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Impact of Biochar Application on Carbon Dynamics and Fertility of Soils Over-fertilization with Compost

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Abstract

In Taiwan, farmers often apply excess compost to ensure adequate crop yield in highly frequent tillage, highly weathered, and lower fertility soils. The potential of biochar (BC) for diminishing soil C mineralization, and improving soil nutrient availability in compost over-fertilized soil is promising, but the study is still under-examined. To test the hypothesis, 434 days in vitro C mineralization kinetics of incubation experiment were conducted. Woody BC 0%, 0.5%, 1.0% and 2.0% (w/w) made of lead tree (*Leucaena leucocephala* (Lam.) de. Wit) were added to an Oxisols, and two Inceptisols of Taiwan. In each treatment, 5% swine manure compost (2 times recommended amount) was added and served as the over-fertilized soil. The results indicated that soil type strongly influenced the impact of BC addition on soil carbon mineralization potential. Respiration per unit of total organic carbon (total mineralization coefficient, TMC) of three studied soils significantly decreased with BC addition increased. Principal component analysis (PCA) suggested that for retaining more plant nutrients in addition to the effects of carbon sequestration, it is recommended that farmer could use locally produced biochars and composts in highly weathered and highly frequent tillage soil. Adding 0.5%-1% woody BC in soil should

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be reasonable and appropriate.

Keywords: Biochar; carbon mineralization; over-fertilization soils; compost; Ultisols

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1. Introduction

Problems of soil degradation by erosion, salinization, depletion of soil organic matter (SOM), and nutrient imbalance are the most serious bio-physical constraint limiting agricultural productivity in many parts of the world [1]. It is crucial to the success of soil management and agricultural productivity strategies by maintaining an appropriate level of SOM and ensuring the efficient biological cycling of nutrients [2,3], including the application of organic and inorganic fertilizers combined with knowledge of how to adapt these practices to local conditions, aiming to maximize agronomic use efficiency of the applied nutrients and thus crop productivity [3]. On soils with low nutrient retention capacity the strong rains easily leach available and mobile nutrients rapidly into the subsoil where they are unavailable for most crops [4] rendering conventional fertilization highly inefficient [5]. SOM has clearly declined in the arable lands of Taiwan since last several decades because of highly frequent tillage in association with high air temperature and rainfall, and farmers often apply excess compost to ensure adequate crop yield.

Depending on the mineralization rate, organic fertilizers such as compost, mulch or manure release nutrients in a gradual manner [6] and may therefore be more appropriate for nutrient retention under high-leaching conditions than inorganic fertilizers. Due to the relatively low levels of nutrients (10-20 g N/kg, and less than 10 g P/kg) in compost compared to complete fertilizer, as well as the low plant availability of compost-N and -P, a large amount of compost is needed to meet the crop requirements for N and P [7] and farmers often apply excess compost to ensure adequate crop yield, leading to excessive N and P loading to the environment. In the tropics, however, naturally rapid mineralization of SOM is a limitation on the practical application of organic fertilizers, that is, in addition to repeated application at high dose and cost of application of organic materials, their rapid decomposition and mineralization may make a significant contribution to global warming [8-10]. In addition, excessive manure application often causes heavy metal accumulation (Cu, Pb, Zn, etc.) in the soil, and the soluble fraction of these metals tends to increase due to desorption and remobilization of metals previously bound to the soil matrix, leading to enhanced crop uptake of heavy metals [11]. On acid and highly weathered tropical soils, application of organic fertilizers and charcoal increase nutrient stocks in the rooting zone of crops, reduce nutrient leaching and thus improve crop production [5]. Biochar could be a key input to raise and sustain production and simultaneously to reduce pollution and dependence on fertilizers, and it could also improve soil moisture availability and sequester carbon [12]. BC studies mainly focus on the effects of pure BC addition or artificial fertilizer, and however pure BC does not provide high amount of nutrients in most cases [13]. Incorporation of BC-compost into poor soil is considered as a promising approach to produce a substrate like *terra preta*, and the study result clearly demonstrated a synergistic positive effect of compost and BC mixtures on soil organic-matter content, nutrients levels, and water-storage capacity of a sandy soil under field conditions [13]. BC either helped stabilize manure C or the presence of manure reduced the effect of BC on the mineralization of SOC [14]. The study of Trupiano et al. [15] showed that both BC amendment (65 g/kg) and compost (50 g/kg) addition to a moderately subalkaline (pH 7.1) and clayey soil poor in nutrients induced a positive effect on lettuce plant growth and physiology and on soil chemical and microbiological characteristics; however, no positive synergic or summative effects exerted by compost and BC in combination were observed here compared to the compost alone treatment. In addition, BC, compost and BC-compost blend all resulted in lower environmental impacts than mineral fertilizer from a systems perspective [16].

However, in compost over-fertilized soils little is known about the impact of BC application rates on the carbon mineralization and soil fertility of mixed-soil (BC, compost, and soil) in highly frequent tillage soil systems. In vitro C mineralization kinetics of various BC addition rates in three selected soils were conducted in this study. We hypothesized that BC addition may stabilize compost organic matter, diminish mixed-soil C mineralization, and improve soil nutrient status. The aims of our research were (1) to quantify the effects of woody BC additions on C mineralization and soil fertility, and (2) to evaluate the sustainability of woody BC additions in terms of maintaining high-SOM contents and nutrient availability.

2. Materials and Methods

2.1 Soils characterization

Three representative rural soils derived from different parent material in Taiwan were selected for the incubation experiment. The Pingchen (Pc) soil series is a relict tertiary Oxisols (slightly acidic Oxisols, SAO) in northern Taiwan [17]. The Erhlin (Eh) soil series is an Inceptisols (mildly alkaline Inceptisols, MAI) developed from calcareous slate old alluvial parent material in central Taiwan. The Annei (An) soil series is also an Inceptisols (slightly acid Inceptisols, SAI) developed from calcareous sandstone-shale new alluvial parent material in southern Taiwan. Rice is the commonly grown crops of the sampled fields. The physical and chemical characteristics of the top soils (0-20 cm depth) are presented in Table 1.

Soil pH was determined in soil-to-deionized water ratio of 1:1 (g/mL) and in soil-to-

1N KCl ratio of 1:1 (g/mL) [18] and electrical conductivity (EC) was determined by saturation extract of soil sample [19]. Soil particle-size analysis was determined by pipette method [20]. Soil total C (TC) content was determined by dry combustion [21], using a O · I · Analytical Solid TOC. TSC was assumed to be organic in nature because the low or neutral soil pH preclude carbonates. Soil total nitrogen (TN) contents was extracted by digesting 1.0 g dried and powdered sample using concentrated H_2SO_4 in a Kjeldahl flask using K_2SO_4, $CuSO_4$ and Se powder as catalyst. TN concentration was determined via O · I · Analytical Aurora Model 1030W; content of soil total phosphorus (TP) in the digested solution was determined with ICP-OES (PerkinElmer Optima 2100DV). The exchangeable bases (Ex-K, Na, Ca, Mg), cation exchangeable capacity (CEC) and base saturation percentage (BS%) were measured using the ammonium acetate method at pH 7 [22]. Mehlich-3 extraction [23] was used for analysis of plant available nutrients. Mehlich-3 extractable (M3-) K, Na, Ca, Mg, Fe, Mn, Cu, Pb, Zn, and P values were measured with ICP-OES.

2.2 Studied Biochar (BC)

Biochar (BC) produced from lead tree (*Leucaena leucocephala* (Lam.) de. Wit) in an earth kiln was constructed by Forest Utilization Division, Taiwan Forestry Research Institute [24,25]. The charring for earth kilns typically takes several days and reaches temperatures about 500 to 700°C. The highest temperature in the kiln at the end of carbonization reached above 750°C. The BCs were homogenized and ground to < 2 mm mesh for analyses. The characterization of studied BC was described in the previous studies [26,27] (Table 1).

2.3 Incubation Experiment

In amended soils, laboratory incubation is generally used to obtain accurate information about C-mineralization dynamics [28], and the data can then be fitted to/with kinetic models in order to obtain complementary information such as the C-mineralization rates and the potentially mineralizable C. Therefore, a laboratory aerobic incubation experiment over 434 days was conducted to study and evaluate C-mineralization kinetics in a nonamended (no BC addition) soil (*i.e.* the control) and in three soils amended with three BC application rates. Totally twelve treatments were performed in this study, and each treatment was set up in triplicate. All soil treatments added 5% commercially available swine manure compost as soil fertilizer, 2 times recommended amount of organic fertilizer in Taiwan. The characteristics of swine manure compost were listed in Table 1. The application rate of BC, including 0%, 0.5%, 1.0%, and 2.0% (w/w), equated to field applications of approximately 0, 12, 24, and 48 metric tons/ha, respectively, considering 2400 Mg of soil per hectare (soil bulk density equal to 1.2 Mg/m^3 and an arable soil layer of 20 cm). Twenty-five grams of mixed soil sample was placed in 30 ml plastic containers which were subsequently put into 500 ml plastic jars containing a vessel with 10 ml of distilled water to avoid soil desiccation and a vessel with 10 ml of 1M NaOH solution to trap evolved CO_2. The jars were sealed and incubated at 25°C. Soil moisture contents were adjusted to 60% of field capacity before the incubation stated and maintained throughout the experiment using repeated weighing. The incubation experiment was run for 434 days with 23 times of sampling after 1, 3, 7, 14, 21, 28, 35, 42, 49, 56, 63, 77, 91, 105, 119, 133, 161, 189, 217, 245, 308, 371 and 434 days. After sampling, the vessel with 10 ml of a 1M NaOH solution was removed, resealed, and stored until analysis for CO_2 and replace with fresh NaOH.

A titrimetric determination method was used to quantify evolved CO_2 [29]. The cumulative CO_2 released and C mineralization kinetics was calculated based on the amount of CO_2–C released during different intervals of time in each treatment. In addition, total mineralization coefficient (TMC) was calculated according to Díez et al. [30] and Méndez et al. [31] as follows:

$$\text{TMC (mg } CO_2\text{-C/g C)} = CO_2\text{-C evolved / initial TOC} \quad (1)$$

Where CO_2-C evolved is expressed as mg CO_2-C/100 g soil and initial total organic carbon (TOC) is expressed as g C/100 g soil.

Samples of the BC-treated soil were collected after incubation days 434 for analysis of plant available nutrients using Mehlich-3 extraction (M3-) [23]. M3-K, Na, Ca, Mg, Fe, Mn, Cu, Pb, Zn, and P values were measured with ICP-OES. In order to compare the changes and quantify the impacts of soil-BC amendments on nutrients, soil pH, TC, TN, TP, exchangeable bases (Ex-K, Na, Ca, Mg), and CEC of the BC-treated soil on day 434 were also measured.

2.4 Statistical Analysis

The statistical analyses (calculation of means and standard deviations, differences of means) were performed using SAS 9.2 package. Results were analyzed by analysis of variance (one-way ANOVA) to test the effects of each treatment. The statistical significance of the mean differences was determined using the least-significant-difference (LSD) tests based on a t-test at a 0.05-probability level. The Pearson correlation coefficient (r) calculated and principle component analysis (PCA) was performed using SAS 9.4 software.

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3. Results

3.1 Carbon Mineralization

Addition of woody BC showed significantly reduced CO_2 release on SAO soil, no significantly difference on MAI soil, and significantly increase on SAI soil (Fig. 1 and Table 2). In SAO soil treatments, the CO_2-C release reduced about 8.8%, 7.0% and 9.4% for 0.5%, 1.0% and 2.0% addition rate, respectively. Even no significantly difference in MAI soil treatments, the CO_2-C release reduced about 8.8%, 7.0% and 9.4% for 0.5%, 1.0% and 2.0% addition rate, respectively. In contrast, in SAI soil treatments the CO_2-C release increase about 6.2%, 15.3% and 7.9% for 0.5%, 1.0% and 2.0% addition rate, respectively. Results of the total mineralization coefficient (TMC) indicated significantly reduce trend with BC addition increasing in SAO and MAI soil treatments, but in SAI soil only 2% addition shown significantly decrease in compare with control. The value of TMC was higher in SAI soil treatments, followed by MAI soil treatments, and much lower in SAO soil treatments. TMC value reduced 16.5%, 24.0% and 37.8% for 0.5%, 1.0% and 2.0% addition in SAO soil, respectively. In MAI soil, it reduced 19.6%, 20.7% and 32.5% for 0.5%, 1.0% and 2.0% addition, respectively. In SAI soil, it reduced 0.7%, and 19.8 for 0.5% and 2.0% addition but increased 2.0% for 1.0% addition, respectively. We hypothesized that woody BC addition may stabilize compost organic matter and diminish C mineralization in over-fertilization soils with compost, and the results have shown that addition of woody BC to SAO soil produced favorable effect by decreasing the cumulative amount of CO_2-C evolution, but in SAI soil it produced unfavorable effect by increasing the cumulative amount of CO_2-C evolution. No obviously effect obverted in MAI soil.

3.2 Changes in Soil Properties and Fertility Characteristics

After 434-days incubation, all treatments were analyzed in order to investigate BC addition could result in increasing (enhancing) or decreasing (reducing) effect on soil properties and fertility characteristics in over-fertilization soils (Table 3). The enhancing effect on soil fertility characteristics will suggest that adding BC can retain nutrients in over-fertilization soils, even after 1-year incubation. At the end of this year, more nutrients could be retained in soils suggest that farmer can apply less compost in next year.

At the end of incubation, TC significantly increases with BC addition increase in three soils. The significantly decreases with BC addition increase in CO_2-C evolution and TMC could explain the soil carbon accumulation (sequence) in soils. That is, in this study BC addition evidently reduced C-mineralization and TMC and resulted in more soil C sequestrated in over-fertilization soils with compost. TN content shown significantly increase in 1% and 2% addition of MAI and SAI soils, but it shown slightly decrease in SAO soil. The application of woody BC with high C/N ratio in three over-fertilized soils did not result in obviously soil nitrogen fixation, but in contrast increasing the TN content. The content of TP shown significantly increase in 0.5% and 2.0% of SAO soil and in 2.0% of MAI soil, but significantly decrease in 1.0% and 2.0% addition of SAI soil. The C/N indicated significantly increase with BC addition increasing, the value all less than 10 (Table 3).

The soil pH of SAO soil shown significantly increase in 2.0% addition of three soils, about 0.3 pH unit for SAO soil, 0.1 pH unit for MAI soil, and 0.2 pH unit for SAI soil (Table 3). Within the exchangeable bases, Ca and Mg both shown no significantly difference with control in three soils, but it has obviously increase in MAI and SAI

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soils. Addition of 0.5% BC resulted in significantly increase in K and Na content in SAO soil but decrease in 1.0% and 2.0%. In 2% of MAI and 1.0% and 2.0% of SAI soil shown significantly increase in K content. CEC shown variable changes, that is, significantly increases occurred in 1.0% of MAI soil but significantly decrease occurred in 2.0% of SAI soil.

In SAO soil, soil fertility characteristics the content of M3-P, K, Mg, Fe, Mn shown obviously and significantly decrease with BC addition increasing (Table 4). But in contrast, Ca, Cu, Pb, and Zn shown increase with BC addition increasing, especially in 2.0% addition. The content of Cu, Pb and Zn in SAO soil was about 8~9, 10~12, and 26~30 mg kg^{-1}, respectively, it seems not very high and could not result in plant toxicity. But we should pay more attentions that in SAO soil those metals could not be fixed by BC, and the availability may increase after BC addition. In MAI soil, P, K, Ca, Mg, Fe, and Mn shown increase trend after BC addition, but only K content shown significantly increase in 1.0% and 2.0% addition. Significantly decrease trend of Cu, Pb, and Zn occurred in 0.5%, 1.0% and 2.0% addition (except for Zn in 2.0%). The application of woody BC in over-fertilized MAI soil could retain some nutrients and significantly reduced heavy metal availability. Similar results of K, Cu and Pb could be found in SAI soil. But the content of P in 1.0% addition and Zn content in 0.5and 1.0% shown significantly increase in SAI soil. The content of Ca, Mg, Fe, and Mn shown the decrease trend after BC addition. Adding BC in SAI soil could result in some nutrients decrease and reduce the availability of Cu and Pb, but we should pay attention on the risk of increased Zn availability.

3.3 Principal component analysis

The PCA described substantial differences in soil physicochemical characteristics (pH, TC, TN, TP, M3-P, M3-K, M3-Cu, M3-Pb, and M3-Zn), and cumulative CO_2-C among the subjected BCs (Fig. 2). The PCA identified two primary components of the SAO soil fertility, and PC1 and PC2 accounted for 49.1% and 21.0% of the total variance, respectively. Additionally, PC1 and PC2 explained 43.0% and 19.78%, and 52.3% and 23.3% of the total variance in the MAI and SAI soil, respectively.

The PCA showed two groupings for each of the three soils. The two grouping of SAO soil: pH, TC, TP, M3-Pb, M3-Zn, and M3-Cu (Group 1), and TN, M3-P, M3-K, and cumulative CO_2-C (Group 2). The 2% BC addition clustered near Group 1, while the 0.5% BC addition clustered closer to Group 2. For the MAI soil, two groupings stood out: pH, TC, TN, TP, M3-P, and M3-K (Group 1), and M3-Cu, M3-Pb, M3-Zn, and cumulative CO_2-C (Group 2). The addition of 1% BC clustered near Group 1. Lastly, the PCA for the SAI soil showed two main groupings: pH, TC, TN, M3-P, M3-K, M3-Zn and cumulative CO_2-C (Group 1), and TP, M3-Cu, and M3-Pb (Group 2). Addition of 1% BC clustered closer to Group 1, while 0.5% BC addition clustered closely to Group 2.

4. Discussion

4.1 Effect of BC on Carbon Mineralization

While proper use of compost promotes soil productivity and improves soil quality, excess application degrades soil and water quality and inhibits crop growth [32]. In addition, the effect of BC on net CO_2 emission is clear, both directly through sequestration of BC C and indirectly through altering soil physical, chemical, and microbiological properties [5,33]. The BC used in our study was a high-temperature pyrolysis product of wood with an accumulation of black C. This property makes it very inert and recalcitrant to microbial degradation [34]. In this study, we hypothesized that the addition of relatively "small" amounts of a woody BC to soils with excess swine manure compost application could stabilize compost organic matter and diminish C mineralization. Diminishing C mineralization could contribute to reduce the decomposition of compost organic matter, enhance C sequestration, retain some nutrients, and may reduce the application rate of manure compost in next year.

Carbon mineralization in each soil type was obviously greater in the initial days of the incubation (Fig. 1), especially at the 1st day of incubation, and is like those reported in other studies [35-37]. Nevertheless, swine manure compost contained a significant amount of easily degradable organic C, and consequently, and intense increase in soil microbial activity should have occurred after their application to soil leading to high C mineralization. In addition, the BC treatments were significantly reduced in SAO soil and not significantly difference in MAI soil for C mineralization (Table 2), but significantly increased in SAI soil (1.0% and 2.0% treatments). The study results of Mukome et al. [38] showed that emissions of CO_2 from the interaction of BC with compost organic matter (COM) are dependent on the BC feedstock and pyrolysis temperature, however, the net CO_2 emissions are less for the BC and compost mixtures (compared to compost alone), suggesting that BC may stabilize COM and diminish C mineralization. Moreover, the presence of easily metabolized organic C or additional labile organic carbon sources has been shown to accelerate BC decomposition (or increased soil CO_2 effluxes) [39-42], suggesting that co-metabolism contributes to BC decomposition in soils. Respiration per unit of TOC (TMC) of three studied soils significantly decreased with BC addition increased. The four treatments in SAO soil had significantly lower TMC value than MAI and SAI soil. Méndez et al. [31] suggested that high value of TMC result in a more fragile humus and thus in a lower quality soil. In contrast, the lower TMC means that organic matter is conserved more efficiently and maintains the activity of the microorganisms responsible for soil organic matter biodegradation.

BC amendments clearly had effects on soil CO_2 evolution which varied with soil type. In the coastal saline soil (pH 8.09), the peanut shell derived BC addition increased the cumulative CO_2 emissions and the cumulative SOC mineralization, because of the labile C released from BC and the enhanced microorganism proliferation)[37]; however, the increased C mineralized only accounted for less than 2% in the 0.1%-3% BC treatments, indicating that the BC may enhance the C sequestration in the saline soil. Rogovska et al. [14] indicated that BC additions sometimes increase soil respiration and CO_2 emissions which could partially offset C credits associated with soil BC applications, and there are many uncertainties related to estimation of mineralization rates of BC in soils. In this study, the result of CO_2 evolution and TMC both suggested that in the condition of adding excess swine manure compost in Oxisols higher BC application rate can stabilize and prevent the rapidly mineralization of compost. BC addition in mildly alkaline Inceptisols can stabilize compost organic matter but only slightly decrease the mineralization of compost. In slightly acid Inceptisols, higher BC application rate can stabilize compost organic matter but significantly increase the mineralization of compost.

4.2 Effect of BC on Soil Properties and Fertility Characteristics

In the tropics, naturally rapid mineralization of soil organic matter is a limitation on the practical application of organic fertilizers, despite the application having positive effect in enhancing soil fertility [32]. Thus, the repeated application at high dose of organic materials can cause significant contribution to global warming, plant toxicity, accumulation in plants of heavy metals, and ground and surface water pollution of nutrients leaching. Recently some studies have indicated that the simultaneous application of BC and compost resulted in enhanced soil fertility, water holding capacity, crop yield and C sequestration benefit [43-46]. Schulz and Glaser [46] found that the overall plant growth and soil fertility decreased in the order compost > BC + compost > mineral fertilizer + BC > mineral fertilizer > control. Combination of BC with mineral fertilizer further increased plant growth during one vegetation period but led also to accelerate BC degradation during a second growth period. Combination of BC with compost showed the best plant growth and C sequestration but no effects on N and P retention could be observed. The blending of BC with compost has been suggested to enhance the composting performance by adding more stable C and creating a value-added product (BC-compost blend) that can offset potential negative effects of the composting system and of the pyrolysis BC system [16].

As well as diminishing C mineralization in soils over-fertilization with swine manure compost, the study in further examined the positive or negative effect on the mineralization and availability of soil nutrients and heavy metals after 434 days of incubation. The results suggested that the effect of adding woody BC varied with soil types and elements (Table 4). In SAO soil, 0.5% BC treatment significantly increased TC, TP, C/N ratio, Ex-K, Ex-Na, and M3-Ca, but no negative impact on mixed-soil. The 1% BC treatment significantly increased TC, C/N ratio, M3-Ca and Cu, but significantly decrease M3-P, K, Mg, Fe and Mn. The 2% BC treatment significantly increased TC, TP, C/N ratio, pH, M3-Ca, Cu, Pb, and Zn, but significantly decrease M3-P and Fe. For MAI soil, 0.5% BC treatment significantly increased TC and pH, and showed significantly decrease in M3-Cu, Pb, and Zn. The 1% BC treatment significantly increased TC, TN, C/N ratio, CEC, and M3-K, but the content of M3-Cu, Pb, and Zn has significantly decrease. Including the content of TC, TN, TP, C/N ratio, pH, Ex-K, and M3-K showed significantly increase, but the content of M3-Cu and Pb was significantly decrease. For SAI soil, pH, TC, C/N ratio, and M3-Zn has significantly increase in 0.5% BC treatment. The 1% BC treatment significantly increased pH, Ex-K, TC, TN, C/N ratio, M3-P, K, and Zn, but showed significantly decrease in TP, M3-Cu and Pb. The 2% BC treatment significantly increased pH, Ex-K, TC, TN, C/N ratio, and M3-K, but the content of TP, M3-Cu and Zn was significantly decrease.

Without amendment with compost, the soils used in this study had low plant available contents of some nutrients as well as the low CEC. Soils with low CEC are often low in fertility and vulnerable to soil acidification [45] The CEC of studied soils followed the order: SAI soil > MAI soil > SAO soil. After incubation, the soil pH of four treatments in SAO soil (Table 3) were lower than bulk soil (Table 1), suggesting the low soil buffering capacity and the soil acidification occurred after adding excess manure compost. In a Dystric Cambisols with a loamy-sand texture, a maize (*Zea mays* L.) field trial with five treatments (control, compost, and three BC-compost mixtures with constant compost amount (32.5 Mg/ha) and increasing BC amount, ranging from 5-20 Mg/ha) was conducted [13], and the results demonstrated that total organic C content could be increased by a factor of 2.5 from 0.8 to 2% ($p < 0.01$) at the highest BC-compost level compared with control while TN content only slightly increased, and plant-available Ca, K, P, and Na contents increased by a factor of 2.2, 2.5, 1.2, and 2.8, respectively. Trupiano et al. [15] indicated that compared to the addition of compost alone, the compost and BC combination did not improve soil chemical characteristics, except for an increase in total C and available P content, and these increases could be related to BC capacity to enhance C accumulation and sequestration and to retain and exchange phosphate ions by its positively charged surface sites. The study results of Oldfield et al. [16] suggested that BC recycles C and P, whilst compost recycles C, N, P and K and a blend of both resulted in the recycling of C, N, P and K. In addition, regional differences were found between BC, compost and BC-compost blend, and the BC-compost blend offered benefits related to available nutrients and sequestered C [16].

4.3 BC addition rate effects on soil carbon mineralization and soil fertility

Deteriorating soil fertility and the concomitant decline in agricultural productivity are major concerns in many parts of the world [44], and it is a critical problem in Taiwan. Biochar and biochar-compost applications positively impact soil fertility, for example, through their effect on SOC, CEC and plant available nutrients [43]. Naeem et al. [47] suggested that application of BC in combination with compost and inorganic fertilizers could be a good management strategy to enhance crop productivity and improve soil properties. Agegnehu et al. [44] indicated that as the plants grew, compost and biochar additions significantly reduced leaching of nutrients; separate or combined application of compost and biochar together with fertilizer increased soil fertility and plant growth. Application of compost and biochar improved the retention of water and nutrients by the soil and thereby uptake of water and nutrients by the plants [44].

PCA of soil carbon mineralization and soil fertility from the different BC addition treatments in three soils over-fertilization with compost supported the results discussed above. In SAO soil, 2% BC addition clustered near Group 1 (pH, TC, TP, M3-Pb, M3-Zn, and M3-Cu) whose values were negatively correlated, indicating that 2% BC addition reduced soil C mineralization and stabilized compost organic matter, but slightly promoted the soil pH, the content of TC, TP, M3-Pb, M3-Zn, and M3-Cu (smaller, positive loading scores for PC1). In contrast, the 0.5% BC addition clustered closer to Group 2 whose variables were positively correlated, suggesting that the content of TN, M3-P, and M3-K slightly reduced (smaller, negative scores for PC1) with reducing soil C mineralization. In MAI soil, the addition of 1% BC was similarly clustered near the negatively correlated Group 1 (pH, TC, TN, TP, M3-P, and M3-K), indicting its positive contribution in soil fertility. In SAI soil, 1% BC addition clustered closer to Group 1 whose variables were positively correlated, suggesting that pH and the content of TC, TN, M3-P, M3-K, and M3-Zn of slightly promoted (smaller, positive scores for PC1) with increasing soil C mineralization. In contrast, the 0.5% BC addition clustered closely to Group 2 whose values were negatively correlated, indicating that 0.5% BC addition increased soil C mineralization and cannot stabilized compost organic matter, but slightly reduced the content of TP, M3-Pb, and M3-Cu (smaller, negative loading scores for PC1). The application of woody BC has potential for stabilizing compost organic matter, diminishing soil C mineralization, and improving soil nutrient availability in such soil over-fertilization with compost, but depending on soil type and application rate. Addition BC in SAO soil and MAI soil led to substantial improvement in physicochemical properties, as well as the significant and insignificant lower C mineralization, respectively (Fig. 1 and Table 2). The 0.5% BC addition would reduce the content of available P and K, and 2% addition could result in the risk of Cu, Pb, and Zn in SAO soil. In MAI soil, 1% addition would increase pH and the content of TC, TN, TP, M3-P, and M3-K. In contrast, BC addition in SAI soil resulted in significant higher C mineralization. Addition 1% BC would result in the increase in soil pH and the content of TC, TN, M3-P, M3-K, and M3-Zn, but 0.5% BC addition would reduce the content of TP, M3-Cu, and M3-Pb.

PCA of the soil properties measured in Speratti et al. [48] found that both BC feedstocks had positive correlations between Ca, Fe, and Mn. Metals such as Fe and Mn, along with lower soil pH, can contribute to the formation of organo-mineral and/or organo-metallic associations that decrease BC mineralization [49]. This can increase BC-C stability in the soil which may improve soil structure [50]. In this study, the content of free Fe oxides (Dithionate-citrate-bicarbonate extractable) was very high (43.1 g/kg) in SAO soil, followed by MAI soil and SAI soil, 8.80 g/kg and 6.96 g/kg, respectively. Along with lower soil pH (< pH 6.0), BC, compost, and soil Fe oxides can contribute to the formation of organo-mineral and/or organo-metallic associations that improve soil structure, stabilize compost organic matter, and decrease mixed-soil C mineralization in SAO soil. The soil pH in MAI soil was highest, the potential of BC showed insignificance between control and BC treatments but has minor reduced after BC addition treatments. After BC addition, the mixed-soil C mineralization showed significant increase and can contribute to less formation of organo-mineral and/or organo-metallic associations because of the lower Fe oxides and higher soil pH (7.1~7.2). The study results of Berek et al. [51], adding two biochars at 2% (w/w) made of lac tree wood and mixed wood (scrapped wood and tree trimmings) with and without vermicompost or thermocompost at 2% (w/w) in Hawai'i highly weathered soils (Ultisols and Oxisols), indicated that soil acidity, nutrient in the soils, plant growth and

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nutrient uptake were improved by the amendments compared to the control. Berek et al. [51] also suggested that increases in nutrients and reduced soil acidity by the additions of biochar combined with compost were the probable cause, and locally produced biochars and composts be used to improve plant nutrient availability in the highly weathered soils is recommended.

5. Conclusions

The capacity of woody BC in compost over-fertilized soils to stabilize compost organic matter, diminish C mineralization and improve nutrient availability was assessed in three highly weathered and frequent tillage soils of Taiwan (Oxisols, SAO; and Inceptisols, MAI and SAI). The effect of BC addition varied strongly according to the soil type. Soil carbon mineralization significantly reduce with BC addition increase in SAO soil, and has insignificant change in MAI soil, but significantly increase in SAI soil. Respiration per unit of TOC (TMC) showed significantly decrease with BC addition increase. In this study, higher BC application rate can stabilize and prevent the rapidly mineralization of swine manure compost. The soil pH, exchangeable bases and CEC only showed minor increase with BC addition increase. The positive effect of BC addition on soil fertility including TC, TN, TP, M3-P, K, Mg, Fe, Mn, Pb and Zn, but has slightly positive and negative effect on extractable Ca and Cu. For improving soil nutrient availability, adding BC generally increased the levels of plant macronutrients and reduced the concentrations of micronutrients. Principal component analysis indicates that adding BC has positive impact on diminishing soil carbon mineralization (carbon sequestration), sustaining soil fertility and preventing heavy metals contamination in compost over-fertilized soil, and suggests that adding 0.5% woody BC in SAO soil and adding 1% in MAI and SAI soil should be reasonable and appropriate in Taiwan.

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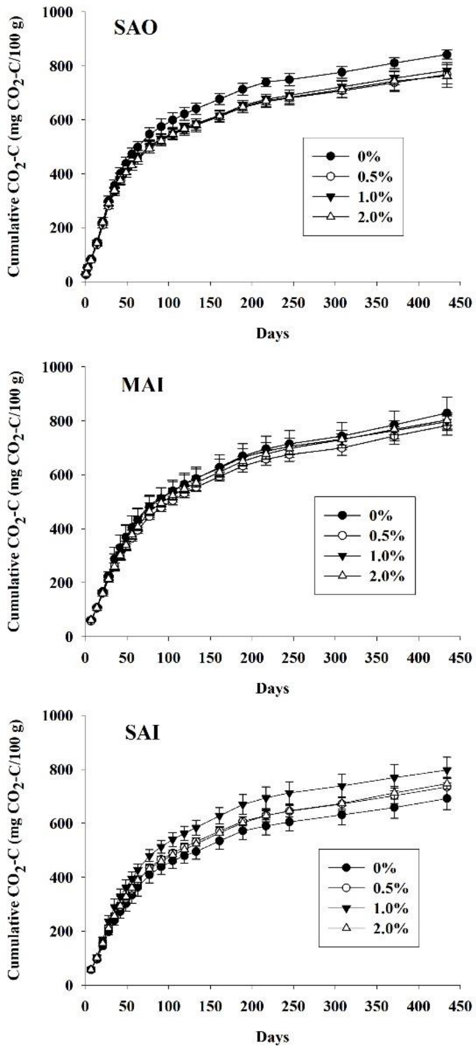

Figure 1. Cumulative CO_2-C (mg CO_2-C/100 g soil) from the three studied soils treated with 0%, 0.5%, 1.0%, and 2.0% woody BC. Error bars indicated the standard deviation of the mean.

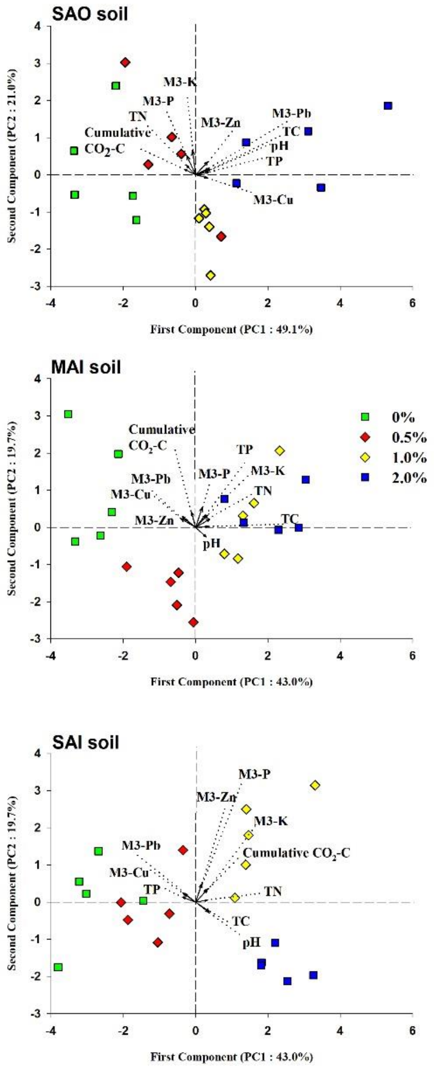

Figure 2. Principal component analysis based on the soil chemical characteristics and cumulative CO_2-C (mg CO_2-C/100g soil) after 434-d incubation period in SAO, MAI, and SAI soils treated with 0%, 0.5%, 1.0%, and 2.0% woody BC.

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Table 1. Characteristics of biochar, compost, and three studied soils.

Characteristics	**Biochar (BC)**	**Compost**	**Pc Soil (SAO)**	**Eh Soil (MAI)**	**An Soil (SAI)**
pH	9.9[1]	8.41[1]	6.1/5.0[3]	7.5/7.2[3]	6.5/6.2[3]
EC (dS/m)	0.77[1]/1.36[2]	3.79[1]	0.45	2.21	0.81
Sand (%)			11	24	33
Silt (%)			30	36	33
Clay (%)			59	39	34
Soil Texture			Clay	Clay loam	Clay loam
Total C (%)	82.5	23.3	2.03	1.11	0.94
Total N (g/kg)	6.99	22.6	2.71	2.32	1.58
Total P (g/kg)	0.55	10.2	1.16	0.98	0.77
Ex. K (cmol(+)/kg soil)	1.91	6.43	0.32	0.29	0.21
Ex. Na (cmol(+)/kg soil)	1.26	1.09	0.31	0.26	0.37
Ex. Ca (cmol(+)/kg soil)	3.62	2.70	4.85	2.94	2.24
Ex. Mg (cmol(+)/kg soil)	0.40	2.72	0.64	0.80	0.36
CEC (cmol(+)/kg soil)	5.20	19.7	8.58	11.5	14.2
BS (%)	100	69	71	37	22
M3-P (mg/kg)	96.6	6874	163	236	94.0
M3-K (mg/kg)	616	8911	68.4	108	94.1
M3-Ca (g/kg)	4.09	14.5	2.03	8.22	2.99
M3-Mg (mg/kg)	278	3972	143	344	401
M3-Fe (mg/kg)	65.5	396	524	589	1199
M3-Mn (mg/kg)	20.9	188	29.0	213	185
M3-Cu (mg/kg)	0.02	6.22	9.77	9.95	3.17
M3-Pb (mg/kg)	ND[4]	1.23	10.8	11.7	1.54
M3-Zn (mg/kg)	0.35	62.4	20.4	7.98	5.28

[1] The pH and electrical conductivity (EC) of biochar and compost were measured using 1:5 solid: solution ratio after shaking for 30 min in deionized water; [2] Biochar EC was measured after shaking biochar-water mixtures (1:5 solid: solution ratio) for 24 hr; [3] Soil pH was determined in soil-to-deionized water ratio of 1:1 (g mL^{-1}) and in soil-to-1N KCl ratio of 1:1 (g mL^{-1}); [4] ND = not detected.

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Table 2. CO_2-C evolved (mg C/100 g dry weight) and total mineralization coefficient (TMC) for control and amended soils after incubation experiment[1].

Rate	CO_2 evolved (mg C/100 g dry weight)	TMC (mg CO_2-C/g C)
SAO Soil		
0%	842 ± 8.7 A	333 ± 3.4 A
0.5%	768 ± 18 B	278 ± 6.4 B
1.0%	783 ± 15 B	253 ± 4.7 C
2.0%	763 ± 21 B	207 ± 5.7 D
MAI Soil		
0%	829 ± 30 A	526 ± 19 A
0.5%	782 ± 18 A	423 ± 9.6 B
1.0%	797 ± 17 A	417 ± 8.7 B
2.0%	803 ± 10 A	355 ± 4.5 C
SAI Soil		
0%	692 ± 20 C	455 ± 14 A
0.5%	735 ± 18 BC	452 ± 11 A
1.0%	798 ± 24 A	464 ± 14 A
2.0%	747 ± 10 B	365 ± 4.9 B

[1] Each value is the average ± standard deviation form three independent experiments. Means compared within a column followed by a different uppercase letter are significantly different at $p < 0.05$ using a one-way ANOVA (multiple comparisons vs. studied soil + 0% biochar as a control).

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Table 3. Mean values of total soil carbon (TC), nitrogen (TN), and phosphorus (TP), soil pH, exchangeable bases (K, Na, Ca, and Mg), and cation exchangeable capacity (CEC) of four treatments of three soils after 434-day incubations[1].

Rate	pH	Ex-K	Ex-Na	Ex-Ca	Ex-Mg	CEC	TSC	TSN	TSP	C/N
		--------------coml(+)/kg soil--------------					-----------g/kg-----------			
SAO Soil										
0%	5.66 b	2.55 b	0.72 b	14.9 a	3.58 a	16.4 a	23.9 c	4.37 ab	1.55 c	5.5 c
0.5%	5.75 b	2.87 a	0.91 a	15.0 a	3.73 a	16.4 a	28.0 b	4.43 a	1.77 b	6.3 b
1.0%	5.76 b	2.40 b	0.73 b	14.4 a	3.36 a	16.0 a	31.8 a	4.28 b	1.69 bc	7.4 a
2.0%	5.93 a	2.55 b	0.63 b	15.5 a	3.41 a	16.3 a	34.5 a	4.27 b	2.21 a	8.1 a
MAI Soil										
0%	7.53 c	2.64 b	0.66 a	22.9 a	3.37 a	9.7 b	18.2 c	3.64 b	0.88 bc	5.0 c
0.5%	7.58 b	2.92 b	0.68 a	25.5 a	3.78 a	10.1 b	21.9 b	3.62 b	0.75 c	6.0 bc
1.0%	7.58 bc	2.92 ab	0.68 a	25.5 a	3.78 a	10.7 a	22.2 b	4.06 a	1.05 ab	5.5 b
2.0%	7.65 a	3.24 a	0.76 a	25.9 a	3.75 a	10.0 b	32.4 a	4.15 a	1.18 a	7.8 a
SAI Soil										
0%	7.04 c	2.14 c	0.59 a	13.9 a	4.24 a	13.4 a	13.7 c	2.86 b	1.26 a	4.8 c
0.5%	7.11 b	2.30 bc	0.54 a	15.3 a	4.52 a	13.3 a	18.3 b	2.89 b	1.11 a	6.3 b
1.0%	7.14 b	2.61 a	0.62 a	15.6 a	4.56 a	13.6 a	21.4 b	3.06 a	0.88 b	7.0 b
2.0%	7.24 a	2.45 ab	0.54 a	14.9 a	4.23 a	12.8 b	26.6 a	3.07 a	0.64 c	8.7 a

[1] Each value is the average form three independent experiments. Means compared within a column followed by a different lowercase letter are significantly different at p < 0.05 using a one-way ANOVA (multiple comparisons vs. studied soil + 0% biochar as a control).

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Table 4. Mean values of soil fertility characteristics (Mehlich 3 extraction) (mg/kg) of four treatments of three soils after 434-day incubations[1].

Rate	P	K	Ca	Mg	Fe	Mn	Cu	Pb	Zn
SAO Soil									
0%	645 a	461 a	2701 b	533 a	953 a	5.7 ab	8.64 c	10.3 b	26.8 b
0.5%	653 a	467 a	3216 a	556 a	948 a	37.2 a	9.02 bc	10.2 b	28.6 b
1.0%	486 b	408 b	3118 a	444 b	739 b	31.6 c	9.36 ab	11.0 b	27.8 b
2.0%	537 b	457 a	3188 a	474 ab	777 b	3.5 bc	9.83 a	12.3 a	30.6 a
MAI Soil									
0%	769 ab	474 c	7594 a	636 ab	694 ab	286 a	8.73 a	12.9 a	12.2 a
0.5%	671 b	481 bc	7799 a	611 b	621 b	271 a	7.79 b	11.4 b	10.6 b
1.0%	832 a	545 a	7142 a	712 a	739 a	310 a	7.60 b	10.7 b	10.3 b
2.0%	795 a	534 ab	7697 a	660 ab	707 ab	301 a	7.66 b	11.3 b	11.1 ab
SAI Soil									
0%	476 b	384 c	3569 a	750 a	1257 a	197 a	1.70 a	0.84 a	9.48 c
0.5%	462 b	392 bc	3292 a	712 a	1147 a	186 a	1.66 a	0.67 ab	10.1 b
1.0%	564 a	474 a	3313 a	759 a	1200 a	196 a	1.54 b	0.57 bc	11.1 a
2.0%	470 b	437 ab	3648 a	726 a	1183 a	194 a	1.29 c	0.48 c	9.53 bc

[1] Each value is the average form three independent experiments. Means compared within a column followed by a different lowercase letter are significantly different at $p < 0.05$ using a one-way ANOVA (multiple comparisons vs. studied soil + 0% biochar as a control).