Effect of sugarcane-bagasse biochar on retention of ammonium and nitrate in soils cropped with Komatsuna (*Brassica rapa*)

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Introduction

Treatment of sugarcane bagasse

There has been an increasing trend towards more efficient utilization of sugarcane bagasse (SB). One of the efficient utilizations of SB is to use as adsorbent in carbonized form biochar (SBB) produced from pyrolysis of biomass.

Biochar as an adsorbent

Biochar can adsorb ammonium, nitrate, and phosphate(1). However, adsorption capacity depends on physicochemical properties of biochar which are mainly determined by feedstock and carbonization temperature(2).

Nitrogen (N) loss from agricultural soil

The overuse and low use efficiency of N fertilizers have caused serious environmental problems(3). N leaching from agricultural soils is the main N loss pathway in forms of ammonium and nitrate(4).

Objectives

To investigate the effect of sugarcane-bagasse biochar on retention of ammonium and nitrate in soils cropped with Komatsuna (*Brassica rapa*).

- Physicochemical properties of SBB
- Ammonium and nitrate adsorption capacity of SBB
- Ammonium and nitrate leaching in column with Komatsuna

Materials and Methods

Study 1. Physicochemical Properties Study

- **Pore structure analysis** (Micromeritics ASAP 2020)
  - Brunauer-Emmett-Teller (BET) surface area
  - Pore size distribution
- **Thermogravimetric analysis** (SDT Q600)
  - Ash, volatile matter, and fixed carbon
- **Point of zero charge** (Mass titration)
- **The surface functional groups** (Boehm titration)

Study 2. Adsorption Study

- **Adsorption kinetics** (Pseudo-second -order equation ①)
- **Adsorption isotherm** (Langmuir equation ②)

$$q_t = \frac{tkq_e^2}{1+tK_2q_e} \cdots ①$$

$$q_e = q_m\frac{K_LC_e}{1+K_LC_e} \cdots ②$$

q_t: Amount of adsorption at time t
q_e: Amount of adsorption at equilibrium status
k : Adsorption kinetic constant

q_e: Amount of adsorption at equilibrium status
q_m: Amount of maximum adsorption
k_L : Adsorption isotherm constant
C_e: Equilibrium concentration of solution

- **Analytical Parameters**
  - Ammonium (Indophenol blue methods @640 nm)
  - Nitrate (Ultraviolet spectrophotometric methods @220 nm)

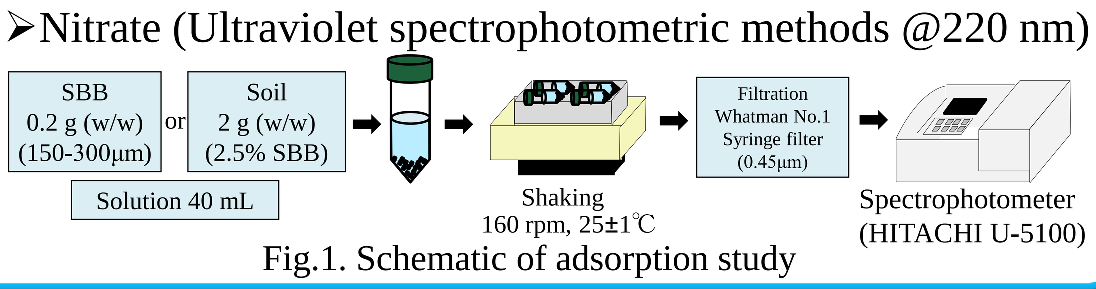

Fig.1. Schematic of adsorption study

Study 3. Column Leaching Study

- **Column** (PVC, D_i=15 cm, H=25 cm)
- **Metering liquid feeding pump** (EYELA, SMP-23 model)
  - 500 mL (500mL/hr, once every 3 days)
- **Experimental treatments** (plant = Brassica rapa)
  - ① Soil (S)
  - ② Soil+Chem. Fertil. (C)
  - ③ C+Plant (CP)
  - ④ C+SBB400 (C4)
  - ⑤ C+SBB800 (C8)
  - ⑥ C4+Plant (P4)
  - ⑦ C8+Plant (P8)

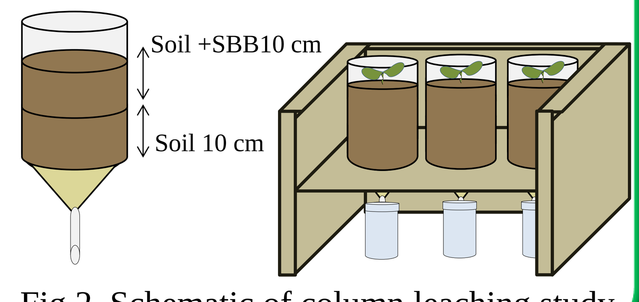

Fig.2. Schematic of column leaching study

Soil and Biochar

- **Calcareous dark red soil** (Miyako island, Okinawa, Japan)
  - Fallow soil (0-15 cm) (24º46′ N, 125º19′E)
  - Oven dried (45°C) with 2 mm sieved for adsorption study
  - Moist soil with 10 mm sieved for leaching study
- **Sugarcane-bagasse biochar** (Miyako island)
  - Carbonized under oxygen limitation
  - Carbonization temperature with 400ºC (SBB400) and 800ºC (SBB800)
  - Oven dried (105°C) with 150-300 μm sieved for physicochemical properties study and adsorption study
  - Oven dried (105°C) with 2 mm sieved for leaching study

Results and Discussions

Study 1. Physicochemical Properties Study

Table 1. Chemical properties of soil and SBBs.

Parameter	Unit	Soil	SBB400	SBB800
pH		6.8	8.5	9.1
EC	μS cm^{-1}	24.6	n.d.	n.d.
T-N	g kg^{-1}	1.6	9.3	10.1
T-C	g kg^{-1}	14.6	499.6	602.8
NH^+_4-N	mg kg^{-1}	0.3	n.d.	n.d.
NO^-_3-N	mg kg^{-1}	8.5	2.1	1.1
NO^-_2-N	mg kg^{-1}	0.2	0.0	0.1
pH_{pzc}		n.d.	7.4	8.2
Volatile matter	%	n.d.	26.6	7.4
Fixed carbon	%	n.d.	53.1	18.9
Ash	%	n.d.	20.3	73.7
Acidic functional group	mmol g^{-1}	n.d.	1.5	0.8
Basic functional group	mmol g^{-1}	n.d.	0.1	0.2

Table 2. Physical properties of SBBs.

Parameter	Unit	SBB400	SBB800
BET surface area (S_{BET})	m^2 g^{-1}	207.3	283.9
Micropore surface area	m^2 g^{-1}	162.3	215.0
Total pore volume (V_p)	cm^3 g^{-1}	0.121	0.144
Micropore volume†	cm^3 g^{-1}	0.075	0.099
Average pore diameter (D_p)‡	nm	2.33	1.97

† T-plot method ‡ $D_p = 4000*V_p*S_{BET}^{-1}$

- **SBB400 had a high acid functional groups (AFGs; Table 1) → NH_4^+-N adsorption capability via cation exchange(5)**
- **SBB800 had high total pore and micropore volumes (Table 2) → High water-holding capacity in pores**

Study 2. Adsorption Study

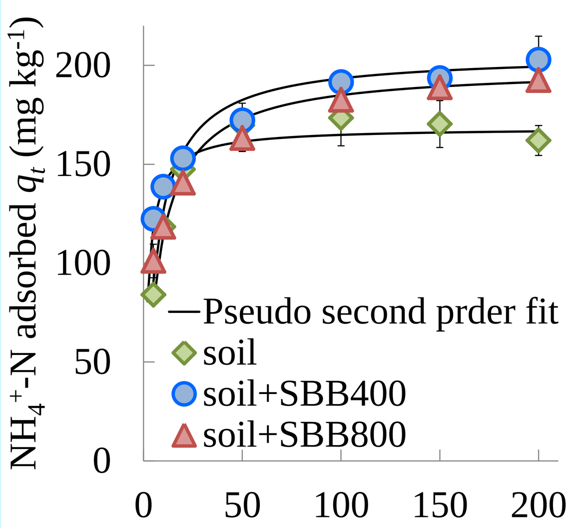

Fig.3. Adsorption kinetics of NH_4^+-N on calcareous dark red soil with SBB400 and SBB800.

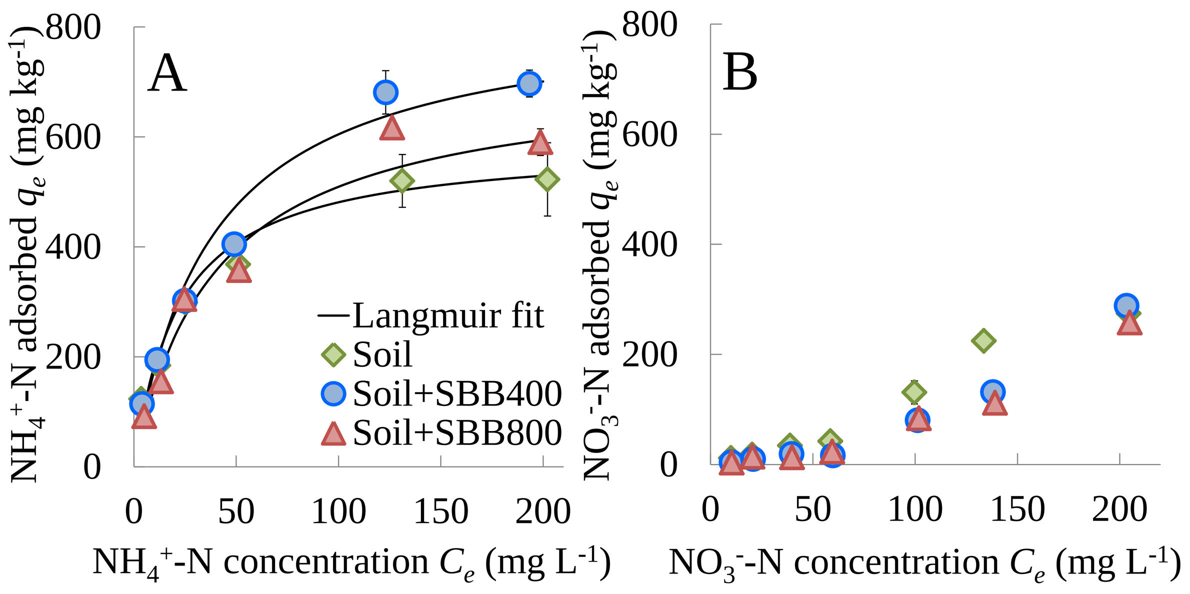

Fig.4. Adsorption isotherms of A: NH_4^+-N and B: NO_3^--N on calcareous dark red soil with SBB400 and SBB800.

Table 3. Langmuir isotherm model parameter for NH^+_4-N adsorption.

	Langmuir isotherm model		
	K_L (mg kg^{-1})	q_m (L mg^{-1})	r^2
Soil	0.45	588.23	0.994
Soil + SBB400	0.03	833.33	0.983
Soil + SBB800	0.02	714.32	0.983

- **NH_4^+-N adsorption process on SBB400 and soil → Electrostatic adsorption (Fig.3 and Fig.4.A)**
- **Soil+SBB400 had a higher NH_4^+-N adsorption capacity (Fig.4.A) than soil+SBB800.**
  → High AFGs content
- **NO_3^--N adsorption result for soil+SBBs showed weak adsorption behavior.**
  → Nitrate is considered to be only weakly attracted to the soil(7).
  Soil+SBB800 were negatively-charged (Table 1. pH_{pzc})

Study 3. Column Leaching Study

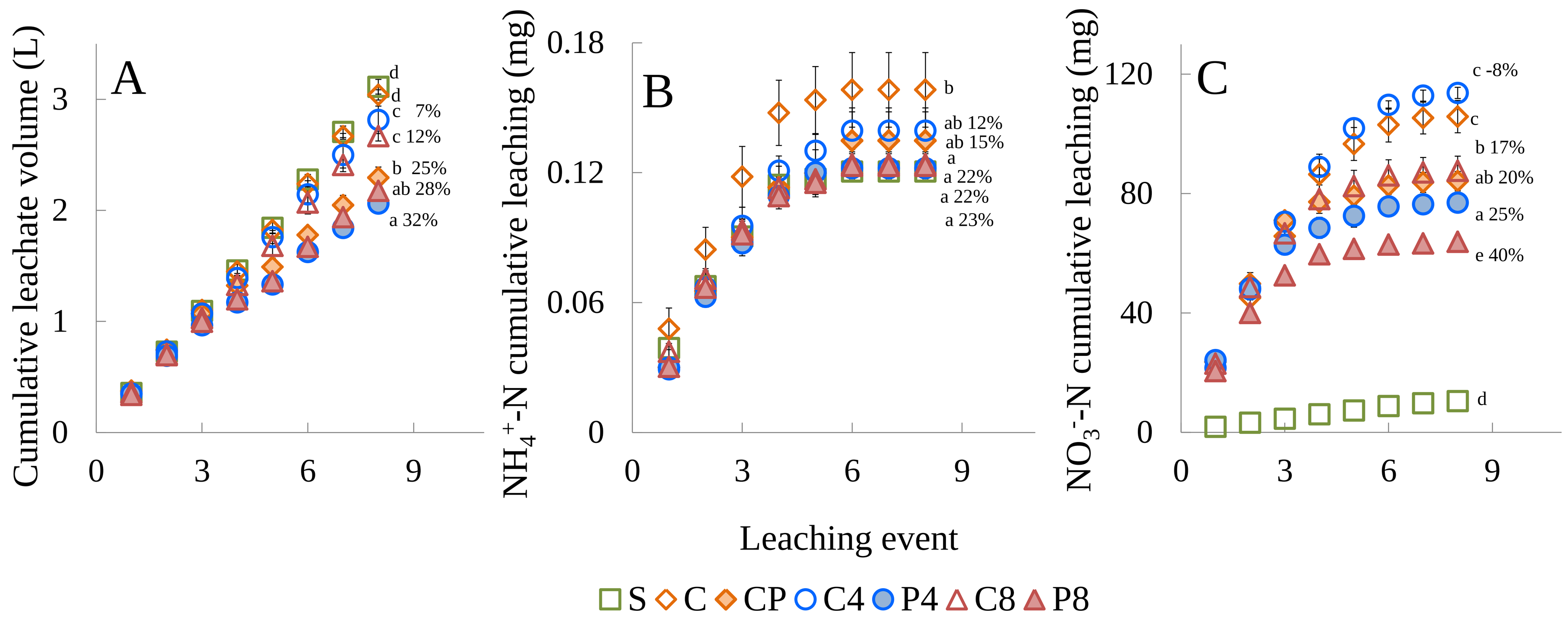

Fig.5. Cumulative quantity of A: leachate volume, B: NH^+_4-N, and C: NO^-_3-N leached from column over 8 leaching event for S, C, CP, C4, P4, C8, and P8.

- **Leachate volume, NH_4^+-N, and NO_3^--N in CP, P4, and P8 were reduced compared with C, C4, and C8, respectively (Fig.5.A). → Plant uptake**
- **NH_4^+-N cumulative leaching were low (Fig.5.B) compared with NO_3^--N cumulative leaching (Fig.5.C). → Adsorption on NH_4^+-N through electrostatic adsorption on SBBs (Fig.4.A).**
- **NO_3^--N in C8 and P8 were significantly reduced compared with C and CP, respectively (Fig.5.C, Table 4). → SBB800 adsorption NO_3^--N through physical process (Table 2).**

Table 4. Cumulative NH_4^+-N and NO^-_3-N leaching

	NH_4^+-N (mg)	NO_3^--N (mg)
S	0.12 ab	10.5 d
C	0.16 b	105.7 c
CP	0.14 ab	84.1 ab
C4	0.12 ab	113.7 c
P4	0.12 a	76.9 a
C8	0.12 a	87.6 b
P8	0.12 a	63.8 e

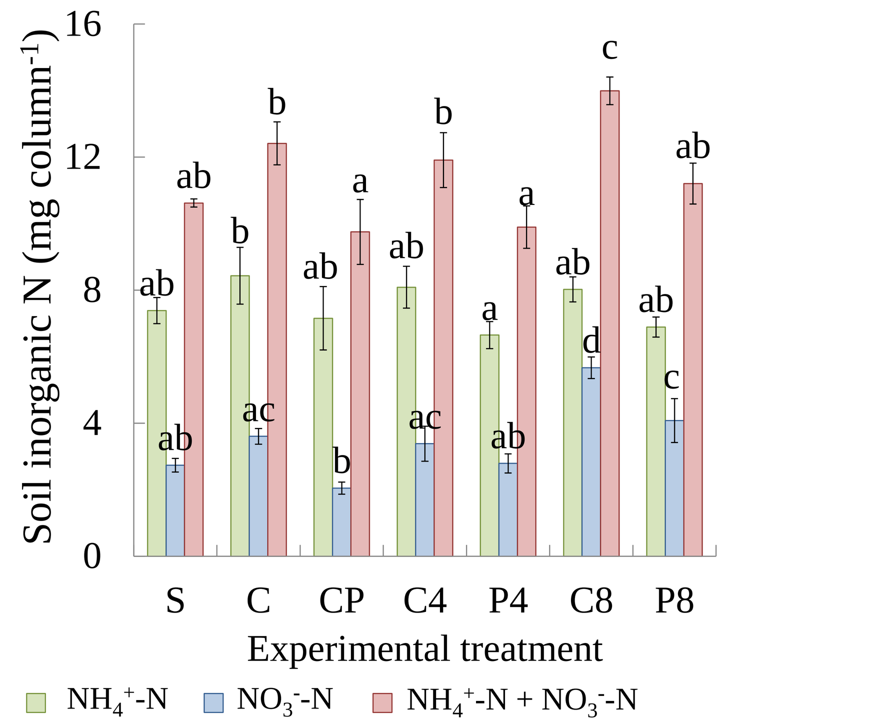

Fig.6. Soil NH^+_4-N, NO^-_3-N, and NH^+_4-N+NO^-_3-N in columns after 8 leaching event for S, C, CP, C4, P4, C8, and P8.

Retention of total NH_4^+-N and NO_3^--N in SBB800-amended soil significantly increased compared with other treatments (Fig. 6).

→ Soil water retention was increased by high SBB800's pore volumes (Table 2. and Fig.5.A)

Conclusions

SBB400 exhibited NH^+_4-N adsorption capability via cation exchange reaction due to high AFGs contents. Although not significant, NH^+_4-N leaching was reduced from SBB400-amended soils compared to non-amended soil. However, cumulative amounts of NH^+_4-N leaching from soils were much smaller than cumulative amounts of NO_3^--N leaching from soils in all treatments.

NO_3^--N leaching in SBB800-amended soil was significantly reduced because of increased water retention capacity due to high pore volume of SBB800.

It is indicated that the application of sugarcane-bagasse biochar to soils may reduce N leaching from soils and possibly contribute to N fertilizer use efficiency.

Acknowledgements

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