.102 0.137</td>
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<tr>
<td></td>
<td>Leachate</td>
<td>1 0.885**</td>
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**Fig. 5** Saturated hydraulic conductivities obtained with the different treatments. The bars represent the arithmetic mean of three replicates, and the error bars are the standard deviations. The bars with the same letter were not significantly different at p < 0.05.

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fine-textured soil (Liu et al., 2016). However, all 2% biochar treatments significantly decreased the amount of leached nitrate, and A2% and C2% had little effect on the leachate volume, but B2% significantly increased the leachate volume (Fig. 2 and 4).

In detail, the C columns were homogeneous, i.e., the total mass of the biochar and the flow path through the biochar-soil mixture layers in these columns were 2-fold greater than those of the A and B soil columns. Due to these differences, the C application pattern at the 1% and 2% doses exerted prominent effects on mitigating nitrate leaching (Fig. 3). However, the increased tortuosity might have decreased the K (Liu et al., 2016), and thus, C1% and C2% slightly reduced K.

The A2% and B2% columns were homogeneous and exhibited opposite double-layer soil interfaces. In the A2% soil column, water was suspended from continued infiltration and thus accumulated at the interface until the energy level increased to a value higher than that of the underlying soil (Hillel and Baker, 1988). This short stagnation might give the biochar more time to adsorb nitrate and retain water (Yuan et al., 2016; Zbang et al., 2016), which would simultaneously result in decreased nitrate leaching and a lower K. In the B2% soil column, the upper layer of soil acted as a buffer zone that intercepted and diluted the nitrate solution accessible to the underlying biochar-soil mixed layer. Moreover, the infiltration of water into the interface produced fast-flowing wetting fingers (Hill and Parlange, 1972), which increased the water migration rate (Li et al., 2016). The B2% column structure might give the biochar a greater opportunity to capture nitrate, particularly when the pores inside the biochar particles are filled with solution (Uzoma et al., 2011). Finally, the B2% treatment both reduced the leaching of nitrate and increased the K.

**4.2. Ammonium leaching**

The total mass of ammonium leached was notably lower than that of nitrate lost under all the treatments, which agrees with the results of previous studies (Lehmann et al., 2003; Xu et al., 2016). This finding was obtained because ammonium might be readily adsorbed onto negatively charged clay minerals in silty clay soil (Xu et al., 2016). Nevertheless, biochar has the potential to reduce ammonium leaching through ammonium sorption (Kizito et al., 2015). Indeed, the total masses of ammonium that leached from the specific biochar treatments were significantly (12.6–30.8%) lower than those obtained with the CK (Fig. 3c).

It is becoming increasingly apparent that the surface groups of biochar may play a more important role than its surface area and porosity (Bargmann et al., 2014; Spokas et al., 2012). Additionally, Takaya et al. (2016) indicated that biochars with high surface areas do not possess better ammonium adsorption capacities than low-surface-area biochars. This finding suggests that physisorption might not be the dominant mechanism for ammonium adsorption (Pratiwi et al., 2016; Takaya et al., 2016). Zheng et al. (2013) and Gai et al. (2014) revealed that CEC is the most important factor affecting ammonium adsorption onto biochar. The CEC value of the biochar used in this study was 32.57 cmol kg\(^{-1}\), which is 58% higher than that of the soil (20.60 cmol kg\(^{-1}\)). Thus, the CEC of the biochar-soil mixture was most likely higher than that of the soil (Li et al., 2016). The increase in the CEC value of the soil caused by the biochar application might have been the main factor responsible for the observed reduction in ammonium leaching, as suggested by previous studies (Lehmann et al., 2003; Sika and Hardie, 2014; Zheng et al., 2013).

Furthermore, in our study, the mitigation of ammonium leaching by biochar was significantly influenced by the biochar application method (Table 2). Additionally, ammonium leaching was positively correlated with the leachate volume in the first 6-h leaching (Table 3), which indicated that the changes in K due to the biochar might have affected ammonium leaching similarly to nitrate leaching. In detail, ammonium leaching in the homogeneous C columns was similar to nitrate leaching. The strong chemical adsorption for ammonium and the weak decrease in K obtained with C2% and C1% significantly decreased ammonium leaching at the different leaching stages (Fig. 3). The highest K obtained with C4% had no effect on ammonium leaching, even though the C4% column had abundant biochar particles.

In the heterogeneous A and B columns, the ammonium leaching results were inconsistent with the nitrate leaching results. Ammonium leaching was reduced by A1% but increased by B1% (Fig. 3), and this difference might be attributed to the relatively low ammonium adsorption capacity of biochar at low doses coupled with the lower K obtained with A1%, which was not the case for B1% (Fig. 5). However, the relatively high ammonium adsorption capacity of the biochar-soil mixture obtained with the 2% application rate coupled with the “buffer effect” of the upper layer of soil resulted in a decrease in ammonium leaching obtained with B2%. Nevertheless, B4% had no effect on ammonium leaching, likely because the high soil K limited the ability of the biochar to capture more ammonium in a manner similar to that observed with C4%.

The A2% column presented no protection by “buffer layer” soil, and the negatively charged sites on the biochar surface may be rapidly occupied by ammonium or other cations during the first leaching stage (Pratiwi et al., 2016; Takaya et al., 2016). Additionally, the solution that accumulated above the interface would persistently increase the ammonium concentration (Liu et al., 2016). This phenomenon might explain the increased ammonium leaching observed with the A2%
treatment in the later leaching stage. However, with a biochar application rate of 4%, the accumulation of a high volume of ammonium solution in the surface layer causes many biochar particles to adsorb ammonium and accelerate the flow rate. Thus, A4% had a positive effect on mitigating ammonium leaching and increasing the $K$ at each stage (Fig. 4).

4.3. Saturated hydraulic conductivity

In summary, both the biochar application rate and the application pattern had a significant effect on the $K_{sat}$ (Table 2). All the 4% rate biochar treatments increased $K_{sat}$, but the 2% and 1% treatments, with the exception of A1% and B2%, had no significant effect on $K_{sat}$ (Fig. 5). These findings indicate that without changing the application pattern, only a high application rate could increase the $K_{sat}$ of silty clay soil. Similar results have also been observed by researchers who have focused on the effects of biochar on $K_{sat}$ of fine-textured soil (Castellini et al., 2015; Kameyama et al., 2012). For example, Kameyama et al. (2012) indicated a column experiment and found that $K_{sat}$ of clay increased significantly only by higher-concentration bagasse biochar treatments (5–10%). Ajayi et al. (2016) reported that the addition of 2% hardwood biochar did not significantly influence $K_{sat}$ of silty substrates, whereas biochar dosages of 5 and 10% significantly increased $K_{sat}$.

$K_{sat}$ is correlated with soil properties, such as particle hydrophobicity, pore connectivity, pore size, porosity and tortuosity (Ajayi et al., 2016; Carman, 1997; Liu et al., 2016). According to Kinney et al. (2012), who reported that apple branch biochars produced at pyrolysis temperatures exceeding 400 °C are consistently hydrophilic, our apple branch biochar, which was pyrolyzed at 450 °C, is most likely hydrophilic. Additionally, these researchers found that biochar pyrolyzed at 400–500 °C shows the highest field capacity. Hence, the apple branch biochar particles might have caused a low intrapore entry pressure, which facilitated the formation of water-penetrable intrapore and thus contributed to the increased $K_{sat}$. However, porous biochar could change the pore size, and the porosity of a biochar-soil mixture is affected by both the pores inside the biochar and the pores between the biochar and soil particles (Liu et al., 2016; Masiello et al., 2015). Lim et al. (2016) indicated that the effect of biochar on the soil $K_{sat}$ is not due to the internal porosity of the biochar but mainly to differences in particle packing (tortuosity). Similarly, Liu et al. (2016) suggested that the $K_{sat}$ of biochar-amended soil is mainly controlled by the pores between the biochar and soil particles. Hence, the pore shapes and connectivities may better explain the effect of biochar on the soil $K_{sat}$.

The uniform addition of low doses (e.g., 1% of biochar) to fine-textured soil may cause the silt and clay particles surrounding the biochar to fill the intrapore and thereby create smaller pores (Liu et al., 2016). Additionally, denser packing may decrease the pore throat size between the particles and the pore connectivity and thereby increase the tortuosity (Liu et al., 2016; Zhang et al., 2016). This phenomenon might be the main reason for the decrease in $K_{sat}$ obtained with C1%. When the biochar application rate reached 2%, the increased porosity may increase pore connectivity and the numbers of flow paths, which may offset the impact of narrow pore throat size. Thus, C2% had no effects on $K_{sat}$. However, the addition of biochar to silty clay soil at high rates (4%) could cause the formation of substantial numbers of large pores (Castellini et al., 2015) and increase the size and connectivity of the pores between particles (Barnes et al., 2014; Herath et al., 2013), thereby inducing an overall increase in the $K_{sat}$.

Furthermore, a layered structure would complicate the hydraulic process, as was observed with the A and B application patterns (Miller and Gardner, 1962). The addition of biochar at a 1–2% dose (A1% and A2%) into the surface layer decreased $K_{sat}$ to lower levels than those observed with the other treatments (Fig. 5) because the finer particles of subsoil could create a low-permeability layer to make water preferentially move horizontally rather than infiltrate vertically (Liu et al., 2016). In contrast, the B2% column presented a finer texture layer overlying a coarser texture later and is characterized by the production of fast-flowing wetting fingers on the interface, which promotes water infiltration (Hillel and Baker, 1988). The hydrophilic and porous biochar would decrease the intrapore entry pressure of the subsoil and accelerate the water flow (Liu et al., 2016), thereby increasing the $K_{sat}$ of the whole column. Additionally, the B2% and B4% effects on $K_{sat}$ were not significantly different, indicating that $K$ of the topsoil may dominate $K_{sat}$ of the whole column at a biochar concentration higher than a threshold. Therefore, the addition of biochar into subsurface soil at the 2% rate was identified as the best option for increasing $K_{sat}$ of silty clay soil.

4.4. Implications for field application

Overall, the B2% treatment yielded a win-win situation by simultaneously mitigating N leaching and increasing $K_{sat}$ and this result has implications for the field application of biochar. The adoption of a suitable biochar application method coupled with other cultivation measures may further maximize the benefits of biochar with minimum energy expenditure.

For example, deep tillage coupled with porous and hydrophilic biochar in the field may elicit or even strengthen multiple benefits, such as disrupting root-restricting soil layers, increasing water storage, decreasing nutrient leaching, facilitating the uptake of subsurface water and resources, and sequestering more carbon (Alcántara et al., 2016; Baumhardt et al., 2008; Doty et al., 1975; Lehmann et al., 2003; Schneider et al., 2017). Additionally, deep plowing would turn soil horizons to yield a complete or semicomplete inversion of the soil profile such that the subsoil horizons end up at the soil surface and the topsoil horizons end up buried in the deep soil (Schneider et al., 2017). Hence, biochar could be simply applied by placing it on the surface soil, and subsequent deep plowing would mix the biochar into subsurface soil.

Additionally, it is widely recognized that deep-placed fertilizer can decrease NH$_3$ volatilization and improve N use efficiency compared with surface broadcasting (Li et al., 2018; Miah et al., 2016; Yao et al., 2018). Indeed, the addition of biochar into subsurface soil is similar to deep-banding in the rhizosphere (Lehmann and Joseph, 2009). Hence, in an orchard system, biochar could be applied in holes near plants, or biochar and fertilizer could be directly added to the subsurface soil during the transplantation of saplings. Therefore, the application of biochar with fertilizer to roots might improve the water status and further reduce N loss.

5. Conclusions

The choice of biochar application method has significant effects on both N leaching and K in silty clay soil, and there is a balance between N leaching and the soil K. Regardless of the biochar application pattern, a high (4%) biochar addition rate resulted in substantial nitrate leaching due to a high K, but the same finding was not obtained for ammonium leaching. All the 2% biochar treatments significantly mitigated N leaching, but only the mixing of 2% biochar into the subsurface soil (B2%) effectively reduced N leaching and increased $K_{sat}$ simultaneously. Therefore, B2% is the recommended biochar application method for mitigating N leaching and increasing $K_{sat}$ in silty clay soil.

Acknowledgements

This work was supported by the National Key Technology R&D Program of China (2016YFC0501605 and 2015BAD22B01), the Doctor’s Scientific Research Startup Project (YDBK2017-25) and the Open Foundation of State Key Laboratory of Soil Erosion and Dryland Farming on the Loess Plateau (A314021402-1813). We especially thank the reviewers for their valuable suggestions, which improved the...
quality of this manuscript.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.still.2018.06.006.

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