Substrate Quality Effects on Decomposition of Three Livestock Manure Composts with Similar Stability Degree in an Acid Loamy Soil

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Decomposition of compost applied to soils is affected basically by its biological stability; but, many other chemical properties of the compost may also influence compost organic-C mineralization. This study was conducted to investigate the principal substrate quality factors of composts that determine C mineralization of compost with similar stability degree (SD). Three composts samples with similar SD but different chemical properties such as pH, C/N, K_2SO_4-extractable C, and molar ratio of NH_4^+ to NO_3^- were mixed with an acid loamy soil and CO_2 emission was monitored during the laboratory incubation for 100 days. Temporal pattern of cumulative compost organic-C mineralization expressed as % of total organic C ($C_{\% \ TOC}$) followed double exponential first order kinetics model and the $C_{\% \ TOC}$ ranged from 4.8 to 11.8% at the end of incubation. The pattern of $C_{\% \ TOC}$ among the composts was not coincident with the SD pattern (40.1 to 58.6%) of the composts; e.g. compost with the lowest SD resulted in the least $C_{\% \ TOC}$ and *vice versa*. This result indicates that SD of compost can not serve as a concrete predictor of compost mineralization as SD is subject not only to maturity of compost but also to characteristics of co-composting materials such as rice hull (low SD) and sawdust (high SD). Meanwhile, such pattern of $C_{\% \ TOC}$ collaborated with pH, C/N, K_2SO_4-extractable C, and molar ratio of NH_4^+ to NO_3^- of the composts that are regarded as chemical indices of the progress of composting. Therefore, for better prediction of compost mineralization in soils, it is necessary to consider both SD and other chemical indices (pH, C/N, and molar ratio of NH_4^+ to NO_3^-).

Key words: CO_2 emission, First-order kinetics, Mineralizable C pool, Mineralization rate, Livestock manure compost, Stability degree

Introduction

Composting converts livestock manure into a biochemically stable organic material that can be readily stored, easily handled, and uniformly applied to soils with little odor (Tittarelli et al., 2007). The application of compost supplies plants with nutrients, maintains soil organic matter levels, and ultimately improves plant growth (Stamatiadis et al., 1999; Courtney and Mullen, 2008). As nutrients in the composts become available via microbial decomposition of various fractions of organic matter, the understanding of C mineralization in compost-amended soils is critical to estimating the levels of nutrient release from composts

(Castellanos and Pratt, 1981).

The characteristics of C mineralization of compost in soils have been evaluated by determining soil CO_2 respiration in incubation experiments (e.g. Bernal et al., 1998; Busby et al., 2007). First-order kinetic models are generally utilized to describe C mineralization due to their versatility, frequently with the separation of organic C into two pools with different biodegradability; these are referred to as the rapidly decomposable and slowly decomposable pools (Boyle and Paul, 1989; Hadas and Portnoy, 1994; Bernal et al., 1998; Aslam et al., 2008). The pool sizes of the mineralizable C fractions and their mineralization rates can be determined by fitting the kinetic equations to cumulative soil respiration curves (Bernal et al., 1998).

Carbon mineralization, which is expressed in terms of the quantity of CO_2-C generated from soils amended with organic materials, including manure, municipal solid waste,

and their compost, depends largely on the compounds composition (e.g. lignin and cellulose) of the organics employed (e.g. Levi-Minzi, et al., 1990; Ajwa and Tabatabai, 1994). For composts, organic C mineralization in the compost-amended soils is believed to be affected principally by the biological stability of the compost; e.g. a greater production of CO_2 with less stable compost (Bernal et al., 1998; García-Gómez et al., 2003; Aslam et al., 2008). For example, Bernal et al. (1998) previously suggested that when C mineralized is higher than 25% of the total organic C (TOC) applied, the composts could be assumed to be at a low degree of stability.

However, it is still doubtable if C mineralization of compost amended in soils is determined primarily by compost stability as not only stability but also other substrate (compost) quality including C/N, available N concentration (NH_4^+ and NO_3^-), and extractable organic C may certainly influence compost organic-C mineralization particularly when the composts being applied are biologically stable; i.e. less than 25% of TOC of compost is subject to decomposition according to Bernal et al. (1998). Therefore, this study was conducted to investigate the principal substrate quality factors of composts that determine C mineralization of compost in soils when the composts being applied are biologically stable judging from their stability degree.

Materials and Methods

Soil   Soil samples were collected from the surface layer (0 to 15 cm) of the agricultural soils in the experimental farm at the Jeonnam Agricultural Research & Extension Service (126°49′46″E, 35°01′24″N). The soil was classified as Ultisol (fine, mesic family of Typic Hapludults) in the USA Soil Taxonomy. The collected soils were air-dried, passed through a 2-mm sieve, and utilized for the analysis of selected properties and for the incubation study (Table 1).

Composts   Ten compost samples were purchased from local companies. The compost samples were freeze-dried, crushed (<2 mm), and analyzed for stability degree (SD) following the procedures provided by López et al. (2010) that is modified from Klason lignin method. Briefly, SD was calculated as % of resistant organic matter (ROM) to total organic matter (TOM) of compost; ROM represents OM fractions that are not hydrolysable by acid (H_2SO_4), and the detailed procedures are provided in López et al. (2010). Among the ten composts, three composts were

Table 1. Selected physico-chemical properties of soils used.

Properties[†]	Ultisol
Texture	Loam (23.4:45.2:31.4)
$pH_{1:5}$	5.6 (0.2)
Total organic C (g C kg^{-1})	19.1 (0.8)
Total N (g N kg^{-1})	2.4 (0.1)
K_2SO_4-extractable organic C (g C kg^{-1})	0.22 (0.01)
KCl-extractable NH_4^+ (mg N kg^{-1})	8.5 (0.3)
KCl-extractable NO_3^- (mg N kg^{-1})	357.3 (14.3)
C/N	8.0 (0.3)
WHC (kg kg^{-1})	0.38 (0.02)

[†]All analyses were conducted on triplicate samples for each soil. Texture was in USDA classifications and the values in parentheses are the % distributions of clay:silt:sand determined by the pipette method (Gee and Bauder, 1986); pH at a 1-to-5 ratio of soil-to-water; total organic C and N concentrations via a combustion method (Nelson and Sommers, 1996); K_2SO_4-extractable organic C with a TOC analyzer after K_2SO_4 extraction at 1-to-5 of soil-to-K_2SO_4 (1 mole L^{-1}) ratio (Choi and Chang, 2005); KCl-extractable NH_4^+ and NO_3^- concentrations using the steam distillation method after KCl extraction at a 1-to-5 soil-to-KCl (2 mole L^{-1}) ratio (Mulvaney, 1996); WHC (water holding capacity) with the gravimetric method using a funnel (Fierer and Schimel, 2002).

selected that showed relatively high SD over 40% for incubation experiment. The selected composts were analyzed for pH, total organic C, total N, C/N, K_2SO_4-extractable organic C, and KCl-extractable N (NH_4^+ and NO_3^-) (Table 2). Comparing among the composts, compost A had a relatively low pH, C/N, extractable C, and molar ratio of NH_4^+ to NO_3^- (Table 2).

Laboratory Incubation   A laboratory incubation was conducted using 1-L Mason jars. A total of 12 jars were prepared: four treatments (one without composts and three for composts)×three replicates. Thirty grams of soil (dry basis) were placed in a 100-mL beaker and distilled water was added to bring the moisture content to 60% of the water holding capacity (WHC) of the soil, and then pre-incubated for 5 days at $25 \pm 1\ ℃$ in darkness to restore the microbial activity of the soils. Afterwards, each 1 g of compost was mixed with the soil (30 g) for compost treatments, and the moisture content of the mixture was re-adjusted to 60% WHC. The application rate of compost is equivalent to 8.86, 9.89, and 11.17 g C kg^{-1} soil for composts A, B, and C, respectively. Both the beaker containing the soils and a 25-mL vial containing 20 mL of

Table 2 Selected chemical properties of composts used[†].

Compost	Composting materials	Stability Degree	$pH_{1:10}$	Total organic C	Total N	C/N	K_2SO_4 extractable C	KCl extractable N		
								NH_4^+	NO_3^-	NH_4^+/NO_3^-
	v/v % composition	%		g C kg^{-1}	g N kg^{-1}		g C kg^{-1}	------ g N kg^{-1} ------		
A	Pig manure (50) Rice hull (30)/Sawdust (20)	40.1 (0.9)	8.1 (0.1)	265.7 (17.8)	23.0 (1.5)	11.5 (0.8)	1.7 (0.0)	0.8 (0.06)	2.5 (0.17)	0.3 (0.02)
B	Cattle and pig manure (50) Sawdust (50)	49.7 (2.3)	9.2 (0.2)	296.6 (5.3)	13.7 (0.2)	21.7 (0.4)	4.1 (0.07)	0.5 (0.01)	0.04 (0.001)	10.9 (0.2)
C	Pig manure (45) Sawdust (55)	58.6 (4.8)	8.9 (0.3)	335.2 (11.4)	14.6 (0.5)	22.9 (0.8)	4.8 (0.5)	0.2 (0.01)	0.004 (0.000)	55.8 (1.9)

[†]All analyses were conducted on triplicate compost samples. pH was measured at a 1-to-10 ratio of compost-to-water; organic C and total N concentrations with a combustion method (Nelson and Sommers, 1996); K_2SO_4-extractable organic C with a TOC analyzer after K_2SO_4 extraction at 1-to-10 of soil-to-K_2SO_4 (0.5 mole L^{-1}) ratio (Choi and Chang, 2005); KCl-extractable NH_4^+ and NO_3^- concentrations using the steam distillation method after KCl extraction at 1-to-10 of soil-to-KCl (2 mole L^{-1}) ratio (Mulvaney, 1996), respectively.

1 N NaOH (CO_2 trap) were placed into the Mason jars, and the jars were sealed with air-tight screw-top lids. The jars were incubated for 100 days in darkness at 25 ± 1℃. During incubation, the jars were opened for 10 minutes every other day to maintain an adequate O_2 level. In a previous study, the CO_2 loss during the aeration was estimated to be negligible (Lee et al., 2011). At 7, 21, 35, 49, 75, and 100 days of incubation, the vial containing the NaOH solution was removed from the jar and utilized for the analysis of CO_2, and a new vial with fresh NaOH solution was placed back in the jar at each sampling (except the last sampling at 100 days). Soil water content was adjusted by adding distilled water to the initial weight of the soil container at each sampling.

CO_2 Measurement and Calculation The amount of CO_2-C trapped in the NaOH solution was determined via the titration of the solution with 1 N HCl solution after the addition of 20 mL of 1 N $BaCl_2$ (Choi and Chang, 2005). The rate of CO_2 emission was expressed as mg C kg^{-1} soil day^{-1}. The amount of C emitted as CO_2 from the applied compost was calculated as the difference in the amount of CO_2-C evolved between the compost-amended soil and the control soil without compost, and the priming effect (influence of added compost on soil C mineralization in this study) was assumed to be negligible (Sinha et al., 1977; Bernal et al., 1998). The cumulative CO_2-C (C_{cum}) emitted over the 100-day incubation was calculated. For comparison among the composts, the C_{cum} was expressed as the % of added total organic C (TOC) of the composts ($C_{\%TOC}$).

Kinetic Model Fitting To estimate the pool size of mineralizable organic C and the mineralization rate constant, the data on cumulative CO_2-C evolution was fitted to the double exponential first-order kinetic model with the Fit Curve procedures of SigmaPlot 10.0 (Systat Software Inc., IL), which uses the Marquardt-Levenberg algorithm and an iterative process to determine the parameter values that minimize the residual sum of squares. The double exponential model separates the mineralizable organic C into rapidly and slowly mineralizable pools as follows:

$$C_{\%TOC} = C_R[1-exp(-k_Rt)]+ C_S[1-exp(-k_St)]$$

in which $C_{\%TOC}$ is the cumulative % of C mineralized from the compost at time t; C_R and C_S are the sizes of rapid and slow pools of mineralizable organic C (as % of TOC), respectively; and k_R and k_S are the corresponding mineralization rate constants (day^{-1}) for each pool. Generally, the automatically estimated parameters proved acceptable; however, in some cases, particularly in cases in which k_R and k_S were greater than a few orders of magnitude, the manual adjustment of the initial k_R and k_S values was required to generate sensible results (Wang et al., 2004).

Statistical Analysis One-way ANOVA on C_{cum}, $C_{\%TOC}$, and kinetics parameters (C_0, k_0, C_R, k_R, C_S, and k_S) was conducted to evaluate the effects of compost type using the GLM procedure in the SPSS 17.0 package (SPSS Inc., Chicago. IL, USA). When the treatment effects were significant, the means were separated by Duncan's multiple range tests. The significance of the first-order kinetic

model was analyzed by an *F*-test. The level of significance established for all statistical tests was $\alpha = 0.05$.

Results and Discussion

Temporal Pattern of CO₂ Emission Rate The maximum rate of C mineralization was noted during the first week of incubation particularly for the treatments with composts B and C; thereafter, the C mineralization rate gradually decreased with elapse of incubation time (Fig. 1). Such temporal pattern of C mineralization, an initial flush of CO_2-C followed by a gradual decrease or relatively constant mineralization rate, is not unusual and reported by other studies (e.g. Levi-Minizi et al., 1990; Ajwa and Tabatabai, 1994; Bernal et al., 1998; Aslam et al., 2008). The initial flush of CO_2 emission is believed to represent the presence of readily decomposable organic carbon (e.g. K_2SO_4 extractable organic C in our study) in the composts that stimulates microbial activities in the soils immediately

after application of the composts (Bernal et al., 1998). Therefore, the diminutive CO_2 peak of the soil with compost A during the early incubation period could be attributed primarily to its low K_2SO_4 extractable organic C (1.7 g C kg^{-1}, see Table 2). A steady emission of CO_2 from organics-amended soils following the initial flush is also widely reported and ascribed to depletion of readily decomposable organic C during the early incubation period (Bernal and Kirchmann, 1992; Kirchmann and Lundvall, 1993; Bernal et al., 1998; Rochette et al., 2006).

Cumulative CO₂ Emission and Its Relation with Substrate Quality The C_{cum} over time exhibited an exponential pattern (small figure in Fig. 1a) and were 165.7, 595.0, 1333.9, and 1478.1 mg C kg^{-1} for control, compost A, B, and C, respectively, at the end of incubation, and these were significantly ($P<0.001$) different among the treatments (Table 3). The greatest C_{cum} for compost C followed by compost B and A is well corresponding to the amount of C applied as compost: 8.86, 9.89, and 11.17 g C kg^{-1} soil for composts A, B, and C, respectively. Therefore, to investigate the effect of substrate quality on compost organic-C mineralization, it was necessary to express the C_{cum} as % of TOC of compost ($C_{\%TOC}$), and the values were 4.8, 11.8, and 11.7% for compost A, B, and C, respectively (Table 3). These values are within the range of 2.0 to 39.0% reported for matured composts by Bernal et al. (1998) and Helgason et al. (2005), but lower than the values (from 21 to 62%) reported for a variety of non-composted organic materials, including plant residues, animal manure, and sewage sludge (Ajwa and Tabatabai, 1994). Through an
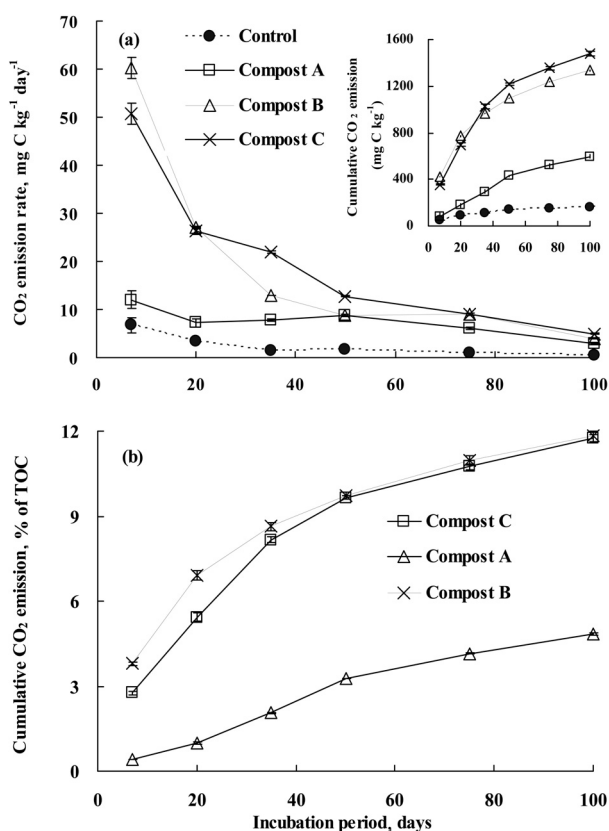

Fig. 1. (a) CO₂ emission rate from the soil amended with or without composts (cumulative CO₂ emission from both soil and compost is depicted in the small figure) and (b) cumulative CO₂ emission only from compost expressed as % of total organic C (TOC) of compost applied. Vertical bars are standard errors of the means.

Table 3. The cumulative amount of C mineralized (mg CO₂-C kg^{-1}) from the composts amended in the soils during the 100 days of incubation and its percentage relative to the total organic C (% of TOC) in the composts.

Treatment	Cumulative CO₂-C	
	Amount per soil	Percentage of compost TOC
	mg CO₂-Ckg^{-1}	% of TOC
Control	165.7 (1.1)a	Not applicable
Compost A	595.0 (3.9)b	4.8 (0.03)a
Compost B	1333.9 (18.3)c	11.8 (0.18)b
Compost C	1478.1 (14.5)c	11.7 (0.12)b
Effects	*Probability > F*	
Treatment	<0.001	<0.001

Values followed by the same letter are not statistically different at $\alpha = 0.05$.

incubation study using compost samples at different stages of composting (from initial to maturity stages), Bernal et al. (1998) suggested that a $C_{\%TOC}$ of over 25% after 70 days of incubation might indicate the pre-maturity of the composts. Therefore, all of the composts utilized in this study could be considered to be mature or stable.

Meanwhile, considering the lower SD of compost A (40.1%, see Table 2) than composts B (49.7%) and C (58.6%), such a low $C_{\%TOC}$ value of compost A is notable. Assuming that the three composts used in our study are biological stable judging from the $C_{\%TOC}$ as suggested by Bernal et al. (1998), such discordant relationship between SD and $C_{\%TOC}$ suggests that other factors can be more critical for C mineralization of compost. In the present study, the considerably lower $C_{\%TOC}$ of compost A than those of composts B and C collaborates with its low pH, C/N, K_2SO_4-extractable C, and NH_4^+/NO_3^- (Table 2). First of all, K_2SO_4-extractable C concentrations of composts A, B, and C were 1.7, 4.1, and 4.8 g C kg^{-1} (Table 2) and these amounts are equivalent to 0.63, 1.38, and 1.42% of TOC. As K_2SO_4-extractable C is considered to be readily decomposable organic C pool, therefore, the low extractable C concentration of compost A might have led to diminutive $C_{\%TOC}$ (Choi and Chang, 2005).

Meanwhile, pH, C/N, and NH_4^+/NO_3^- are closely associated with progress of composting stages and therefore, they may serve indicators of compost maturity and thus decomposability of the composts (Tittarelli et al., 2007). As the pH of the composting mixture tends to increase via the mineralization of organic N and protonation (R-NH$_2$ → NH_4^+ + OH$^-$) in the initial stage, followed by a progressive reduction as the result of nitrification (NH_4^+ → NO_3^- + 2H$^+$) and organic acid production, pre-matured compost may show a relatively high pH (Kim et al., 2008; Leconte et al., 2009). In this context, it is plausible that compost A (pH 8.1) is regarded as more mature than compost B (9.2) and C (8.9). The narrow C/N of compost seems to be another indicator of high maturity of compost A as the C/N of composting materials tends to decrease with the progress of microbial decomposition of the materials due to the faster loss of C relative to N (Kim et al., 2008). Regarding the molar ratio of NH_4^+ to NO_3^-, Helgason et al. (2005) reported that C mineralization of cattle manure composts applied to soils is proportional to the NH_4^+-to-NO_3^- ratio of the composts. This is attributable to the fact that active nitrification (oxidation of NH_4^+ to NO_3^-) occurs during the middle or late phase of composting following early decomposition of organic matter (Kim et al., 2008). Therefore, the lower NH_4^+-to-NO_3^- ratio of compost A represents changes in the concentrations of NH_4^+ (decrease) and NO_3^- (increase) with compost maturing.

The discrepancy between SD and maturity indices of composts observed in our study could be due to different type and mixing rate of co-composting materials such as rice hull and sawdust (Table 2). For compost A, rice hull and sawdust were mixed with pig manure at 30 and 20 v/v %, respectively; meanwhile for composts B and C, 50 and 55 v/v % of sawdust were mixed with livestock manure (Table 2). López et al. (2010) investigated SD of 25 types of composting materials including rice hull and wood materials and reported that SD of rice hull was 33% that is much lower than that (around 60%) wood materials. In the present study, the lower SD of compost A compared with those of composts B and C should be primarily due to relatively low SD of rice hull that used as co-composting materials. In this context, as our results in combination

Table 4. Parameter values (C_R, rapidly mineralizable C pool; C_S, slowly mineralizable C pool; k_R, mineralization rate constant of C_R; k_S, mineralization rate constant of C_S) of the double first-order equation model and *F*-values for CO_2-C mineralization of the composts in three soils.

Treatment	Rapid pool		Slow pool		F[†]
	C_R	k_R	C_S	k_S	
	% of TOC	day^{-1}	% of TOC	day^{-1}	
Compost A	5.2b	0.016a	6.1a	0.003a	67.7[**]
Compost B	4.5b	0.144b	9.8b	0.020b	7924.1[***]
Compost C	2.2a	0.132b	11.6b	0.026b	369.2[***]
Effects	*Probability > F*				
Treatment	<0.001	<0.001	<0.001	<0.001	

Values followed by the same letter are not statistically different at α=0.05.
[†] [*]P<0.05, [**]P<0.01, [***]P<0.001

with López et al. (2010) suggest that SD of compost is subject to not only compost maturity but also the type of co-composting materials, SD of compost alone can not be used in predicting compost organic-C mineralization. Therefore, other substrate quality indices such as pH, C/N, and NH_4^+/NO_3^- also needs to be considered to better predict compost decomposition.

Mineralization Kinetics   Overall, C mineralization was well fit with the double exponential first-order kinetic model, and the total mineralizable organic C pool in the composts was separated successfully into rapidly and slowly mineralizable (Table 4). The sizes of rapid (C_R) and slow pool (C_S) of mineralizable C of composts A, B, and C were 5.2, 4.5, and 2.2% and 6.1, 9.8, and 11.6% of TOC, respectively, and therefore, total mineralizable C ($C_{total}=C_R+C_S$) of composts A, B, and C were 11.3, 14.3, and 13.8%, respectively. Comparing with the $C_{\%TOC}$ of composts A (4.8%), B (11.8%), and C (11.7%), the geater C_{total} values than the $C_{\%TOC}$ indicates that mineralization of compost organic-C has not been completed during the 100-day incubation. Particularly for compost A, virtually the same value of $C_{\%TOC}$ to C_R suggests that only rapid pool was undergone decomposition. Meanwhile, the higher $C_{\%TOC}$ than C_R for composts B and C implies that mineralization of C_R has been completed and some part of C_S was experienced microbial decomposition.

The mineralization rate of the rapid pool (k_R) ranged between 0.016 and 0.144 day^{-1}, and this was much greater than the mineralization rate of the slow pool (k_S, from 0.003 to 0.026 day^{-1}) (Table 4). These indicate that the composts utilized in our study were heterogeneous, and consisted of organic C pools with differing biodegradability (Bernal and Kirchmann, 1992; Ajwa and Tabatabai, 1994; Bernal et al. 1998). For compost A, the much small values of both k_R and k_S well collaborates with the lower $C_{\%TOC}$ than other composts (Table 3).

Conclusion

Our study shows that C mineralization of compost was not correlated with SD but with other chemical indices associated with the progress of composting (maturity) such as pH, C/N, extractable C, and molar ratio of NH_4^+ to NO_3^-. The mal-linkage between C mineralization and SD of composts was attributed to the different types (rice hull and sawdust) of co-composting materials due to their dissimilar SD (sawdust > rice hull) before initiation of composting. Therefore, it is suggested that both SD and other chemical indices (pH, C/N, extractable C, and molar ratio of NH_4^+ to NO_3^-) needs to be considered for better prediction of C mineralization from compost-amended soils.

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