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Full Length Article

Effects of Fresh and Aged Maize Straw-Derived Biochars on Inorganic Nitrogen Adsorption in Aqueous Solution and Leaching from Calcareous Clay Soil

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Abstract

Biochar's production and application in soils has been suggested as a means of abating climate change by sequestering carbon, while simultaneously providing energy and increasing crop yields. However, little is known about the effects of aged biochars on ammonium (NH_4^+) and nitrate (NO_3^-) adsorption and leaching from arable calcareous clay soil. Based on the physicochemical analyses of the fresh and spontaneously aged maize straw-derived biochars (prepared at 400 and 600°C, designated as F400, F600, A400, and A600, respectively), the effects of the four kinds of biochars on NH_4^+ and NO_3^- adsorption in aqueous solution and their leaching from calcareous clay soil were explored. Results showed that the aged biochars (A400 and A600) decreased pH and mean pore size, but increased carboxyl amount and specific surface area compared with the fresh biochars (F400 and F600). NH_4^+ adsorption capacity of the biochars was as follows A400 > A600/F400 > F600, with the maximum of 4.20 mg NH_4^+-N/g biochar at A400. Though biochar NO_3^- adsorption capacity showed the similar trend as NH_4^+, the variations were significantly large, indicating the instability of NO_3^- adsorption by biochar. The column leaching experiment showed that both the fresh and aged biochars inhibited inorganic N leaching. For NH_4^+, though all the biochars postponed the occurrence of leaching peak compared with control, A400 and A600 showed much stronger ability than F400 and F600 to delay the leaching peak occurring. However, for NO_3^-, the leaching peak of A400 and A600 occurred at the same leaching event as control, while F400 and F600 even brought the leaching peak forward. Furthermore, the distribution profiles of potential ammonia-oxidation rate and ammonia-oxidizing bacteria amount in soil column after leaching indicated that A400 and A600 possessed relatively stronger ability than F400 and F600 to retain NH_4^+ transportation into the deep layers of soil column. In all, the spontaneous aging process enhanced the inorganic N adsorption capacity and retention ability of maize straw-derived biochars. © 2020 Friends Science Publishers

Keywords: Biochar; Inorganic N; Adsorption; Leaching; Calcareous clay soil

Introduction

Excessive application of fertilizer has caused the release of nitrogen (N) from agricultural fields to aquatic systems. Leaching of nutrients from soils may deplete soil fertility, accelerate soil acidification, and most importantly impose a threat to environmental health (Ozacar 2003; Laird *et al.* 2010). It is therefore very important to develop effective technologies to hold N in soils.

Biochar is a carbonaceous material produced during the pyrolysis of biomass (Hussain *et al.* 2017). An option to reduce N leaching could be the application of biochar to soils (El-Naggar *et al.* 2019). The adsorption of inorganic N on biochars has been paid much attention. Biochar displayed strong adsorption ability of NH_4^+ in several studies (Dempster *et al.* 2012; Yao *et al.* 2012). Placing biochar into soil has also been shown to inhibit the leaching of NH_4^+ under fertilization condition (Ding *et al.* 2010; Dempster *et al.* 2012). However, some studies showed that biochar could reduce NO_3^- leaching (Dempster *et al.* 2012; Yao *et al.* 2012), while increased leaching of NO_3^- with biochar has also been reported somewhere (Laird *et al.* 2010; Kameyama *et al.* 2012). Moreover, some literatures indicated that significant biochar NO_3^- adsorption only occurred at relatively higher pyrolysis temperatures (>600°C) (Dempster *et al.* 2012; Kameyama *et al.* 2012). The statements for biochar NH_4^+ adsorption were consistent, but contradictory for NO_3^- adsorption.

As a matter of fact, biochar surface properties are likely to be gradually altered during environmental exposure. In soils, due to its strong affinity for organic matter and inorganic mineral ions, biochar is likely to

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undergo a series of biogeochemical reactions and physical processes that will result in the alteration of its properties with time (aging) (Cheng *et al.* 2008; Farrell *et al.* 2013; Ren *et al.* 2016; Sarma *et al.* 2018). This implies that these changes have potential effects for altering biochar adsorption capacity of inorganic N and the physicochemical properties of biochar amended soils. However, most of the existing laboratory and field studies focused on freshly produced biochars, and there is a little information on the study of aged biochar and its impact on inorganic N adsorption and leaching from calcareous clay soil.

On the other hand, in most of the studies, artificial aging methods were used to examine the effects of simulation aging processes on biochar properties (Liu *et al.* 2013; Qian and Chen 2014). However, biochar aging occurred under natural ambient conditions is ordinary and dramatic during biochar production, storage, transportation to farmland, and final agricultural application because of the frequent rainfall, illumination, and aeration. Therefore, the spontaneous aging process was carried out in our study to prepare the corresponding aged biochars. The objective of the study was to explore the effects of fresh and aged maize straw-derived biochars on NH_4^+ and NO_3^- adsorption in aqueous solution and leaching from calcareous clay soil.

Materials and Methods

Soil

The soil was collected from the surface layer (0–20 cm) of a farmland in the suburb of Jinzhong, Shanxi Province, China, locating at the southeastern margin of Loess Plateau. The detailed information about the soil was showed in our previous paper (Wang *et al.* 2018).

Biochar

Fresh biochar production: Maize (*Zea mays* L.) straw was collected from the same area as the soil in harvesting season. The straw was air-dried at room temperature and ground to pass a 10-mesh sieve. The ground straw was then placed in a quartz boat of the tube furnace (SK-G10123K, Tianjin Zhonghuan Lab Furnace Co., Ltd., Tianjin, China). The pyrolysis temperature was raised to 400°C (approximately 5°C/min) and 600°C (approximately 10°C/min) respectively with a N_2 flow rate of 150 ml/min. The final temperature was maintained for 2 h, and then the biochars were allowed to cool to room temperature and ground to pass through a 2-mm sieve, which were hereafter referred to as the fresh biochars (F400 and F600).

Biochar aging incubation: The fresh biochars (F400 and F600) were incubated in open vessels at room temperature (25 ± 2°C) in the dark and at 77.7% water content by weight. The water evaporation from the open vessels was compensated by weight using deionized water every day. After 50 d incubation, the biochar samples were air-dried and mixed thoroughly to storage, which were defined as the aged biochars and referred to as A400 and A600, respectively.

Biochar characteristic determination: To explore the effects of aging incubation on biochar properties, the fresh and aged biochar characteristics were determined. The pH was determined by shaking the glass bottle contained 1.0 g of biochar with 15 mL deionized water fiercely by hand for 1 min, and then after 30-min settlement, the supernatant was measured with an electrode (Mettler Toledo Delta 320). The amount of acidic/alkaline oxygen-containing functional groups of biochar was determined by Boehm titration method (Boehm 1994). The specific surface area, total pore volume, and mean pore size of the biochar were evaluated using the Sorption Analyzer (Quadrasorb SI, America Quantachrome) N_2 adsorption Brunauer-Emmet-Teller (BET) technique.

Biochar adsorption capacity of ammonium and nitrate in aqueous solution

Batch adsorption experiment was conducted in 250 mL conical flask with stopper. About 1.0 g of fresh or aged maize straw-derived biochar was added into the vessels and mixed with 100 mL 100 mg N/l NH_4^+ or NO_3^- solution. The vessels without either biochar or nutrient elements were also included as experimental controls. The mixtures were shaken at 170 rpm in a mechanical shaker for 240 min at a constant temperature of 25 ± 0.5°C. The inorganic N concentrations of the suspension at the time zero were presumed as 100 mg/L. Subsequently, at the time points 1, 5, 20, 40, 60, 90, 150, and 240 min after incubation the homogenous suspensions were collected from the conical flasks. And then the collected samples were filtered through 0.45 µm cellulose acetate membrane filters. The concentrations of NH_4^+-N and NO_3^--N in the supernatants were measured using the colormetric method (APHA *et al.* 2012), using a dual beam UV/VIS spectrophotometer (UV-5100B, Shanghai Metash Instruments Co., Ltd., Shanghai, China). Inorganic N adsorbed by biochar was calculated based on the initial and final aqueous concentrations. All the experiments were carried out in triplicate.

Ammonium and nitrate leaching from soil column amended with biochar

All the fresh and aged maize straw-derived biochars (F400, F600, A400, and A600) were selected to study their effects on inorganic N retention and transportation in the calcareous clay soil. Soil columns were made of plexiglass cylinders measuring 30 cm in height and 10 cm in diameter. A screw cap with a hole in the middle allowing water drainage was fitted to the bottom end of the column. Then, the screw cap was covered with some quartz sand with the thickness of 3 cm (soaked in 2.0 mol/l H_2SO_4 overnight and washed with deionized water), which was enclosed by nylon net (70 µm pore size) to prevent quartz sand loss. The calcareous clay

soil with (F400, F600, A400, and A600; 2% mass fractions by dry weight) or without biochars was packed into the column with the depth of 40 cm (0–15 cm: homogeneous soil-biochar mixture; 15–40 cm: original soil sample) and the bulk density of 1.20 g cm^{-3} (equal to the field soil after ploughed). An appropriate filter-paper was placed on the surface of the soil in each column to homodisperse the source water and to retard water evaporation. Altogether, the experiment consisted of five treatments with three replicates (n = 15).

Initially, the columns were flushed with deionized water to reach a saturated state to precondition the soil-biochar mixture, which lasted for a week. We compensated water loss due to evaporation by adding the appropriate amount of deionized water through weighing every day. Then a nutrient solution containing 0.8999 g NH_4Cl (equal to 300 kg N/ha) was sprayed onto the surface of the soil. Thereafter, the columns were leached with 300 mL deionized water by dripping, which lasted for 3 h. The leachate from each column was collected in 400 mL polyethylene bottles for about 6 h after the start of leaching. The bottles had a cap with a small hole drilled through it that allowed the drain tube to be inserted into the bottle so that evaporative water loss was minimized. We called this process a leaching event. The leaching events were repeated for 16 times with an interval of 3 days in the first 30 days and 2 days in the later 10 days. Between adjacent leaching events when the soil was idle, the loss of water through evaporation was compensated by adding deionized water through the weighing method. The leaching experiment was carried out at room temperature (25 ± 2°C).

All the leachate samples were immediately filtered through 0.45 μm cellulose acetate membrane filters for further analyses. The volume of the leachate collected from each column was determined gravimetrically (assuming the density is 1.0 g/mL). The NH_4^+-N and NO_3^--N concentrations in leachate samples were measured using the same method as described above.

Column layered soil sample analyses

Immediately after the 16 leaching events, the topsoil (0–2 cm) and the layered soil samples of 3–7, 8–12, 18–22, 23–27, 28–32, and 38–42 cm in the column, which were defined as 0, 5, 10, 20, 25, 30, and 40 cm depth soil samples, were collected with a spade. The potential ammonia-oxidation rate of the layered soil samples was measured using a modified chlorate inhibition method (Kurola *et al.* 2005). The dilution-plate method was used to quantify the amount of ammonia-oxidizing bacteria (AOB) in the layered soil sample (Lin 2010; Wang *et al.* 2018).

Data analysis

The variance between any triplicate measurements in this study was smaller than 5%, and the average value ± standard deviation was reported. The graphing was performed using OriginPro 8.0 software.

Results

Physicochemical properties of maize straw-derived biochars before and after aging

All the fresh and aged maize straw-derived biochars prepared at 400 and 600°C (designated as F400, F600, A400, and A600, respectively) were alkaline (10.3–11.7). The pH of the biochars prepared at 600°C (11.7 and 10.5 for the fresh and aged biochar, respectively) was much higher than that prepared at 400°C (10.6 and 10.3). After 50 d aging incubation, the aged biochars showed decreased pH (400°C: 0.3 units; 600°C: 1.2 units) and mean pore size (400°C: 75.1% of the fresh biochar; 600°C: 29.6% of the fresh biochar), but increased carboxyl amount (400°C: 0.031 mmol/g; 600°C: 0.102 mmol/g) and specific surface area (400°C: 2.42 times of the fresh biochar; 600°C: 15.3 times of the fresh biochar) (Table 1).

Ammonium and nitrate adsorption kinetics of fresh and aged maize straw-derived biochars

Ammonium: NH_4^+-N adsorption amount of the four kinds of biochars increased sharply in the first 5 min, and then increased slowly until to 40 min, then reached to be stable. The biochar prepared at 400°C showed relatively stronger NH_4^+ adsorption capacity than that of the biochar prepared at 600°C either for the fresh or aged biochars. Moreover, the aged biochar showed relatively stronger NH_4^+ adsorption capacity than fresh ones either for the 400 or 600°C produced biochars. Therefore, the order of the NH_4^+ adsorption capacity of the biochars was as follows A400 > A600/F400 > F600 (existing some counterchanges between F400 and A600). The result may be attributed to the more carboxyl of biochar prepared at 400°C than 600°C (fresh biochars: 0.182 ± 0.068 *vs.* 0.086 ± 0.009 mmol/g; aged biochars: 0.213 ± 0.152 *vs.* 0.188 ± 0.018 mmol/g) and biochar aging process increased carboxyl amount (400°C: 0.182 ± 0.068 to 0.213 ± 0.152 mmol/g; 600°C: 0.086 ± 0.009 to 0.188 ± 0.018 mmol/g) and specific surface area (400°C: 2.42 to 5.85 m^2/g; 600°C: 1.33 to 20.4 m^2/g). Particularly, A400 showed the maximum balance adsorption amount of NH_4^+-N (4.20 mg NH_4^+-N/g biochar) (Fig. 1).

Nitrate: Being different from NH_4^+, NO_3^--N adsorption amount of the four kinds of biochars increased sharply in the first 5 min, and then increased slowly until to 20 min, then decreased slowly with fluctuations and reached to be stable. However, the order of the NO_3^- adsorption capacity of the biochars was the same as NH_4^+, A400 > A600/F400 > F600 (existing some counterchanges between F400 and A600). A400 also showed the maximum balance adsorption amount of NO_3^--N (0.56 mg NO_3^--N/g biochar) (Fig. 2).

Table 1: The physicochemical property of the fresh and aged maize straw-derived biochars

	F400	F600	A400	A600
pH (H_2O)*	10.6 ± 0.04	11.7 ± 0.06	10.3 ± 0.04	10.5 ± 0.06
Carboxyl (mmol/g)	0.182 ± 0.068	0.086 ± 0.009	0.213 ± 0.152	0.188 ± 0.018
Carbonyl (mmol/g)	0.222 ± 0.108	0.239 ± 0.004	0.207 ± 0.092	0.206 ± 0.009
Phenolic hydroxyl (mmol/g)	0.538 ± 0.138	0.625 ± 0.005	0.517 ± 0.085	0.342 ± 0.006
Total acidic oxygen-containing functional group (mmol/g)	0.942 ± 0.038	0.950 ± 0.018	0.937 ± 0.048	0.736 ± 0.015
Total alkaline oxygen-containing functional group (mmol/g)	1.065 ± 0.020	1.216 ± 0.004	0.935 ± 0.025	0.945 ± 0.011
Specific surface area (m^2/g)	2.42	1.33	5.85	20.4
Total pore volume (cm^3/g)	0.0107	0.0064	0.0194	0.029
Mean pore size (nm)	17.7	19.1	13.3	5.66

*: Biochar: water = 1 g: 15 mL; F400/F600: fresh biochar prepared at 400/600°C; A400/A600: aged biochar prepared at 400/600°C

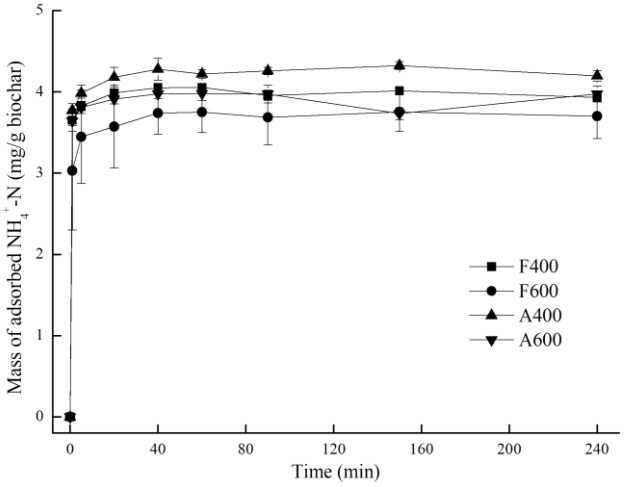

Fig. 1: The ammonium adsorption abilities of the fresh and aged maize straw-derived biochars

Nonetheless, though NO_3^- adsorption capacity of the four kinds of biochars showed the similar trend as NH_4^+, the variations were significantly large, indicating the instability of biochar NO_3^- adsorption process. Moreover, the adsorption amount of NH_4^+-N of the four kinds of biochars was 7.50–10.6 times more than that of NO_3^--N.

Effects of fresh and aged maize straw-derived biochars on ammonium and nitrate leaching from soil column

Ammonium: During the 16 leaching events, the mass of leached NH_4^+-N peaked at the fourth, seventh, sixth, ninth, and ninth leaching for the control, F400, F600, A400, and A600 treatment, respectively. All the biochars postponed NH_4^+ leaching peak occurring compared with control. Particularly, A400 and A600 showed much stronger capacity than F400 and F600 to delay the leaching peak occurring. Compared with control, the maximum of leached NH_4^+-N was reduced by 19.4, 17.1, 28.1 and 26.0% for F400, F600, A400, and A600 treatments, respectively; the cumulative mass of leached NH_4^+-N was reduced by 20.9, 26.2, 24.3 and 24.5% for F400, F600, A400, and A600 treatments, respectively. Remarkably, maize straw-derived biochar incorporation inhibited NH_4^+ leaching from calcareous clay soil and postponed the leaching peak occurring, especially for the aged biochars (Fig. 3).

Nitrate: Like NH_4^+, both the fresh and aged biochars inhibited NO_3^- leaching during the column leaching experiment. However, being different with NH_4^+, NO_3^--N leaching peak of A400 and A600 treatments occurred at the same leaching event as control (the sixth), while NO_3^--N leaching peak of F400 and F600 treatments was even advanced (the fifth). Compared with control, the maximum of leached NO_3^--N was reduced by 22.0, 20.5, 27.1 and 24.3% for F400, F600, A400, and A600 treatments, respectively. The results indicated that both the fresh and aged biochars inhibited NO_3^- leaching. However, all the four kinds of biochars incorporation did not postpone NO_3^--N leaching peak occurring (Fig. 4).

Profiles of potential ammonia-oxidation rate and AOB amount in soil column after leaching

Potential ammonia-oxidation rate: In the control soil column, the potential ammonia-oxidation rate (PAR) varied in the range of 41.4–62.2 nmol N/g DW/h, with the minimum occurred at the 20-cm depth and the maximum occurred at the surface soil. In the fresh biochar incorporated soil column, the PAR decreased significantly ($P < 0.05$) from the surface layer until to the 20 cm depth (F400: 121.6 to 29.9 nmol N/g DW/h; F600: 125.5 to 29.0 nmol N/g DW/h). However, there was no significant ($P > 0.05$) difference in the deep layer soil samples (below 20 cm depth). Nonetheless, in the aged biochar incorporated soil column, the PAR decreased sharply and significantly ($P < 0.05$) from the surface until to the deep layer (A400, 146.5 to 6.35 nmol N/g DW/h; A600, 146.3 to 10.1 nmol N/g DW/h) (Fig. 5).

The PARs were always in the order of control > F400/F600 > A400/A600 in the subsurface and deep layers of the soil column. While in the surface layer, the situation was reversed. This phenomenon may be due to biochars' retention capacity of NH_4^+ (as the substrate of ammonia-oxidizing microbes) in the surface soil, and the aged biochars possessing relatively stronger capacity of retarding NH_4^+ transportation into the deep layers of soil column than fresh ones.

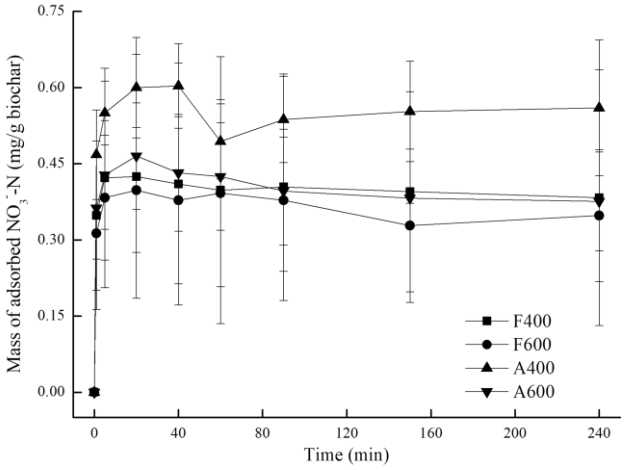

Fig. 2: The nitrate adsorption abilities of the fresh and aged maize straw-derived biochars

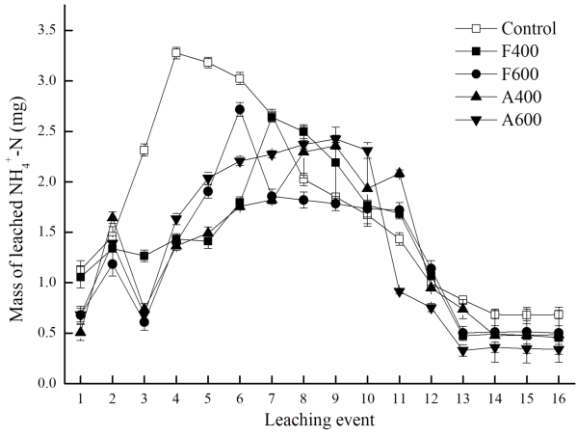

Fig. 3: The variation of the mass of leached NH_4^+-N during the 16 leaching events

AOB amount: The profile of ammonia-oxidizing bacteria (AOB) amount in soil column was in the same pattern as PAR for all the five treatments. In the control, the AOB amount varied in the range of 3.43×10^5 – 4.82×10^5 individual/g DW, with the minimum occurred at 20 cm depth and the maximum occurred at the surface layer. In the fresh biochar incorporated soil column, the AOB amount decreased significantly ($P < 0.05$) from the surface to the 20 cm depth (F400: 1.08×10^6 to 2.54×10^5 individual/g DW; F600: 1.11×10^6 to 2.44×10^5 individual/g DW). However, there was no significant ($P > 0.05$) difference in the deep layer soil samples (below 20 cm depth) (F400: varied in the range of 2.25×10^5 to 2.48×10^5 individual/g DW; F600: varied in the range of 2.18×10^5 to 2.31×10^5 individual/g DW). In the aged biochar incorporated soil column, the AOB amount decreased sharply and significantly ($P < 0.05$) from the surface until to the deep layer (A400: 1.16×10^6 to 4.85×10^4 individual/g DW; A600: 1.11×10^6 to 7.16×10^4 individual/g DW) (Fig. 6).

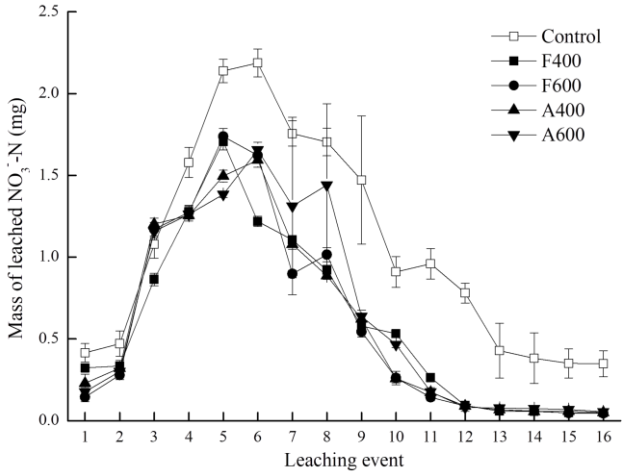

Fig. 4: The variation of the mass of leached NO_3^--N during the 16 leaching events

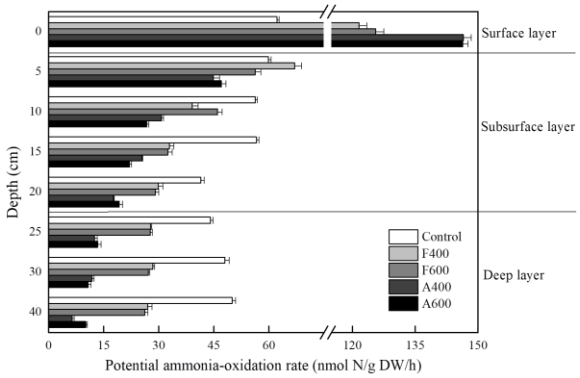

Fig. 5: The profile of potential ammonia-oxidation rate of the layered soil samples in columns after leaching

The reason for the distribution pattern of AOB amount in the soil columns incorporated with and without fresh/aged biochars may result from the distribution characteristic of NH_4^+, which is the substrate of AOB. And the discrepant profile of NH_4^+ in the layered soil samples in columns after leaching was attributed to the different soil amended materials (the fresh or aged maize straw-derived biochars).

Discussion

The spontaneous aging process occurring at room temperature and certain water condition decreased the pH and mean pore size of the maize straw-derived biochars, but increased the carboxyl amount and specific surface area. Moreover, the aging process also enhanced the biochar adsorption ability of NH_4^+ and NO_3^- in aqueous solution, especially for the biochar prepared at 400°C. Furthermore, the aged biochars showed relatively stronger ability to retard NH_4^+ transportation into the deep layers of soil column

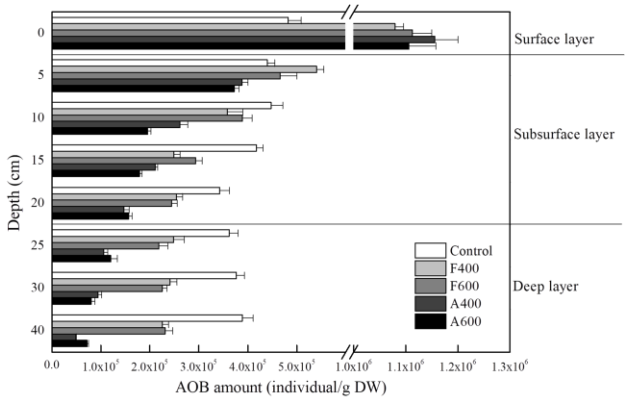

Fig. 6: The profile of AOB amount of the layered soil samples in columns after leaching

compared with the fresh biochars.

Aging typically results in the increased amount of carboxyl functional group on the biochar surface (Lin *et al.* 2012; Sorrenti *et al.* 2016), which coincides with a decrease of biochar pH. In agreement with our study, Olivier (2011) showed that the acidic oxygen-containing functional group content of biochar increased after oxidized by H_2O_2, promoting more surface acid sites formation on biochar surface. Similar trends were also observed in other studies of field-weathered biochars (Joseph *et al.* 2010; Jones *et al.* 2012) and laboratory-aged biochar (Yao *et al.* 2010). However, both carbonyl and phenolic hydroxyl functional groups on the biochar surface were decreased. Correspondingly, Wiedner *et al.* (2015) also indicated that the phenolic groups of three composted biochars decreased up to 22%. Moreover, aging influences the cation exchange capacity (CEC) of biochar-amended soil (Steiner *et al.* 2007; Major *et al.* 2010), which may influence the adsorption of inorganic N in soil.

For both NH_4^+ and NO_3^-, the aged maize straw-derived biochar showed stronger adsorption capacity than fresh biochar, especially for the biochar prepared at 400°C. In accordance with our study, Singh *et al.* (2010) also suggested that the N sorption capacity of biochar increases over time due to surface oxidation. The reason for this phenomenon would be aging caused increases in both CEC and anion exchange capacity (AEC), and specific surface area, so they are thus likely to adsorb large amounts of NH_4^+ and NO_3^- (Bakshi *et al.* 2016). However, other study also showed that the AEC of biochar decreases rapidly on their oxidation (Cheng *et al.* 2008) or did not change significantly with aging (Lawrinenko *et al.* 2016). The inconsistent effect of aging on AEC of biochar may come from the different feedstock, charring temperature and techniques during biochar production.

Both the fresh and aged maize straw-derived biochar inhibited NH_4^+ and NO_3^- leaching from the calcareous soil column compared with control in our study. However, A400 and A600 showed relatively stronger retention ability than F400 and F600 to postpone inorganic N leaching peak occurring, especially for NH_4^+ (Fig. 3 and 4). The reason for this phenomenon may be the enhanced adsorption ability of biochar after aging as shown in our study (Fig. 1 and 2). Consistent with our study, Singh *et al.* (2010) speculated that the increased effectiveness of wood or poultry manure biochars in reducing NH_4^+ leaching over time was due to increased adsorption capacity of biochars through oxidative reactions on the biochar surfaces with aging.

Furthermore, the profiles of the potential ammonia-oxidation rate (PAR) and ammonia-oxidizing bacteria (AOB) amount of the layered soil samples in columns at the end of the leaching experiment in our study also indicated that the aged biochars showed relatively stronger ability to hold NH_4^+, retarding NH_4^+ transportation into the deep layers of soil column (Fig. 5 and 6). In the surface layer of soil column (0–2 cm), both PAR and AOB amount of the aged biochar-amended soil were much larger than that of fresh biochar amended. Given that NH_4^+ is the substrate of AOB and the reactant of nitrification process, the results indicated that the aged biochars possessed relatively stronger NH_4^+ holding capacity. Moreover, in the subsurface and deep layers of soil column (below the depth of 5 cm), both PAR and AOB amount of the aged biochar treatments were much smaller than that of fresh biochar amended, and the difference became larger and larger as depth increasing, indicating the aged biochar retarded NH_4^+ transportation into the deep layers of soil column.

During the leaching experiment, both the fresh and aged biochars postponed NH_4^+ leaching peak occurring, while NO_3^- leaching peak of the aged biochars treatment occurred at the same leaching event as control, and the fresh biochars treatment even brought the NO_3^- leaching peak forward compared with control (Fig. 3–4). The obvious different performance of NH_4^+ and NO_3^- leaching from the calcareous soil columns amended with biochars in our study may result from the different biochar adsorption abilities of NH_4^+ and NO_3^-. Our study showed that the adsorption ability of NH_4^+ of either the fresh or aged biochars was 7.50–10.6 times more than that of NO_3^-. Concurrently, Kameyama *et al.* (2012) also concluded that NO_3^- was only weakly adsorbed onto biochar compared with NH_4^+, and it could be desorbed by water infiltration.

Conclusion

Aging process decreased the pH and mean pore size but increased the carboxyl amount and specific surface area of the maize straw-derived biochars. The aged biochar prepared at 400°C showed the strongest adsorption ability on both NH_4^+ and NO_3^-, while the fresh biochar prepared at 600°C showed the weakest adsorption ability on inorganic N.

All the four kinds of biochars inhibited the leaching of NH_4^+ and NO_3^- from the calcareous soil column compared with control. Moreover, the aged biochars showed much

stronger ability than fresh biochars to delay the leaching peak occurring. The distribution profiles of potential ammonia-oxidation rate and AOB amount in soil column indicated that the aged biochars possessed relatively stronger ability to retain NH_4^+ transportation into the deep layers of soil column compared with the fresh biochars. In all, the spontaneous aging process enhanced the inorganic N adsorption capacity and retention ability of maize straw-derived biochars.

Acknowledgements

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