



Effects of Sugarcane Bagasse Biochar on Ammonium and Nitrate Adsorption and Leaching in a Japanese Tropical Soil Cropped with Japanese Mustard Spinach (*Brassica rapa*)

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Authors' contributions

This work was carried out in collaboration among all authors. Author SK conceptualized the study, did study investigation, performed methodology, did formal analysis, validation, data curation, wrote, reviewed and edited the manuscript. Author YK investigated the study, reviewed and edited the manuscript. Author SS conceptualized and investigated the study, performed methodology, did data validation, reviewed and edited the manuscript and supervised the study. All authors read and approved the final manuscript.

Article Information

DOI: <https://doi.org/10.9734/ajsspn/2024/v10i3357>

Open Peer Review History:

This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: <https://www.sdiarticle5.com/review-history/121319>

Original Research Article

Received: 10/06/2024

Accepted: 13/08/2024

Published: 19/08/2024

ABSTRACT

This study investigated the dynamics of ammonium-nitrogen ($\text{NH}_4^+\text{-N}$) and nitrate-nitrogen ($\text{NO}_3^-\text{-N}$) adsorption and leaching in a Japanese tropical soil amended with sugarcane bagasse biochars (SBBs) in the presence of plant. Adsorption and column leaching studies were conducted in a

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laboratory in Japan, and the column study was performed for 21 days. Biochar was produced from sugarcane bagasse at the maximum pyrolysis temperatures of 400°C (SBB400) and 800°C (SBB800) for use in the experiments. Adsorption isotherms for $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ were developed for soil only, SBB400-amended soil, and SBB800-amended soil. Column leaching study included 6 treatments: fertilizer only, fertilizer and plant, fertilizer and SBB400, fertilizer and SBB400 and plant, fertilizer and SBB800, fertilizer and SBB800 and plant. This study showed that soil and SBBs-amended soils fitted well into the Langmuir adsorption model for $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ ($r^2= 0.983\text{--}0.994$ and $0.956\text{--}0.970$, respectively). Application of SBBs to soil significantly decreased cumulative $\text{NH}_4^+\text{-N}$ leached from the soil ($P < 0.05$) because of increased adsorption capacity due to high acid functional groups and increased soil water holding capacity (WHC) due to high specific surface areas and pore volumes, regardless of the presence of plant. However, the SBBs application did not affect the adsorption capacity for $\text{NO}_3^-\text{-N}$ because of negatively charged surfaces. However, cumulative $\text{NO}_3^-\text{-N}$ leached was significantly reduced ($P < 0.05$) due to increased soil WHC, regardless of the presence of plant. Therefore, more soil water contents retained and less $\text{NO}_3^-\text{-N}$ leached from the soil may have contributed to greater plant growth with the SBBs application. This study showed that the SBBs application to soil could enhance adsorption capacity for $\text{NH}_4^+\text{-N}$ but not for $\text{NO}_3^-\text{-N}$, nevertheless increase soil WHC and reduce leaching of both $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$, thus contributed to increased plant growth.

Keywords: Column leaching; langmuir; point of zero charge; surface functional groups.

1. INTRODUCTION

Sound fertilizer management on agricultural lands is one of the most crucial practices for high yields, high cost performance, and low environmental impacts. However, farmers often apply more amounts of fertilizer, particularly nitrogen (N), than amounts required for the maximum crop growth [1]. As a result, decrease in long-term crop yields, low N utilization efficiency demanding high fertilizer cost, and severe environmental pollution particularly caused by nitrate-nitrogen ($\text{NO}_3^-\text{-N}$) in watersheds may occur [2]. It is critical to reduce $\text{NO}_3^-\text{-N}$ leaching from agricultural fields to watersheds to reduce and prevent environmental pollution. It has been shown that increasing soil water retention capacity [3], enhancing soil microbial activity for immobilization [4], and increasing soil $\text{NO}_3^-\text{-N}$ adsorption capacity [5] are effective practices to reduce $\text{NO}_3^-\text{-N}$ leaching to watershed.

Biochars, when incorporated into soils, have been shown to increase soil water retention capacity, enhance soil microbial activity for immobilization, and increase soil $\text{NO}_3^-\text{-N}$ adsorption capacity [6,7,8]. Consequently, $\text{NO}_3^-\text{-N}$ leaching has shown to be reduced by incorporating biochars to the soil [9]. It was shown that $\text{NO}_3^-\text{-N}$ leaching from biochar- and biosolids-amended soils was reduced to levels equivalent to or below control (no amendments) [10]. On the other hand, there have been studies that showed an increase in $\text{NO}_3^-\text{-N}$ leaching

despite a decrease of ammonium-nitrogen ($\text{NH}_4^+\text{-N}$) leaching when biochars were incorporated in the soil [11]. It has been reported that the application of 0.5% (w/w) biochar to the surface soils reduced cumulative $\text{NH}_4^+\text{-N}$ leaching by 15.2% [12]. It appears that the effects of the biochar application to soils on $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ adsorption and leaching behaviors largely depend on different physicochemical properties of the soils and biochars involved. Of those properties, adsorption capacity of the biochar for $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ may be one of the determining factors, and greatly varies particularly by pyrolysis temperature of the biochar [13].

However, only a few studies have investigated the ability and mechanism of the biochar to retain $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ based on their adsorption capacity for biochars with different pyrolysis temperatures. In addition, $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ adsorption and leaching behaviors in soils when cropped with plants after the biochar application are not well understood. Therefore, the objectives of this study focused on clarification of the dynamics of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ adsorption and leaching in a Japanese tropical soil amended with biochars derived from sugarcane bagasse under the presence of plant.

2. MATERIALS AND METHODS

2.1 Preparation of Soil and Biochar

A dark red soil classified as Typic Hapludalf was collected from a fallow field (15 cm surface layer)

in Miyako Island, Okinawa Prefecture, Japan. After transferred to the laboratory in Tokyo, some were frozen in a freezer (-30°C) until further analyses, and some others were passed through a 10 mm sieve without being dried for the column leaching experiment. The remaining samples were dried in an oven at 45°C , passed through a 2 mm sieve, and stored until further analyses.

The biochar used in this study was produced using sugarcane (*Saccharum* L) bagasse collected from a sugar factory in Miyako Island. Sugarcane bagasse biochar (SBB) was pyrolyzed at the maximum temperatures of 400°C (SBB400) and 800°C (SBB800) under limited oxygen condition. Both SBBs were sieved by 150–300 μm size for characterization and 2 mm size for adsorption experiments and column leaching experiment.

2.2 Characterizations of Soil and Biochar

The pH and electrical conductivity (EC) of the soil sample were determined in a 1:2.5 and 1:5 soil:water suspension, respectively. Soil $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and nitrite-nitrogen ($\text{NO}_2^-\text{-N}$) were extracted from 3.0 g of the thawed field-moist soil with 30 mL of 2 mol L^{-1} KCl solution in a centrifuge tube [14]. The concentration of $\text{NH}_4^+\text{-N}$ in the extractant was determined by an indophenol blue method [15] using a spectrophotometer (U-5100, HITACHI) at 640 nm. The concentrations of $\text{NO}_3^-\text{-N}$ and $\text{NO}_2^-\text{-N}$ were determined by a cadmium-copper column reduction method [15] using an auto analyzer (SWAAT, BL-TECH) at 550 nm. Total carbon (TC) and total N (TN) of the soil were analyzed by the dry oxidation method [16] with a CHN recorder (A1110, CE Instrument).

The pH of the biochars was determined in a 1:100 biochar:hot deionized water suspension [17]. The TC and TN of the biochars were analyzed by the dry oxidation method. Biochar $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and $\text{NO}_2^-\text{-N}$ were analyzed with the same procedure as the soil samples. The point of zero charge (pH_{PZC}) of the biochars was determined by a mass titration method [18]. Analysis by thermal gravimetric analysis (TGA) was employed for determination of volatile matter, fixed C, and ash contents of the biochars using a simultaneous differential thermogravimetry (Q600, TA Instruments; [19]). Surface functional groups (SFGs) were analyzed by Boehm titration method for determination of acid and basic SFGs [20]. The acid SFGs consist of carboxyl, lactone, and hydroxyl groups.

Surface area and pore size distribution of the biochars were measured by N_2 gas adsorption at 77K using Advanced Systems Analysis Program (ASAP 2010, Micromeritics). The Brunauer Emmett Teller (BET) method was used to estimate the surface areas (S_{BET}) [21]. Total pore volume (V_p) was estimated from the amount of N_2 adsorbed at a relative pressure. Average pore size micropore (D_p) was estimated from V_p and S_{BET} by the following equation (1), assuming a cylindrical pore shape.

$$D_p = \frac{4000V_p}{S_{\text{BET}}} \quad (1)$$

Micropore volume (V_{mic}) was estimated by the t-plot method. Mesopore (V_{meso}) and macropore (V_{mac}) volumes were estimated by difference of V_p and V_{mic} .

2.3 Adsorption Isotherms Experiment

Adsorption isotherms for $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ were developed on soil only, SBB400-amended soil, and SBB800-amended soil, respectively. The SSBs were amended at a rate of 2.5% (w/w), and all experiments were performed in triplicate. Mixtures of 2.0 g of soil without or with 0.05 g of biochar and 40 mL of $\text{NH}_4^+\text{-N}$ or $\text{NO}_3^-\text{-N}$ solutions with 10, 20, 40, 60, 160, and 240 mg $\text{NH}_4^+\text{-N}$ L^{-1} or 10, 20, 40, 60, and 100 mg $\text{NO}_3^-\text{-N}$ L^{-1} were shaken at 160 strokes min^{-1} at room temperature ($25^{\circ}\text{C} \pm 1^{\circ}\text{C}$) for 200 or 60 min, respectively (determined from the previously performed kinetics experiment; data not shown). The suspension was filtered through Whatman No.1 filter paper and 0.45 μm pore size nylon membrane filter. The concentrations of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ in the filtrate were analyzed by indophenol blue method using the spectrophotometer at 640 nm and ultraviolet spectrophotometer method at 220 nm, respectively [22].

Adsorption isotherm data for $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ were fitted to Langmuir isotherm equation (2) [23] and Freundlich isotherm equation (3) [24].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

$$q_e = K_F C_e^{1/n} \quad (3)$$

Where q_e is the amount adsorbed on the adsorbent at equilibrium status (mg kg^{-1}), K_L is the adsorption isotherm constant (L mg^{-1}), q_m is

the maximum adsorption capacity (mg kg^{-1}), K_F is Freundlich constant, $1/n$ is non-linear constant, and C_e is equilibrium concentration of solutions (mg L^{-1}).

2.4 Column Leaching Experiment

PVC columns were repacked with 3.8 kg (on dry weight based) of the field-moist soil, pre-sieved by 10 mm size, to the height of 20 cm. Glass microfiber filter (Whatman GF/A filter) and pebbles were placed on the bottom of the columns to prevent soil loss during the experiment. Chemical fertilizers 905–706–233 kg N–P₂O₅–K₂O ha⁻¹ and/or each of SBB400 and SBB800 (at a rate of 2.5% w/w) were mixed thoroughly in the top 10 cm layer of the repacked soil. After the column was repacked, 2.0 L of distilled water was applied using a peristaltic pump to the maximum water holding capacity (WHC). A total of 9 seeds of Japanese mustard spinach (*Brassica rapa*) were planted per column, and thinned to 5 individuals after 6 days after germination. The experiment was performed in triplicate with the following treatments: (1) soil with chemical fertilizers added (C), (2) soil with chemical fertilizers added and planted (P), (3) soil with chemical fertilizers and SBB400 added (C400), (4) soil with chemical fertilizers and SBB400 added and planted (P400), (5) soil with chemical fertilizers and SBB800 added (C800), and (6) soil with chemical fertilizers and SBB800 added and planted (P800).

Leaching events were started a day after thinning of the plant. Five-hundred milliliters of distilled water were introduced on the top of each column for one hour using the peristaltic pump at every leaching event. The column was leached in every 3 days for 21 days. Leachate volume and pH of the leachates were recorded immediately after the collection. Leachates pH was adjusted between 2 and 3 by adding a few drops of concentrated sulfuric acid to suppress microbial activity, and the leachates were stored in a refrigerator at 5°C until further analyses. The NH₄⁺-N in the leachates were determined by the indophenol blue method, and NO₃⁻-N and NO₂⁻-N were determined by the cadmium-copper column reduction method [22].

2.5 Statistical Analyses

Statistical analyses were performed using the statistical software, Statistica 6.1 (StatSoft). Treatment effects were analyzed by one-way analysis of variance (ANOVA). A Tukey honestly

significant difference (HSD) analysis was performed for multiple comparisons of the treatment effects. Statistical significances were determined at $P = 0.05$.

3. RESULTS AND DISCUSSION

3.1 Soil and Biochars Characterizations

The dark red soil used in this study from Miyako Island had a near neutral pH 6.77 (Table 1), which was in the range of pH of similar soils found elsewhere, where surface (0 to 15 cm) soils ($n = 25$) collected from Miyako Island with pH 6.6 [25]. However, it has been reported that a calcareous dark red soil had a high pH value (8.0) because of the presence of many coral limestone fragments that contributed to calcium ions [6]. It appeared that pH of the dark red soil from Miyako Island could vary from neutral to alkaline depending on sampling locations. Total C (14.6 g kg⁻¹) and C/N ratio (9.01) of the soil used in this study were similar with the previous study (13.4 g kg⁻¹ and 8.38, respectively [6]).

Both pH of SBB400 and SBB800 used in this study were alkaline being 8.45 and 9.14, respectively (Table 2), which were in the range of pH values found elsewhere, where sugarcane bagasse collected from Miyako Island was pyrolyzed at 400°C and 800°C showing pH of 5.0 and 9.8, respectively [6]. It was shown that SBBs pyrolyzed at 300°C, 450°C, and 600°C had pH values of 7.2, 7.9, and 7.9, respectively [26]. The pH_{PZC} values of SBB400 and SBB800 were 7.38 and 8.18, respectively (Fig. 1; Table 2), and lower than respective pH values, which indicated that both SBB400 and SBB800 surfaces were negatively charged. It was shown that the biochar surface was positively and negatively charged when the pH_{PZC} was higher and lower than pH of the biochar surface, respectively [27]. Therefore, it was suggested that SBB400 and SBB800 used in this study might possess cation exchange capacity due to negatively charged surfaces.

Volatile matter, fixed C, and ash contents of SBB400 were 26.6%, 53.1%, and 20.3%, respectively, and those of SBB800 were 7.40%, 18.9%, and 73.7%, respectively (Fig. 2; Table 2). Higher pyrolysis temperature yielded lower volatile matter of SBBs, which was in line with the previous studies [28]. However, higher pyrolysis temperatures are expected to produce biochars with higher fixed C contents [29]. One of the reasons why fixed C

content of SBB800 was lower and ash content was higher than those of SBB400 could be attributed to biochar with ash content of more than 20% generally tends to have a decreased amount of fixed C after pyrolysis [30].

Table 1. Selected physicochemical properties of the soil used

pH [†]	EC	TC [‡]	TN [‡]	C/N	NH ₄ ⁺ -N [§]	NO ₃ ⁻ -N [§]	NO ₂ ⁻ -N [§]	Bulk density	Porosity
	μS cm ⁻¹	g kg ⁻¹	g kg ⁻¹		mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	g cm ⁻³	%
6.77	24.6	14.6	1.62	9.01	0.321	8.51	0.160	1.08	56.8

[†] pH (soil:water = 1:2)

[‡] Dumas dry oxidation method [16]

[§] Extracted by 2 mol L⁻¹ KCl [14]

Table 2. Selected Chemical Properties of the Bagasse Biochars used

Biochar [†]	pH [‡]	pH _{PZC} [§]	TC [¶]	TN [¶]	C/N	NH ₄ ⁺ -N [#]	NO ₃ ⁻ -N [#]	NO ₂ ⁻ -N [#]
			g kg ⁻¹	g kg ⁻¹		mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹
SBB400	8.45	7.38	500	9.28	53.8	18.4	2.12	0.01
SBB800	9.14	8.18	603	10.1	59.7	7.20	1.11	0.09

Biochar [†]	Volatile matter ^{††}	Fixed C ^{††}	Ash ^{††}	Carboxyl	Lactone	Hydroxyl	Acid SFGs ^{††}	Basic SFGs ^{††}
	%	%	%	mmol g ⁻¹	mmol g ⁻¹	mmol g ⁻¹	mmol g ⁻¹	mmol g ⁻¹
SBB400	26.6	53.1	20.3	0.26	0.26	0.98	1.50	0.10
SBB800	7.40	18.9	73.7	0.11	0.15	0.59	0.85	0.20

[†] SBB400 and SBB800 are bagasse biochar pyrolyzed at 400°C and 800°C, respectively.

[‡] pH (biochar:hot water = 1:100)

[§] Mass titration method [18]

[¶] Dumas dry oxidation method [16]

[#] Extracted by 2 mol L⁻¹ KCl [14]

^{††} Measured by simultaneous differential thermogravimetry [19]

^{††} SFGs: surface functional groups. Boehm titration method [20]

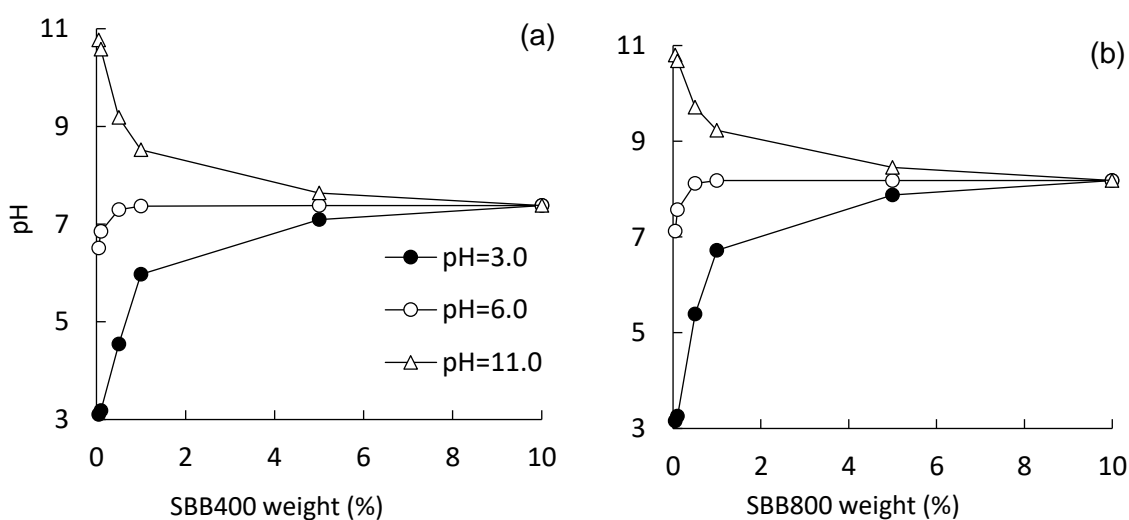


Fig. 1. (a) Mass titration curves for SBB400. (b) Mass titration curves for SBB800
 SBB400 and SBB800 are bagasse biochar pyrolyzed at 400°C and 800°C, respectively

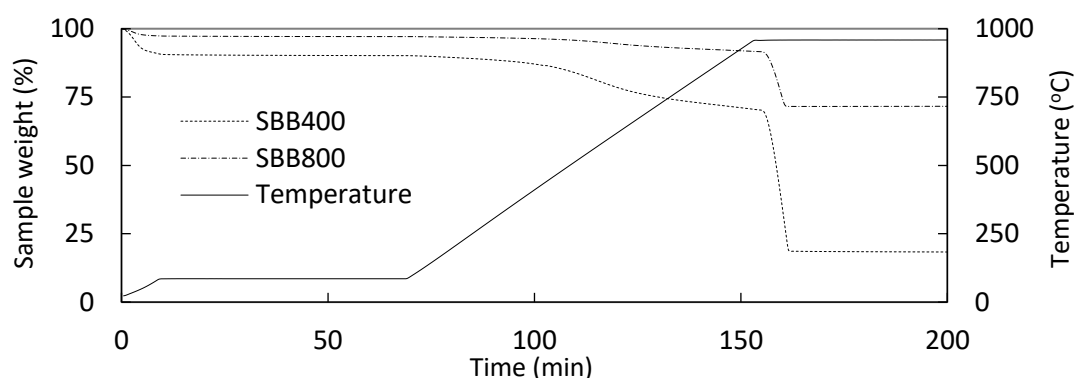


Fig. 2. Thermal gravimetric curves for SBB400 and SBB800
SBB400 and SBB800 are bagasse biochar pyrolyzed at 400°C and 800°C, respectively

Table 3. Selected Physical Properties of the Bagasse Biochars used

Biochar [†]	Micropore surface area (S_{mic}) $m^2 g^{-1}$	Meso¯opore surface area ($S_{meso\&mac}$) $m^2 g^{-1}$	BET surface area (S_{BET}) [‡] $m^2 g^{-1}$	
SBB400	162	45.0	207	
SBB800	215	68.8	284	
Biochar [†]	Micropore volume (V_{mic}) $cm^3 g^{-1}$	Meso¯opore volume ($V_{meso\&mac}$) $cm^3 g^{-1}$	Total pore volume (V_p) $cm^3 g^{-1}$	Average pore diameter (D_p) nm
SBB400	0.075	0.046	0.121	2.33
SBB800	0.099	0.045	0.144	1.97

[†] SBB400 and SBB800 are bagasse biochar pyrolyzed at 400°C and 800°C, respectively.

[‡] Brunauer Emmett Teller (BET) method [21]

It was shown that the carboxyl and hydroxyl groups were dominant contributors in the adsorption of NH_4^+ -N on biochar [31]. The total acid functional groups including the carboxyl, lactone, and hydroxyl groups of SBB400 (1.50 mmol g^{-1}) were higher than those of SBB800 (0.85 mmol g^{-1}) possibly due to its higher volatile matter content (Table 2; [32]). It appeared that SBB400 used in this study could have a higher NH_4^+ -N adsorption capacity compared with SBB800. On the other hand, the total basic functional groups of SBB800 (0.20 mmol g^{-1}) were slightly higher than those of SBB400 (0.10 mmol g^{-1}). This indicated that SBB800 used in this study could have a higher NO_3^- -N adsorption capacity than SBB400. The NO_3^- -N adsorption on the biochar surfaces increased with increasing total basic surface functional groups [33].

The BET surface area of SBB800 ($284 \text{ m}^2 \text{ g}^{-1}$) was higher than that of SBB400 ($207 \text{ m}^2 \text{ g}^{-1}$) due likely to higher pyrolysis temperature (Table 3). This result was in line with the previous studies that demonstrated that raising the pyrolysis temperature increased S_{BET} of biochar, derived

from various sources such as rice husk, rice straw, applewood chips, and oakwood, which attributed to increased evolution of volatile matters thus increased pore structures in the biochars [34]. This study also showed that the micropore in SBB800 was more developed than in SBB400 due to higher pyrolysis temperature. Therefore, the greater surface areas, the higher micropore volumes, and the lower average pore diameters were developed in SBB800 than SBB400, suggesting that SBB800 could have higher WHC than SBB400.

3.2 Ammonium and Nitrate Adsorption capacity of Soil and Biochar-Amended Soils

All adsorption isotherms of the soils without or with SBBs used in this study for NH_4^+ -N were fitted to Langmuir adsorption model (Fig. 3a; $r^2 = 0.983\text{--}0.994$; Table 4). It was shown that the application of both SBBs increased the adsorption capacity for NH_4^+ -N with the maximum adsorption capacities being 588, 833, and 714 mg kg^{-1} for soil, SBB400-amended soil, and SBB800-amended soil, respectively (Table

4). It was evident that the SBB application contributed to increased $\text{NH}_4^+\text{-N}$ adsorption capacity. It was shown that 9 out of 13 biochars with different feedstock including sugarcane bagasse and pyrolysis temperatures ranging from 300°C and 600°C showed positive $\text{NH}_4^+\text{-N}$ adsorption capacity (determined as positive removal rate from one concentration solution up

to 15.7%; [26]). Although the application rate was same (2.5% w/w) for both SBBs in this study, the maximum adsorption capacity was greater with SBB400 than with SBB800 possibly because of higher $\text{NH}_4^+\text{-N}$ adsorption capacity due to greater amounts of the total acid functional groups in SBB400 than in SBB800 (Table 2).

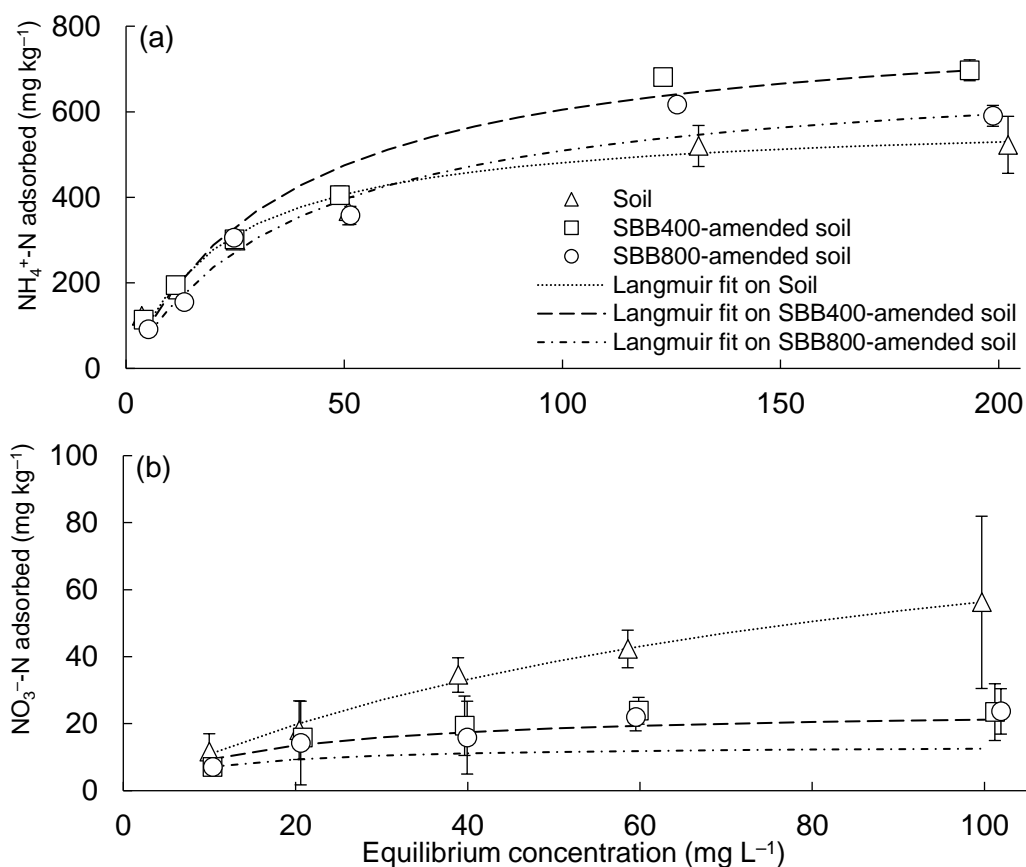


Fig. 3. (a) Adsorption isotherms for $\text{NH}_4^+\text{-N}$ on soil only, SBB400-amended soil, and SBB800-amended soil. (b) Adsorption isotherms for $\text{NO}_3^-\text{-N}$ on soil only, SBB400-amended soil, and SBB800-amended soil

SBB400 and SBB800 are bagasse biochar pyrolyzed at 400°C and 800°C, respectively

Table 4. Langmuir and Correlation Coefficients for Adsorption Isotherms of Soils without and with SBB400 and SBB800 for $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$

Treatment [†]	K_L (L mg^{-1})	q_m (mg kg^{-1})	r^2
$\text{NH}_4^+\text{-N}$			
Soil	0.0449	588	0.994
Soil with SBB400	0.0264	833	0.983
Soil with SBB800	0.0248	714	0.983
$\text{NO}_3^-\text{-N}$			
Soil	0.0115	105	0.956
Soil with SBB400	0.0404	30.5	0.958
Soil with SBB800	0.0311	31.5	0.970

[†] SBB400 and SBB800 are bagasse biochar pyrolyzed at 400°C and 800°C, respectively

Table 5. Cumulative Leachate volume and Soil water content (0–10 and 10–20 cm) in column soils after leaching experiment, and plant dry weight by plant part

Treatment [†]	Cumulative leachate volume	Soil water content		Dry weight		Total
		0–10 cm	10–20 cm	Below ground	Above ground	
	mL	%	%	g	g	g
Non-planted columns						
C	3040 b	13.0 a	16.5 a	–	–	–
C400	2815 a	21.3 b	17.0 a	–	–	–
C800	2668 a	23.3 b	18.3 a	–	–	–
Planted columns						
P	2294 b	15.4 a	17.9 a	0.317 a	2.61 a	2.92 a
P400	2062 a	19.3 b	17.8 a	0.414 ab	2.57 a	2.99 a
P800	2166 a	19.5 b	15.7 a	0.485 b	2.81 a	3.29 a

[†] C: soil with chemical fertilizers added, C400: soil with chemical fertilizers and SBB400 added, C800: soil with chemical fertilizers and SBB800 added, P: soil with chemical fertilizers added and planted, P400: soil with chemical fertilizers and SBB400 added and planted, and P800: soil with chemical fertilizers and SBB800 added and planted

SBB400 and SBB800 are bagasse biochar pyrolyzed at 400°C and 800°C, respectively
Same letters denote non-significance among treatments by Tukey comparison at $P < 0.05$

Similarly, all adsorption isotherms of the soils without or with SBBs used in this study for NO_3^- -N were also fitted to Langmuir adsorption model (Fig. 3b; $r^2 = 0.956$ – 0.970 ; Table 4), although the amounts of adsorption were much lower than those for NH_4^+ -N. It appears that the application of SBBs did not affect or even lower adsorption capacity for NO_3^- -N possibly because both SBBs used in this study were negatively charged on their surfaces because of the total acid functional groups (Table 2). It was shown that 9 out of 13 biochars tested with pyrolysis temperatures of 300°C–600°C showed negative NO_3^- -N adsorption capacity (determined as negative removal rate from one concentration solution), although some high temperature (600°C) biochars showed positive NO_3^- -N adsorption capacity only up to 2.5% [26]. It could be expected that both SBB800 used in this study did not show NO_3^- -N adsorption capacity possibly because the total basic functional groups might not have been high enough to develop positive charges on the surface (Table 2; [35]).

3.3 Water leaching Behaviors and Plant Dry Weight in Soil and Biochar-Amended Soils

Cumulative leachate volumes after 8 leaching events were summed up to 3040, 2815, and 2668 mL for non-planted columns (C, C400, and C800, respectively) and 2294, 2062, and 2166 mL for planted columns (P, P400, and P800, respectively; Table 5). The leachate volumes were smaller from planted columns than non-planted columns possibly because of

transpiration and absorption by the plants [36]. The cumulative leachate volumes from SBBs-amended columns significantly decreased in comparison with those from soil only column regardless of present of the plant (Table 5). Also, soil water contents after all leaching events were significantly higher in SBBs-treated columns than in soil only column for both non-planted and planted columns particularly in the top layer (0–10 cm; Table 5). These results indicate that the application of SBBs may have caused an increase of the soil WHC due to increased specific surface areas and pore volumes (Table 3). In fact, SBB800 with higher WHC due to greater pore volume (Table 3) contained slightly higher water content than SBB400 did. Similar results were observed in the previous studies that says that the cumulative leachate volumes from columns treated with pine (*Pirus radiata* L.) wood biochar (2.5% w/w) and giant reed (*Arundo donax* L.) biochar (5% w/w), respectively, significantly decreased compared with those from non-treated columns [37,38]. It was shown that the application of a wood biochar pyrolyzed at 600°C could be attributed to increased soil water retention during incubation experiment due to high specific surface area of the biochar added [39].

The soil water contents in the biochar-amended soils were higher than the non-amended soil, which could be attributed to increased soil WHC due to its high micro- and meso-porosities caused by the biochar application [40]. However, when maize (*Zea mays* L.) was cropped in the soil amended with the giant reed biochar for 60

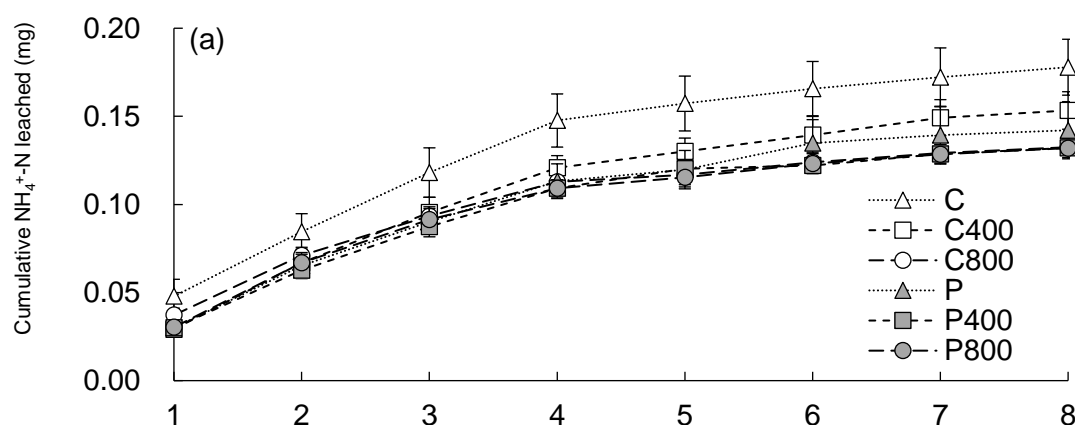
days, the cumulative leachate volume was significantly greater than that from the non-amended soil because it appeared that the biochar application inhibited the plant growth [38]. Another study showed that maize germination was inhibited by the biochar application [41]. On the other hand, in this study, the plant growth both in the belowground and aboveground parts was greater particularly in SBB800-amended soil than the non-amended soil (significantly greater specifically for the belowground; Table 5). This occurred because the plant might have taken up more amounts of water from soil amended with biochar than from soil only.

3.4 Ammonium and Nitrate Leaching Behaviors in soil and Biochar-amended Soils

Cumulative amounts of $\text{NH}_4^+\text{-N}$ leached over 8 leaching events from non-planted columns were 0.18, 0.15, and 0.13 mg column^{-1} , respectively, and from planted columns were 0.14, 0.13, and 0.13 mg column^{-1} , respectively (Fig. 4a). It appears that plant absorption of $\text{NH}_4^+\text{-N}$ caused the lower range of the cumulative $\text{NH}_4^+\text{-N}$ leached from planted columns than that from non-planted columns. Moreover, the application of SBBs resulted in 17% to 28% lower cumulative $\text{NH}_4^+\text{-N}$ leached from non-planted columns and 7% lower from planted columns likely because more $\text{NH}_4^+\text{-N}$ was adsorbed in the soils amended with SBBs compared to soil only (Fig. 3a). Soil $\text{NH}_4^+\text{-N}$ especially in the top layer (0–10 cm) left after the leaching events was greater in SBBs-amended soils than in soil only for both non-planted and planted columns (2.2, 2.8, and 2.6 mg kg^{-1} for C, C400, and C800; 1.7, 2.1, and 2.1 mg kg^{-1} for P, P400, and P800, respectively; Table 6). Also, soil water content especially in the top layer was greater in SBBs-

amended soils than in soil only for both non-planted and planted columns (13.0%, 21.3%, and 23.3% for C, C400, and C800; 15.4%, 19.3%, and 19.5% for P, P400, and P800, respectively; Table 5). It was shown in this study that the reduced $\text{NH}_4^+\text{-N}$ leaching from the soils amended with SBBs could be attributed to increased $\text{NH}_4^+\text{-N}$ adsorption capacity due to high content of the total acid functional groups (Table 2) and increased soil water content with dissolved $\text{NH}_4^+\text{-N}$ regardless of the presence of plant.

Cumulative amounts of $\text{NO}_3^-\text{-N}$ leached over 8 leaching events from non-planted columns were 106, 114, and 87.6 mg column^{-1} , respectively, and from planted columns were 84.1, 76.9, and 63.8 mg column^{-1} , respectively (Fig. 4b). Similarly with $\text{NH}_4^+\text{-N}$, it appears that plant absorption of $\text{NO}_3^-\text{-N}$ caused the lower range of the cumulative $\text{NO}_3^-\text{-N}$ leached from planted columns than that from non-planted columns. However, while the application of SBB400 and SBB800 to planted columns resulted in 8.6% to 24% lower cumulative $\text{NO}_3^-\text{-N}$ leached from soils, respectively, the application of SBB400 and SBB800 to non-planted columns resulted in 8% increase and 17% decrease, respectively, in cumulative $\text{NO}_3^-\text{-N}$ leached from soils. Since SBBs used in this study lowered $\text{NO}_3^-\text{-N}$ adsorption capacity in soils amended with SBBs (Fig. 3b), it appeared that $\text{NO}_3^-\text{-N}$ may have not been adsorbed and leached out from soil amended particularly with SBB400 in non-planted column. The reduced $\text{NO}_3^-\text{-N}$ leaching from the soils amended particularly with SBB800 could be attributed to increased soil water content (0–10 cm; Table 5) containing increased $\text{NO}_3^-\text{-N}$ (0–10 cm; Table 6) through increased soil WHC due to high specific surface areas and pore volumes of SBB800 (Table 3) regardless of the presence of plant.



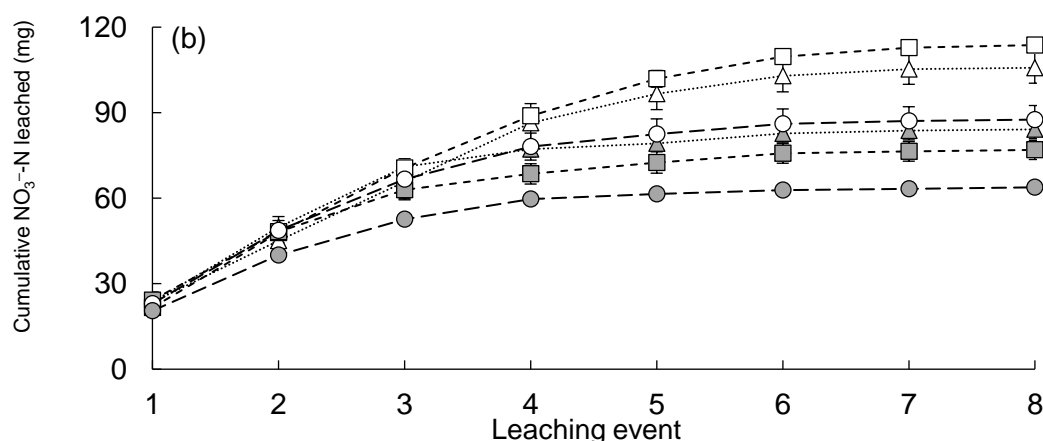


Fig. 4. (a) Cumulative amounts of NH₄⁺-N leached from the columns with 8 leaching events. (b) Cumulative amounts of NO₃⁻-N leached from the columns with 8 leaching events

C: chemical fertilizers, C400: chemical fertilizers and SBB400, C800: chemical fertilizers and SBB800, P: chemical fertilizers and planted, P400: chemical fertilizers, SBB400 and planted, and P800: chemical fertilizers, SBB800 and planted.

SBB400 and SBB800 are bagasse biochar pyrolyzed at 400°C and 800°C, respectively.

Table 6. NH₄⁺-N and NO₃⁻-N concentrations in column soils (0–10 and 10–20 cm) after the leaching event

Treatment [†]	NH ₄ ⁺ -N		NO ₃ ⁻ -N	
	0–10 cm mg kg ⁻¹	10–20 cm mg kg ⁻¹	0–10 cm mg kg ⁻¹	10–20 cm mg kg ⁻¹
Non-planted columns				
C	2.2 a	2.4 b	0.8 a	1.0 b
C400	2.8 b	1.6 a	1.2 a	0.5 a
C800	2.6 b	1.7 a	1.9 b	1.0 b
Planted columns				
P	1.7 a	1.9 a	0.6 a	0.4 a
P400	2.1 b	1.6 a	0.6 a	0.8 b
P800	2.1 b	1.4 a	1.2 b	0.9 b

[†] *C: soil with chemical fertilizers added, C400: soil with chemical fertilizers and SBB400 added, C800: soil with chemical fertilizers and SBB800 added, P: soil with chemical fertilizers added and planted, P400: soil with chemical fertilizers and SBB400 added and planted, and P800: soil with chemical fertilizers and SBB800 added and planted*

SBB400 and SBB800 are bagasse biochar pyrolyzed at 400°C and 800°C, respectively
Same letters denote non-significance among treatments by Tukey comparison at $P < 0.05$

3.5 Effect of Sugarcane Bagasse Biochar Application on Plant Growth

A significant negative correlation was observed between cumulative amounts of NO₃⁻-N leached from soils and the total dry weights of plants grown in the column soils (Fig. 5), which indicated that the reduced NO₃⁻-N leaching caused by the application of SBBs contributed to

the increased plant growth. Biomass production tended to be greater with less cumulative water leached from the soils [42]. Cumulative leachate volumes from soils amended with SBBs were less than that from soil only in this study (Table 5). It appears that the application of SBBs may have contributed to increased water contents, thus reduced water leaching, consequently, increased plant growth.

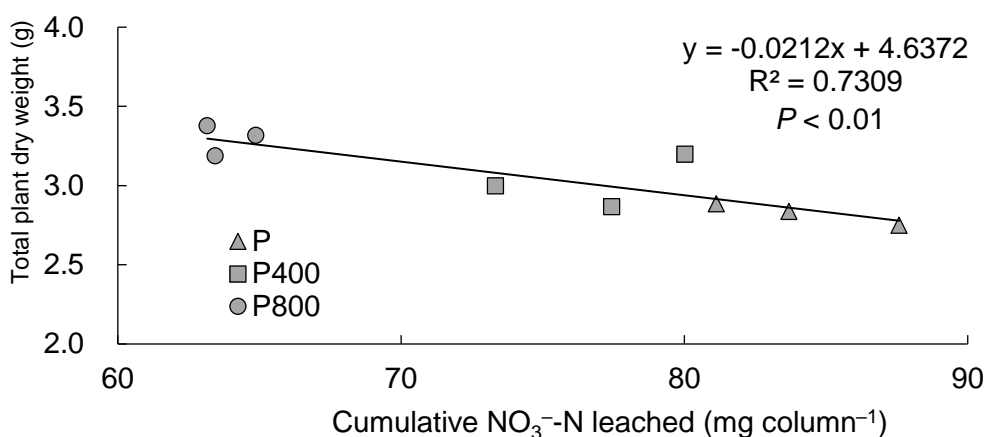


Fig. 5. Relationships between cumulative NO₃⁻-N leached and total plant dry weight grown on soil only, SBB400-amended soil, and SBB800-amended soil
SBB400 and SBB800 are bagasse biochar pyrolyzed at 400°C and 800°C, respectively

4. CONCLUSION

The present study investigated the dynamics of NH₄⁺-N and NO₃⁻-N adsorption and leaching in a Japanese tropical soil amended with SBBs under the presence of plant. The application of sugarcane bagasse biochars significantly decreased cumulative NH₄⁺-N leached from the soil because of increased adsorption capacity through negatively charged surfaces due to high contents of the total acid functional groups and increased soil WHC due to high specific surface areas and pore volumes, regardless of the presence of plant. On the other hand, the application of the SBBs did not affect the adsorption capacity for NO₃⁻-N because of negatively charged surfaces of the SBBs. However, cumulative NO₃⁻-N leached from the soil was significantly reduced mainly because of increased soil WHC, regardless of the presence of plant. More soil water contents retained and less NO₃⁻-N leached from the soil may have contributed to greater plant growth with the SBBs application. The results of this study indicated that the application of the SBBs could enhance adsorption capacity for NH₄⁺-N but not for NO₃⁻-N, however increase soil WHC and reduce leaching of both NH₄⁺-N and NO₃⁻-N, thus contribute to increased plant growth.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

ACKNOWLEDGEMENTS

We thank Dr. Koji Kameyama in National Institute for Rural Engineering for providing sugarcane bagasse, advice, and suggestions especially during experimental preparation. The soil sample was provided by Okinawa Prefectural Agricultural Research Center in Miyako Island through help of Dr. Naoko Miyamaru, to whom we are grateful. The sugarcane bagasse biochars were produced by Nakayasu Ltd., and we thank Mr. Shogo Nakajima for his great support.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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