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The effect of plant residues and biochars on organic matter and nitrogen retention in soil

ผลของเศษพืชและถ่านชีวภาพต่อการกักเก็บอินทรีย์วัตถุและไนโตรเจนในดิน

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Abstract

The excessive use of nitrogen fertilizer leads to soil pollution and groundwater contamination by nitrate leaching. Thus, understanding nutrient retention properties of a soil is important for managing nitrate contamination. The aim of this research was to study the effect of plant residues and biochars on organic matter and nitrogen retention in soil. One percentage (w/w) of each plant residue (mangosteen peel, mangrove bark and neem seed) or biochar (coconut shell, coconut husk and corncob) was incorporated into sandy loam soil amended with 5% (w/w) of nitrogen fertilizer. The pH, organic matter (OM), total nitrogen (TN), available ammonium (avail. NH_4^+) and available nitrate (avail. NO_3^-) of soil samples were analyzed every 7 days, while germination index (GI) of Chinese convolvulus seed (*Ipomoea aquatic* var. *reptans*) was determined once after soil amendment. The result showed that soil amended with coconut husk biochar had highest OM (1.98%), followed by corncob biochar (1.87%) and neem seed (1.84%). The highest avail. NH_4^+ of 34.93 mg N/kg was found in soil amended with coconut shell biochar, but the highest TN of 949.38 mg N/kg was obtained from soil amended with mangrove bark. Lower GI (87.13%) was observed in the former treatment indicating that seed germination can be affected by negative charge of volatile matter, although NH_4^+ adsorption in soil amended with coconut shell biochar is high. However, the

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latter treatment showed the lowest avail. NO_3^- and the highest GI of 45.00 mg N/kg and 123.68%, respectively. Therefore, nitrogen retention in soil amended with mangrove bark is high as phenolic compounds have potential inhibitory effect over nitrification process.

Keywords: Biochar, Mangosteen peel, Mangrove bark, Neem, Nutrient retention

บทคัดย่อ

การใช้ปุ๋ยไนโตรเจนที่มากเกินไปจะทำให้เกิดมลพิษในดิน และการปนเปื้อนของน้ำใต้ดิน โดยการชะล้างไนเตรท ดังนั้นการเข้าใจสมบัติการกักเก็บธาตุอาหารของดินจึงเป็นสิ่งสำคัญสำหรับการจัดการการปนเปื้อนของไนเตรท วัตถุประสงค์ของงานวิจัยนี้จึงทำการศึกษาผลของเศษพืช และถ่านชีวภาพต่อกักเก็บอินทรีย์วัตถุและไนโตรเจนในดิน โดยเศษพืช (เปลือกมังคุด เปลือกโกงกาง และผลสะเดา) หรือถ่านชีวภาพ (กะลามะพร้าว เปลือกมะพร้าว และซังข้าวโพด) อย่างละร้อยละ 1 ร้อยละโดยน้ำหนัก นำมาผสมกับดินร่วนปนทรายที่ปรับปรุงด้วยปุ๋ยไนโตรเจนร้อยละ 5 ร้อยละโดยน้ำหนัก ทำการวิเคราะห์ค่าความเป็นกรดด่าง อินทรีย์วัตถุ (OM) ไนโตรเจนทั้งหมด (TN) แอมโมเนียมที่พืชนำมาใช้ได้ (Avail. NH_4^+) ไนเตรทที่พืชนำมาใช้ได้ (Avail. NO_3^-) ของตัวอย่างดินทุก ๆ 7 วัน ในขณะที่ดัชนีการงอกของเมล็ดผักบุ้งจีน (*Ipomoea aquatic* var. *reptans*) ทำภายหลังจากการผสมลงดิน ผลการวิจัยพบว่าการปรับปรุงดินด้วยถ่านชีวภาพเปลือกมะพร้าวมีค่าอินทรีย์วัตถุสูงสุด (ร้อยละ 1.98) ตามมาด้วยถ่านชีวภาพซังข้าวโพด (ร้อยละ 1.87) และผลสะเดา (ร้อยละ1.84) การปรับปรุงดินด้วยถ่านชีวภาพกะลามะพร้าวพบว่ามีแอมโมเนียมที่พืชนำมาใช้ได้สูงสุดเท่ากับ 34.93 มิลลิกรัมไนโตรเจนต่อกิโลกรัม แต่การปรับปรุงดินด้วยเปลือกไม้โกงกางมีไนโตรเจนทั้งหมดสูงสุด เท่ากับ 949.38 มิลลิกรัมไนโตรเจนต่อกิโลกรัม พบว่าดัชนีการงอกของเมล็ดต่ำ (ร้อยละ 87.13) ซึ่งแสดงให้เห็นว่าการงอกของเมล็ดมีผลมาจากประจุลบของสารระเหย ถึงแม้ว่าการผสมดินด้วยถ่านชีวภาพกะลามะพร้าวจะมีการดูดซับแอมโมเนียมสูงก็ตาม อย่างไรก็ตาม การทดลองถัดมาพบว่าไนเตรทที่พืชนำมาใช้ได้ต่ำสุด และดัชนีการงอกสูงสุดเท่ากับ 45 มิลลิกรัมไนโตรเจนต่อกิโลกรัม และร้อยละ 123.68 ตามลำดับ เพราะฉะนั้น การผสมดินด้วยเปลือกไม้โกงกางมีการกักเก็บไนโตรเจนสูง เนื่องจากสารประกอบฟีนอลิกซึ่งมีความสามารถในการยับยั้งกระบวนการไนตริฟิเคชัน

คำสำคัญ: ถ่านชีวภาพ เปลือกมังคุด เปลือกไม้โกงกาง สะเดา การกักเก็บธาตุอาหาร

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Introduction

Nitrogen is important for plant growth. However, excess use of nitrogen fertilizer in soil could change to nitrate by nitrifying bacteria and leach to underground water. If this underground water was used as a drinking water, it will cause blue baby syndrome in child. (van de Vijver et al., 2013). Plant uses nitrogen in the form of ammonium (NH_4^+) and nitrate (NO_3^-). Ammonium form should be kept in soil because the positive charge of NH_4^+ can be adsorbed on the negative charge of soil. Therefore, controlling nitrification process by inhibition the activity of nitrifying bacteria could reduce the conversion of ammonium (NH_4^+) into nitrate (NO_3^-). It was reported that chemical compounds in plants such as terpenoids, tannins and polyphenols were able to inhibit nitrifying bacteria in soil (Baldwin et al., 1983; Sivropoulou et al., 1995). Generally, polyphenol compounds are found in plant such as tea, mangosteen, clove and grape. Inhibitor from plants have lower cost than chemical inhibitors such as Nitrapyrin (N-Serve), Dicyandiamide (DCD) and Dimethylpyrazole-phosphate (DMPP). Recently, biochar was also used in soil amendment because it has micro-porous structure for improvement of the nutrient adsorption capacity increment of water holding capacity, enhancement of microbial biomass and then change the bacterial community structure of the soil and reduce nitrogen leaching (Zheng et al., 2013; Wang et al., 2015: Xu et al., 2016). Use of 0.5% and 1% biochar mixed with coastal saline could decrease the nitrate leaching by 13-33% in mixed with coastal saline (Sun et al., 2017). Zhang et al. (2015) reported that nutrient element composition in biochar generally includes carbon (C), nitrogen (N), hydrogen (H) and minor elements such as potassium (K), calcium (Ca), sodium (Na) and magnesium (Mg). The adsorption and desorption of nutrient such as nitrogen (N), phosphorus (P), and sulfur (S) associated with the increase in biological activities. Thus, application of biochar could improve soil quality, increase crop production and promote plant growth (Lehmann & Rondon, 2006a; Major et al., 2010; Zhang et al., 2010).

This research used plant residues namely, mangosteen peel (*Garcinia mangostana* Linn.), mangrove bark *(Rhizophora mucronate* Poir.), neem seed *(Azadirachta indica* A. Juss.) and biochars made from coconut shell, coconut husk and corncob as soil amendment. The effect of those materials on the retention of organic matter and nitrogen in sandy loam soil were determined.

Materials and Methods

Soil sample and preparation

Sandy loam soil (Hup Krapong Series soil) from Phetchaburi province, central Thailand was used in this research. Soil samples were collected from surface to a depth of 15 cm, from 15 spots using spade. Then air-dried, crushed and ground by passing 2 mm sieve. Soil samples were kept at room temperature before performing physical and chemical properties as shown in Table 1.

Table 1 Physical and chemical properties of dried soil samples analyzed in this study

Parameter	Value	Methods of analysis	Reference
1. Moisture (%)	1.09	Gravimetric method	AOAC, 2000
2. pH	6.84	WTW, pH3210	Land Development Department, 2010
3. Electrical Conductivity (EC) (mS/cm)	0.05	Lutron, WA-2017SD	Land Development Department, 2010
4. Cation Exchange Capacity (CEC) (Cmol/kg)	0.31	Ammonium acetate	Land Development Department, 2010
5. Organic Matter (OM) (%)	3.17	Walkley and Black method	Walkley and Black, 1947
6. Organic Carbon (OC) (%)	1.87	Walkley and Black method	Walkley and Black, 1947
7. Total nitrogen (mg N/kg)	260	Digestion/Distillation/Titration	Land Development Department, 2005
8. Available NH_4^+ (mg N/kg)	15.9	Distillation (add MgO)/Titration	Land Development Department, 2005
9. Available NO_3^- (mg N/kg)	12.10	Distillation (add devarda alloy)/Titration	Land Development Department, 2005

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Plant residues and biochars preparations

Three plants residues and three biochars were used in this study. Mangosteen peel (*Garcinia mangostana* Linn.) and mangrove bark (*Rhizophora mucronate* Poir.) were air-dried, crushed and ground to pass 2 mm sieve and kept at room temperature. Neem seed (*Azadirachta indica* A. Juss.) was derived from Thaineem Company Limited. It was passed 2 mm sieve and kept at room temperature. Biochars were made from coconut shell, coconut husk, and corncob in a continuously slow pyrolysis reactor at the Energy and Environmental Engineering Center (EEEC), Faculty of Engineering, Kasetsart University Kamphaengsaen Campus. The reactor was heated by stepwise procedure under oxygen limited condition. Biochars were carbonized in reactor at 500 °C. Then they were air-dried, crushed and ground to pass 2 mm sieve and kept at room temperature. Physical and chemical properties of plant residues and biochars, i.e. moisture, pH, electrical conductivity (EC), cation exchange capacity (CEC), total nitrogen (TN), available ammonium (avail. NH_4^+), available nitrate (avail. NO_3^-) and volatile matter, were analyzed as shown in Table 2.

Table 2 Physical and chemical properties of plant residues and biochars.

Parameter	Samples					
	Mango steen peel	Mangrove bark	Neem Seed	Coconut shell biochar	Coconut husk biochar	Corncob biochar
Moisture (%)	11.66	12.04	10.63	4.38	5.30	22.38
pH	4.87	4.92	4.53	9.06	8.29	7.97
EC (mS/cm)	2.63	5.53	4.49	1.23	7.30	2.78
CEC (Cmol/kg)	18.85	23.31	15.55	8.23	12.98	6.26
TN (mg N/kg)	1,586	1,113	1,567	781	690	903
Avail. NH_4^+ (mg N/kg)	11.30	13.28	39.02	28.86	39.36	37.88
Avail. NO_3^- (mg N/kg)	25.41	35.76	30.83	34.10	24.52	31.64
Volatile matter (%)	NA	NA	NA	9.32	1.02	3.28

Note: NA = not analyzed

Organic and nutrient retention analyses

A hundred grams of dried soil was mixed with 0.025 g of $(NH_4)_2SO_4$ solution, and then was amended with 1% (w/w) of each plant residue (mangosteen peel, MG; mangrove bark, MB; neem seed, N) or bichar (coconut shell, CS; coconut husk, CH; corncob biochar, CC). Soil without amendment of any plant residue or biochar was used as a control (NA). Each soil mixture was placed in a 500 ml plastic cylinder with the diameter and height of 7 and 14 cm, respectively. This container was closed with a lid that allows air flow through the 4 small holes and was kept at room temperature for 49 days. The moisture content was controlled at 11±0.5% throughout the experimental period. The experiment was performed using a completely randomized design (CRD) with 3 replications. The pH, OM, TN, avail. NH_4^+ and avail. NO_3^- were analyzed every 7 days.

Germination index determination

The germination capability of Chinese convolvulus (*Ipomoea aquatic* var. *reptans*) was tested by adaptation form the method by Hoekstra et al., (2002). A soil extract was prepared using a ratio of 2 g: 20 ml (soil sample: DI water). A mixture was shaken for 1 h and then was filtered through filter paper No. 1. Twenty seeds of Chinese convolvulus were soaked in 5 ml of soil extract and were kept in dark at room temperature. The control was also done by using deionized water instead of soil extract. After a 5-day soaking, the seed germination was counted and the root length was measured in order to calculate %RSG (relative seed germination), %RRG (relative root growth) and %GI (germination index) as shown in the equation (1) - (3).

$$\%RSG = \frac{\text{number of seeds germinated in soil extract}}{\text{number of seeds germinated in DI water}} \times 100 \quad (1)$$

$$\%RRG = \frac{\text{mean of roots length in soil extract}}{\text{mean of roots length in DI water}} \times 100 \quad (2)$$

$$\%GI = \frac{\%RSG \times \%RRG}{100} \quad (3)$$

Results

Effect of plant residue and biochar amendment to soil on pH

The pH of soil samples during a 49-day amendment with plant residues or biochars were shown in Table 3. The result showed that pH of all treatments gradually decreased during experimental period because hydrogen ion (H^+) was released from organic matter decomposition. Haile et al. (2006) have also reported the decrease in pH of soil amended with neem extract after 3 weeks. Final pH of soil samples ranges from 6.15 to 6.24, suggesting that they were not suitable for growth of nitrifying bacteria (Chena et al., 2006).

Table 3 The pH value of soil samples mixed with plant residues or biochars during 49 days.

pH of sample							
Day	NA	MG	MB	N	CS	CH	CC
0	6.74±0.41	6.63±0.23	6.57±0.26	6.77±0.20	6.64±0.44	6.76±0.28	6.74±0.29
7	6.55±0.27	6.55±0.19	6.44±0.16	6.55±0.11	6.38±0.21	6.59±0.23	6.57±0.24
14	6.42±0.22	6.41±0.14	6.37±0.05	6.55±0.11	6.35±0.33	6.48±0.22	6.53±0.23
21	6.36±0.22	6.40±0.13	6.34±0.06	6.43±0.31	6.32±0.36	6.44±0.22	6.46±0.23
28	6.32±0.79	6.38±0.38	6.32±0.30	6.41±0.28	6.28±0.39	6.38±0.33	6.41±0.24
35	6.28±0.12	6.34±0.27	6.27±0.24	6.33±0.28	6.22±0.69	6.32±0.23	6.38±0.25
42	6.22±0.13	6.26±0.32	6.23±0.33	6.27±0.27	6.20±0.52	6.27±0.37	6.32±0.31
49	6.20±0.54	6.18±0.73	6.15±0.16	6.23±0.11	6.15±0.49	6.19±0.27	6.24±0.37

Note: NA = no amendment, MG = with mangosteen peel, MB = with mangrove bark, N = with neem seed, CS = with coconut shell, CH = with coconut husk, CC = with corncob. (n=3)

Effect of plant residue and biochar amendment to soil on OM retention

The organic matter (OM) of soil samples during a 49-day amendment with plant residues or biochars were shown in Figure 1. The result showed that OM of all samples gradually decreased during experimental period, possibly due to suitable environmental conditions (moisture content 10-12%; temperature 25-30°C; air ventilation) for microbial growth. Microorganisms utilized OM as an energy source. They used the carbon (C), nitrogen (N), phosphorus (P), sulfur (S) and other required nutrients to form new cell materials. After a 49-day amendment (Table 4), the highest and the lowest OM were observed in CH (1.98%) and NA (1.50%), respectively. OM decomposition of soil samples range from 42% to 55%. This finding is comparable to Manaonok et al., (2017), which reported the decrease in OM after a 30-day biochar amendment.

The statistically significant differences ($P<0.05$) were found in MB (949.38 mg N/kg TN; 45.00 mg N/kg avail. NO_3^-) and CS (34.93 mg N/kg avail. NH_4^+; 52.40 mg N/kg avail. NO_3^-), indicating that nitrogen retention in soil amended with mangsteen peel residue or coconut shell biochar is high in comparison with other treatments.

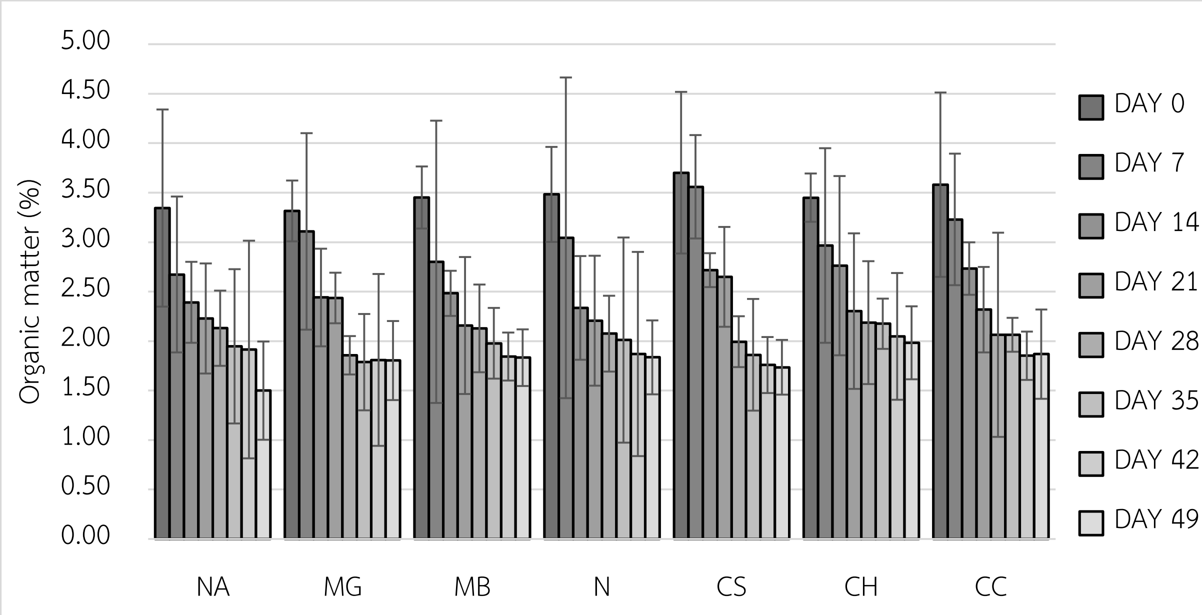

Figure 1 Organic matter (%) of soil samples during a 49-day amendment with plant residues or biochars.

Note: NA = no amendment, MG = with mangosteen peel, MB = with mangrove bark, N = with neem seed, CS = with coconut shell, CH = with coconut husk, CC = with corncob.

Table 4 Organic matter and nitrogen retention in soil amended with plant residues or biochars after a 49-day amendment.

Samples	OM (%)	TN (mg N/kg)	Avail. NH_4^+ (mg N/kg)	Avail NO_3^- (mg N/kg)
NA	1.50 ± 0.50^a	618.22 ± 13.44^a	18.18 ± 0.39^a	73.49 ± 1.16^a
MG	1.80 ± 0.40^a	730.38 ± 87.02^b	18.78 ± 0.67^a	57.43 ± 0.99^b
MB	1.83 ± 0.29^a	949.38 ± 10.52^a	19.28 ± 0.19^a	45.00 ± 5.86^a
N	1.84 ± 0.37^a	714.41 ± 107.21^b	19.07 ± 0.66^a	56.78 ± 2.61^b
CS	1.73 ± 0.28^a	821.75 ± 68.09^b	34.93 ± 0.70^b	52.40 ± 1.05^a
CH	1.98 ± 0.37^a	793.66 ± 2.53^b	18.88 ± 0.85^a	55.32 ± 0.66^b
CC	1.87 ± 0.45^a	797.53 ± 1.88^b	18.89 ± 0.57^a	56.78 ± 2.40^b

Note: [a,b] = *values followed* by the *same letter within* a *column do not differ* significantly at the *5% level*.

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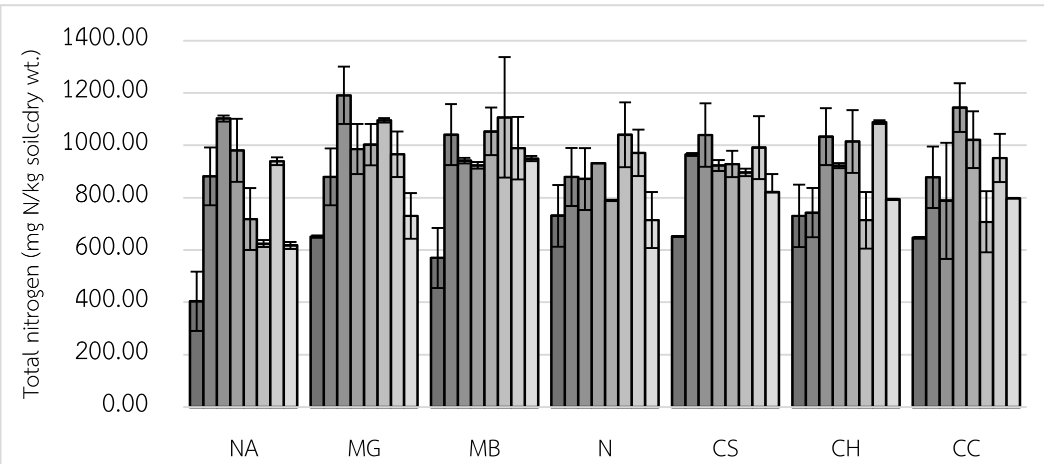
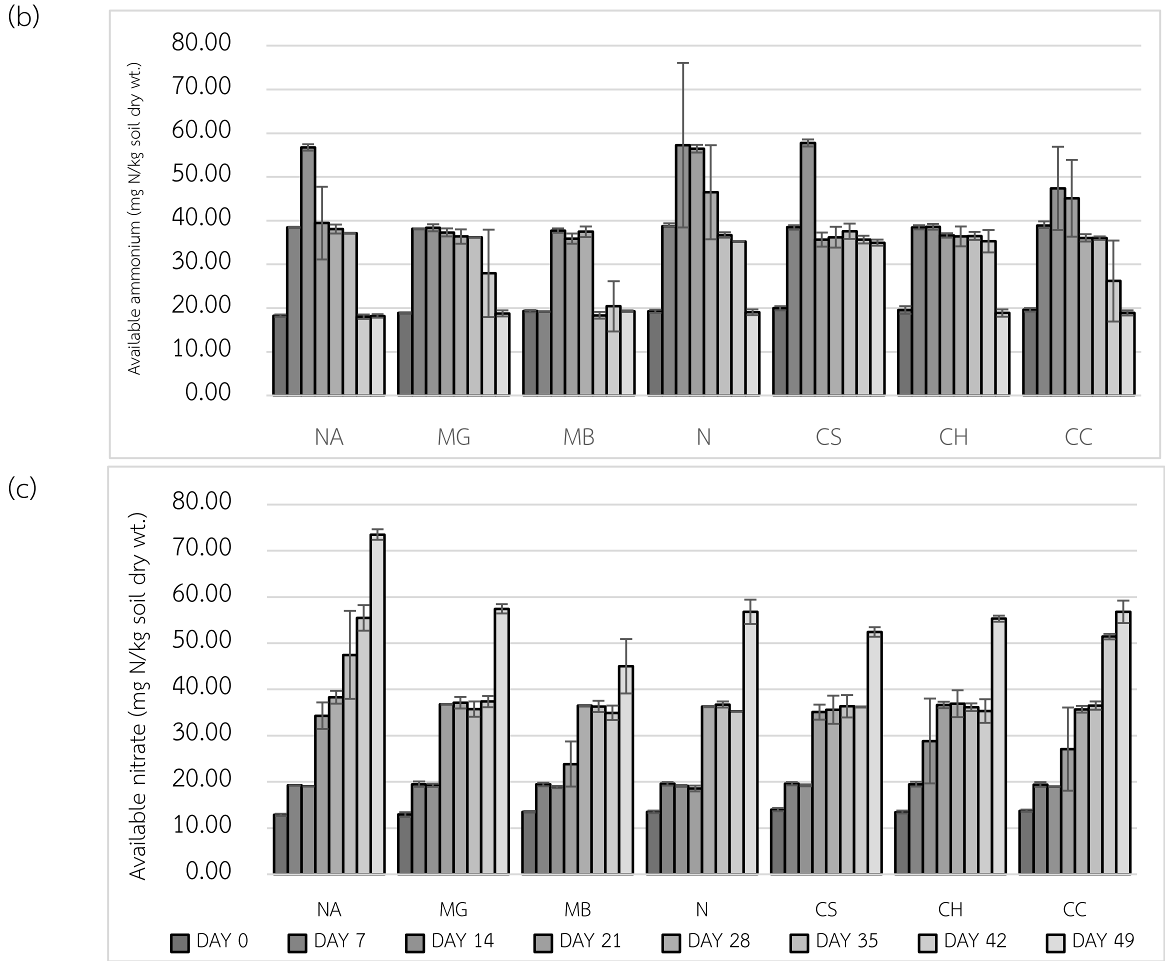
Effect of plant residue and biochar amendment in soil on nitrogen retention

The nitrogen retention of soil samples during a 49-day amendment with plant residues or biochars were shown in Figure 2 (a) – (c). Generally, nitrogen in soil is divided into two main forms which are organic nitrogen and inorganic nitrogen, more than 90% of nitrogen in soil are organic nitrogen (Vityakon, 2004). Microorganisms convert organic nitrogen to inorganic forms by a process called 'mineralization'. The amendment of plant residues and biochars could increase TN of soil (618.22 mg N/kg in NA). Elevated TN levels of 949.38 and 821.75 mg N/kg were obtained from MB and CS, respectively.

Organic nitrogen was converted to ammonia (NH_3) by microorganisms under aerobic condition. Ammonia (NH_3) in the form of ammonium ion (NH_4^+) is normally found in soil because the pH is less than 7.5 (Smith, 2001). Avail. NH_4^+ gradually increased from day 0 to day 14 and eventually decreased (Figure 2 (b)) because it was converted to nitrite (NO_2^-) and nitrate (NO_3^-; Figure 2 (c)) by *Nitrosomonas* spp. and *Nitrobacter* spp., respectively. CS had the highest avail. NH_4^+ of 34.93 mg N/kg, while MB showed the lowest avail. NO_3^- of 45 mg N/kg. Low conversion of ammonium ion (NH_4^+) to nitrate (NO_3^-) in CS might be due to its surface properties, high porosity and negative charge, which were able to adsorb and release positively charge nutrients or NH_4^+ from itself (Lehmann & Rondon, 2006b; Taghizadeh-Toosi et al., 2012). While chemical compounds, terpenoids, tannins and polyphenols, found in MB and other plants might inhibit nitrification process (Baldwin et al., 1983). Haile et al. (2006) have been reported the decrease in NH_4^+ and the increase in NO_3^- that resulted from a 7-day *Eugenia caryphyllata* Thunb amendment.

(a)





2 Nitrogen retention of soil samples during a 49-day amendment with plant residues or biochars.

(a) Total nitrogen (b) Available ammonium (c) Available nitrate

OM and nitrogen retentions (%) of soil samples during a 49-day amendment with plant residues or biochars were shown in Figure 3 and 4. OM retention of soil samples ranged from 45% to 57%, with the highest value observed in CH. High avail. NO_3^- retention found in NA implying that organic nitrogen might be easily converted to inorganic forms (Figure 4). However, the chemical compounds from plant residues such as tannin and alpha-mangostin from mangosteen peel, tannin and triterpenoids from mangrove bark, and nimbin, azadirachtin and salannin from neem seed could inhibit nitrification process (Baldwin et al., 1983; Prasad et al., 1995). Lower avail. NO_3^- retentions were obtained from MB (332.87%) and CS (374.80%), but the latter treatment had the highest avail. NH_4^+ retention (174.94%). Low NO_3^-

concentration can reduce soil nitrate leaching losses. In addition, plants rapidly absorb nitrogen in the form of NO_3^- (Mosier et al., 2004; Marschner and Rengel, 2007). Most samples gave over 100% TN retention, with exception of N (97.68%). These would be due to conversion of organic nitrogen to ammonia (NH_3). As neem seed had a seed coat, it could not be ground to powder in contrast to mangrove bark and coconut shell. In addition, biochar could also release NH_3 from itself (Taghizadeh-Toosi., et al 2012).

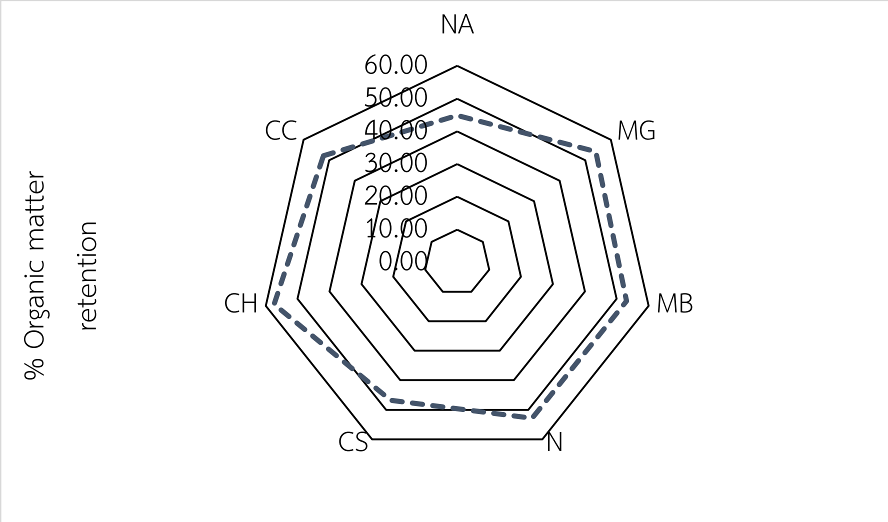


Figure 3 OM retention (%) of soil samples during a 49-day amendment with plant residues or biochars.

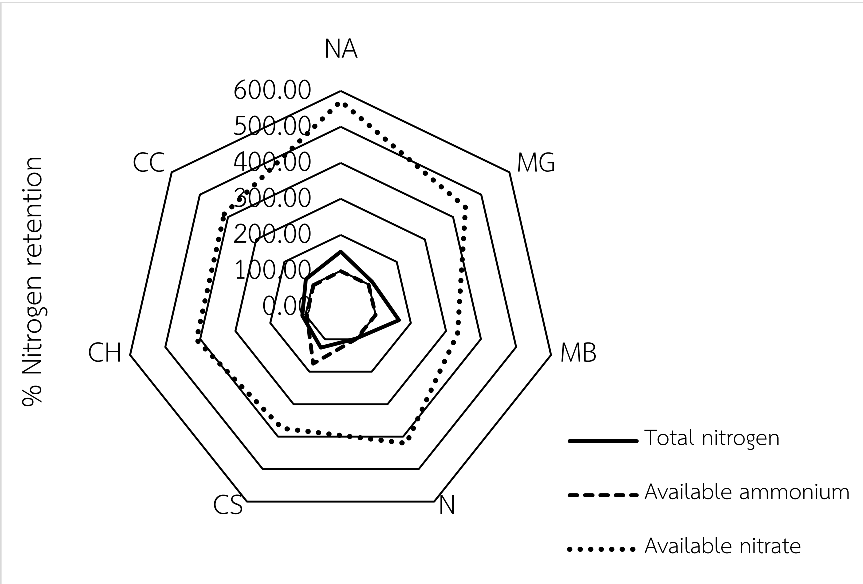


Figure 4 Nitrogen retention (%) of soil samples during a 49-day amendment with plant residues or biochars.

Germination index of plant

The germination index (GI) was used to determine phytotoxicity of biowaste materials affected on seed germination and root length of plants. GI is more than 50% means the toxicity limit (Roe et al., 1997; Wong et al., 2001). GI of soil amended with plant residues or biochars were shown in Figure 5. The highest GI (123.68%) and the highest cation exchange capability (CEC, 23.31 Cmol/kg) were obtained from MB. High nitrogen retention was found in this treatment as tannin and triterpenoid in mangrove bark could inhibit nitrification process (Baldwin et al., 1983). CEC indicated the ability of soil to hold cation nutrients, Ca^{2+}, Mg^{2+}, Na^{2+} and NH_4^+, which was required for plant growth. Therefore, CEC would be important on GI (Ketterings et al., 2007). Lower GI was found in CS because it had the highest volatile matter of 9.32%. Deenik et al. (2009; 2011) have been reported that volatile matter in biochars decreased and inhibited plant growth.

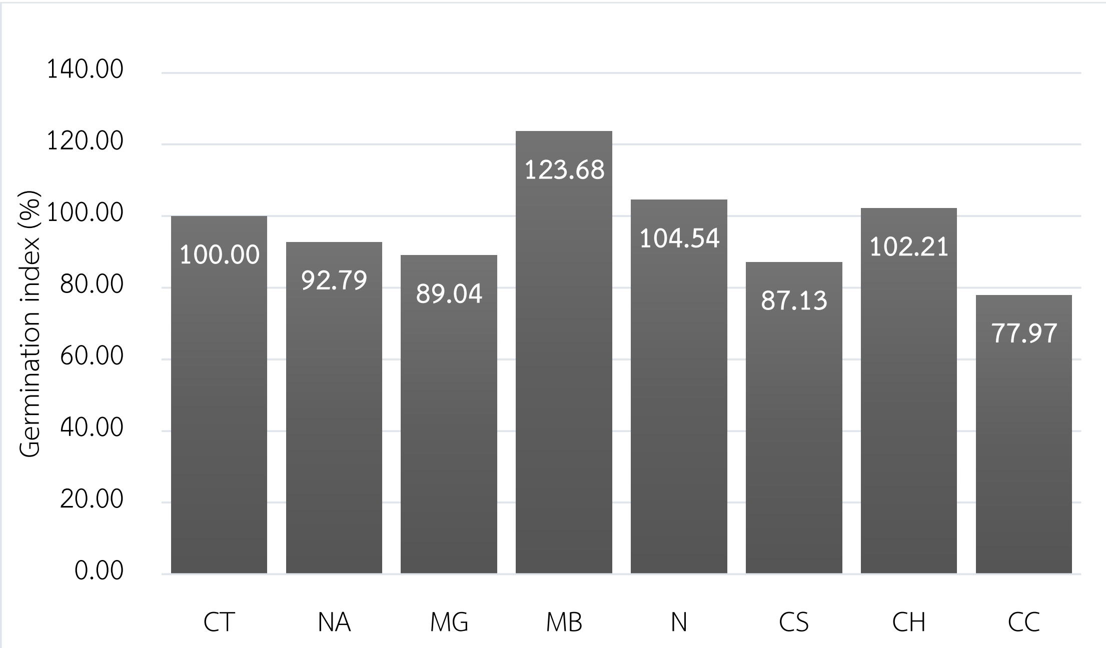


Figure 5 Germination index (GI) of Chinese convolvulus *(Ipomoea aquatic* var. *reptans)* in soil extract and deionized water.

Note: CT = control (DI water), NA = no amendment, MG = with mangosteen peel, MB = with mangrove bark, N = with neem seed, CS = with coconut shell, CH = with coconut husk, CC = with corncob.

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Conclusion

OM and nitrogen retentions of soil amended with plant residues and biochars were examined in this study. The pH of all treatments gradually decreased during experimental period. OM retention of soil samples ranged from 45% to 57%. CS showed the highest avail. NH_4^+ of 34.93 mg N/kg, while MB gave the highest TN of 949.38 mg N/kg. The surface properties of biochars were able to adsorb and release NH_4^+ from itself, whereas the phenolic compound in plant residues could inhibit nitrification process. However, the highest GI of 123.68% was found in MB while lower GI of 87.13% was observed in CS.

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