

Carbon Mineralization Kinetics from Legume Residues Applied to a High Altitude Acidic Soil

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ABSTRACT

An incubation study was conducted for 56 days under room temperature in a high altitude acidic soil (pH = 4.2) to evaluate carbon (C) mineralization from pea (*Pisum sativum L.*) residues and leaves from two agroforestry species (*Calliandra calothyrsus Meisn* and *Gliricidia sepium (Jacq.) Walp.*). Carbon dioxide (CO₂) evolution was measured at 7, 14, 21, 28, 42 and 56 days of incubation. Carbon mineralization was best fit to a sequential decomposition model with a rapid and slow phase, each described by first-order kinetics. Percent rapid, rapid and slow fraction rate constants and half-lives were determined. At the completion of the study, percent decomposition was higher for *Pisum sativum L.* (77.3 %) followed by *Calliandra calothyrsus Meisn* (60.8 %) and *Gliricidia sepium (Jacq.) Walp* (56.7 %). Similarly, higher percent rapid fractions (78 %), higher decomposition rate constants ($k_r = 0.053 \text{ day}^{-1}$; $k_s = 0.012 \text{ day}^{-1}$) and lower half-lives [$t_{0.5}(r) = 13 \text{ days}$; $t_{0.5}(s) = 58 \text{ days}$] were also observed with *Pisum sativum L.* residues. From the findings of this investigation, it appears that the higher lignin content of the two agroforestry species, *Gliricidia sepium (Jacq.) Walp* (6.33 %) and *Calliandra calothyrsus Meisn* (4.16 %) was the limiting factor of their decomposability, as compared to *Pisum sativum L.* which had zero lignin content. This study highlighted pea (*Pisum sativum L.*) residue as the most effective in C mineralization.

Key Words: Carbon dioxide, first-order kinetics, legume residues, lignin, N, C/N.

1. INTRODUCTION

The sustainability of crop production in Burundi is threatened by vicious cycles of declining soil fertility and increasing acidic soils in some regions. Generally, farmers are increasingly concerned about soil fragility and low organic matter in their fields. Some researchers highlighted that incorporation of plant residues may help long term soil fertility as it preserves and improves physical, chemical and biological soil properties through soil organic matter formation and maintenance [7][10][13][14]. Likewise, it was reported that the use of green manure could promote nutrient cycling and improve the synchrony of nutrient release with crop demand [3]. Nowadays, many research works are conducted to understand the pattern of legume leaf decomposition and its release of nutrients [4].

Carbon mineralization has been widely used to estimate organic material mineralization in the soil under controlled conditions [8] [11]. Carbon makes up about 45 % of the elements in the dry plant biomass [15]. Hence, C mineralization as measured by CO₂ evolution is used as a general indicator of the persistence or decomposability of organic materials applied to soil. In addition, a significant correlation between nutrient release, particularly N, P and evolved CO₂ from organic residues has been shown [8][12]. Foregoing research reported that organic materials containing more protein (N) would decompose easily, whereas residues containing more lignin would resist microbial degradation [5]. Our hypothesis is that legume residues with higher lignin content

would decompose slower than residues with lower lignin content. To verify this hypothesis, a study was carried out under controlled laboratory conditions using an acidic soil and two agroforestry species with high lignin content (*Calliandra calothyrsus* Meisn and *Gliricidia sepium* (Jacq.) Walp) and *Pisum sativum* L. with no lignin content. The aim of the study was to comparatively assess the decomposability of pea (*Pisum sativum* L.) residues and leaves from *Calliandra calothyrsus* Meisn and *Gliricidia sepium* (Jacq.) Walp for C mineralization.

1. MATERIAL AND METHODS

1.1. Soil

The soil used in the study was collected from the Ruzibazi Seed Center, a government farm located 50 km South-East of Bujumbura City, in Mukike Commune. Soil physical and chemical analyses included particle size, pH, % C, % N, Cation Exchangeable Capacity (CEC), exchangeable Al^{3+} and H^+ . Soil pH was measured using a 1:1 soil-water mixture. Organic C was determined by the Walkley-Black method [15]. Organic N was measured as described by Bremner and Mulvaney (1982) [2]. Selected physical and chemical properties of the soil are given in Table 1.

Table 1. Selected physico-chemical characteristics of the Ruzibazi soil

Parameter	Ruzibazi
pH	4.2
% C	4.05
% N	0.33
C/N	12.27
CEC (cmol _c /kg)	16.30
Exchangeable Al^{3+} (cmol _c /kg)	2.33
Exchangeable H^+ (cmol _c /kg)	0.37
Clay (%)	64.87
Silt (%)	13.18
Sand (%)	21.95

1.2. Legume leaves

Calliandra calothyrsus Meisn and *Gliricidia sepium* (Jacq.) Walp leaves were collected on living hedges near Bujumbura, while pea (*Pisum sativum* L.) residues were collected after crop harvest in Ruzibazi Seed Center. The organic materials were dried at 70° C to a constant weight before chemical analyses were performed. Total N was determined by digestion with sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) followed by steam distillation [2]. Total C was determined by dry combustion [15]. Total P, K, Ca and Mg were analyzed by ICP spectrometry after digestion of a 0.2 g-sample with HNO_3 and H_2O_2 at 120° C for 3 hours [22]. Selected properties of the legume residues are shown in Table 2.

Table 2. Selected chemical characteristics of legume leaves

Parameter	<i>Gliricidia sepium</i>	<i>Calliandra calothyrsus</i>	<i>Pisum sativum</i>
% C	45.1	45.6	45.2
% N	2.93	3.80	1.37
C/N	15.4	12	33
% Lignin	6.33	4.16	0
% P	0.14	0.25	0.08
% K	1.81	1.36	1.11
% Ca	1.88	0.85	1.41
% Mg	0.35	0.30	0.26

1.3. Incubation procedure

Each incubation vessel (250-mL) was fitted with 2 test tubes each containing 5 mL of 2 N KOH to capture evolved CO_2 . The laboratory incubation was conducted at room temperature ($27 \pm 1^\circ C$) in the soil laboratory of the Faculty of Agricultural Sciences, University of Burundi. Soil samples (50 g d.w basis) from the top-layer (0-15 cm) cultivated field were mixed with legume leaves

to a field application of 1000 kg ha⁻¹, considered realistic under Burundi rural conditions. Fifty (50) mg of organic materials were homogenously mixed with soil. At this rate, 22.55, 22.80 and 22.6 mg C were applied from *Gliricidia sepium* (Jacq.) Walp, *Calliandra calothyrsus* Meisn and *Pisum sativum* L., respectively. The soil was partially air dried at room temperature until it could be crashed and sieved through a 2-mm sieve. Plant materials were cut into approximately 0.5 cm-long sections and were incorporated in soil samples.

The mixtures soil-organic amendments were incubated under aerobic conditions under room temperature during 8 weeks. Soil moisture was set at 60 % water holding capacity (WHC) and respired CO₂ was regularly trapped into alkali solution and titrated with standard HCl.

For each treatment of organic amendments, blank and control, CO₂ sampling was performed at 7, 14, 21, 28, 42 and 56 days of incubation. All incubation vessels were opened and aerated for about 5 minutes at each sampling period to maintain aerobic conditions, while test tubes containing the alkali solution were simultaneously changed and titrated [20][23]. Control soils without organic amendments were set, and empty incubation vessels (blanks) were used as controls for CO₂ absorbed from the atmosphere during the incubation procedure. The total CO₂ collected in the dilute KOH solution was determined by titration to a phenolphthalein indicator endpoint with standardized HCl following precipitation of the carbonates with a BaCl₂ solution, according to the following reactions [19]:



1.4. Calculations

Carbon evolved as CO₂ was estimated as follow [20]:

$$\text{mg C as CO}_2 = (\text{B} - \text{V}) \times \text{N} \times \text{E} \quad (4)$$

Where: B = mL of standard acid for the blank;

V = mL of standard acid for amended treatments;

N = Normality of standard acid;

E = Equivalent weight C (=6).

Soil basal respiration (control unamended soil) was subtracted from the gross respiration to assess the net respiration associated with added organic C mineralization. The total respired CO₂-C quantities were obtained by summing the CO₂-C respired between sampling days. Percentage of decomposition was estimated by calculating the percentage of C added evolved as CO₂ after correction for the CO₂ evolved from unamended soils according to the following Equation (5):

$$\% \text{ C decomposed} = [(\text{X} - \text{Y})/\text{Z}] \times 100 \quad (5)$$

Where: X = mg of C evolved as CO₂ from amended treatments;

Y = mg of C evolved as CO₂ from unamended treatments;

Z = mg of C added in different leguminous leaves.

1.5. Decomposition models

Varied mathematical models have been used to describe C mineralization either from soil organic matter or added organic materials [9][12]. Most models follow the first-order kinetics, for which the magnitude of decomposition is assumed proportional to the quantity of mineralizable C.

Considering the following chemical transformation: C → X, applying the stepwise derivatives and integration will produce the model described by a differential Equation (6a).

$$dC/dt = -k C \rightarrow dC/C = -k dt \quad (6a)$$

which leads to Equation (6b) after some calculations.

$$C_t = C_o e^{-kt} \quad (6b)$$

Where: C_t = Carbon content at time t (day);

C_o = initial C content;

k = first-order rate constant (day⁻¹);

t = time, days.

Equation (6b) describes the simple or one-component exponential model, which assumes that only one form of potentially mineralizable C exists and mineralizes at a rate proportional to its concentration. However, organic materials are not homogenous. They comprise organic fractions of different decomposition potentials: labile and non-labile components. The decomposition models of such organic materials follows a sequential bi-phasic model with an initial rapid phase followed by a slow decomposition phase, each described by first-order kinetics. Using various organic materials under diverse experimental conditions, such models have used by a number of investigators [6][9][12].

The sequential model assumes a complete decomposition of the rapid fraction before the slow fraction decomposition starts. The model is described by Equation (7a) for the rapid fraction and Equation (7b) for the slow fraction:

$$\% \text{ decomposed} = 100 [(1 - \exp(-k_r t_r))] \quad (7a)$$

$$\% \text{ decomposed} = (100 - \% \text{ Rapid}) [1 - \exp(-k_s (t - t_r))] \quad (7b)$$

Where: % Rapid = amount of residue C in the rapid fraction; 100 - % Rapid = amount of the residue C in the slow fraction; k_r = rapid fraction first order rate constant; k_s = slow fraction first order rate constant; t_r (< t) = time (day) for rapid fraction complete decomposition, and
t = time (days).

1.6. Statistical analyses

The incubation study was conducted in a completely randomized design (CRD). Experimental treatments consisted of a blank, a control (soil only) and legume leaves and residues amended treatments. Each treatment was replicated three times. Decomposition of applied organic materials was described by Equation (6b) for the one-component model and Equations (7a) and (7b) for the sequential bi-phasic model.

Decomposition rate constants (k) were estimated by using the Linear Least Squares (LLS). The software used to evaluate the fitness of different models of C decomposition kinetics from legume leaves and residues was JMP IN Version 3.2 [18]. Data were fitted both to the simple (one-component) and bi-phasic exponential models and for each case, decomposition rate constants (k in day^{-1}) and half-lives ($t_{0.5}$ in days) were estimated according to Equation (8).

$$t_{0.5} = 0.693/k \quad (8)$$

2. RESULTS AND DISCUSSION

2.1. Evolved cumulative CO₂-C and Percent C decomposition

In application of Equation (4), Figure 1 below illustrates the quantity of evolved CO₂-C for the control (soil alone), and *Gliricidia sepium* (Jacq.) Walp, *Calliandra calothyrsus* Meisn and *Pisum sativum* L. amended soils. The highest evolved CO₂ was obtained with *Pisum sativum* L. residues followed by *Calliandra calothyrsus* Meisn and *Gliricidia sepium* (Jacq.) Walp leaves. As expected, the control (unamended) soils were characterized by lower quantities of evolved CO₂.

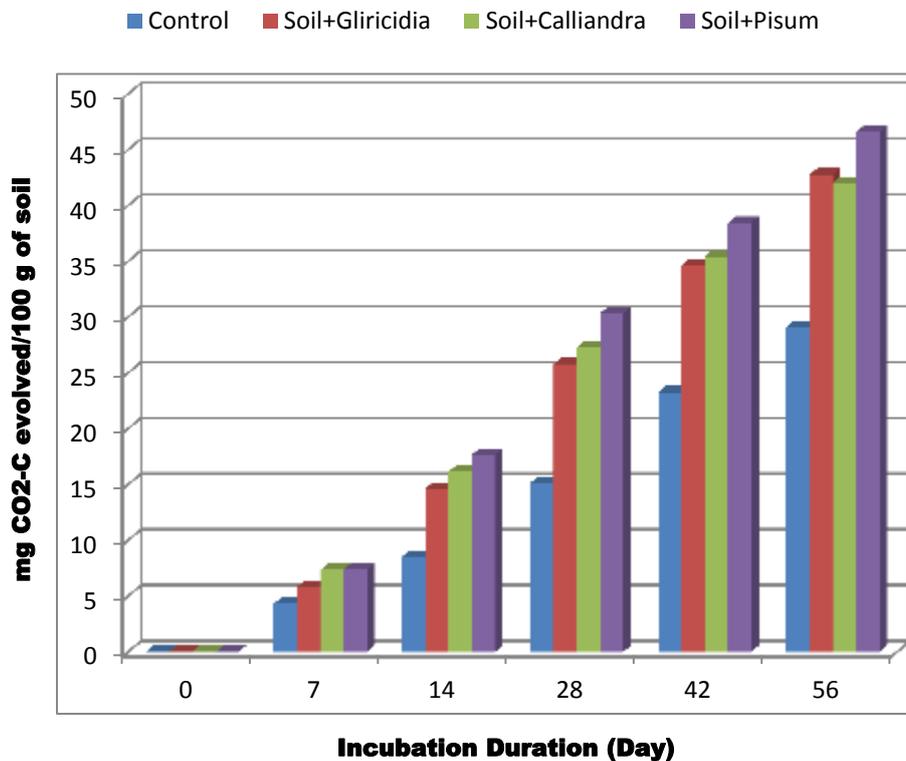


Figure 1. Cumulative CO₂-C evolution from soil-applied organic amendments

At the completion of the 56-day incubation study, percent C decomposition from Equation (5) was as follows (p = 0.006): *Pisum sativum L.* (77.3 %) > *Calliandra calothyrsus Meisn.* (60.8 %) > *Gliricidia sepium (Jacq.) Walp* (56.7 %). This trend is inverse of the lignin content of the organic materials used in the present study, which was higher for *Gliricidia sepium (Jacq.) Walp* (6.33 %) followed by *Calliandra calothyrsus Meisn* (4.16 %), while that of *Pisum sativum L.* was nil (see Table 2 above). Considering the % C mineralization shown in our data, it appears that the % lignin content of the studied organic materials is affecting their decomposability, more than their N content C/N ratios. Hence, our working hypothesis is verified: *Gliricidia sepium (Jacq.) Walp* and *Calliandra calothyrsus Meisn* leaves with higher lignin content decompose slower than legume residues with lower lignin content such as *Pisum sativum L.*

3.2. One-component (simple) exponential model

Most studies on C decomposition kinetics have used the simple (one-component) first-order kinetics as highlighted by Equation (6b). Table 3 shows the first-order kinetics parameters found in our study. First-order rate constants ranged from 0.016 to 0.036 day⁻¹, while half-lives ranged from 19.3 to 43.4 days. Decomposition rate constant was higher and half-life was lower with *Pisum sativum L.* residues than the other two organic materials tested.

Table 3. One-component (simple) exponential models of C decomposition of organic materials applied to Ruzibazi soil.

Organic material	Decomposition model	R ²	Probability	T _{0.5} (day)
Calliandra calothyrsus	Y = 4,493 - 0.016 t	0.61	< 0.0001	43.3
Gliricidia sepium	Y = 4,488 - 0.016 t	0.60	< 0.0002	43.3
Pisum sativum	Y = 4,557 - 0.036 t	0.87	< 0.0001	19.3

For a comparison purpose, Table 4 indicates organic material decomposition parameters (rate constant -k- and half-life -t_{0.5}-) reported in similar studies conducted under various conditions, in Africa and elsewhere.

Table 4. Effect of organic material type and geographic (climate) location on decomposition parameters.

Organic material	k (day ⁻¹)	t _{0.5} (day)	References
Rye straw (Nigeria)	0.04	17.33	Paul & Clark (1988) [16]
Rye straw (England)	0.01	69.30	Paul & Clark (1988)
Wheat straw (Canada)	0.03	23.10	Paul & Clark (1988)
Buried wheat straw (Burundi)	0.0134	57.72	Bicereza (2001) [1]
Surface-applied wheat straw (Burundi)	0.0062	111.77	Bicereza (2001)
Lignin	0.003	231	Paul & Clark (1988)
Natural grass	0.006	115.50	Paul & Clark (1988)

3.3. Biphase (two-component) exponential model

Simple (one-component) first-order equations have been found not to accurately describe substrate C mineralization from initiation to completion, because of the heterogeneity of organic substrates under decomposition [17]. In fact, it must be stressed out that the main components of organic materials include easily oxidizable soluble organic C (sugars, starch, amino acids); proteins, hemicellulose, cellulose and lignin, which, in our understanding, should not metabolize (decompose) in a similar way.

In a study on kinetics of varied added organic matter decomposition in a sandy soil, the superiority of the double exponential model over a simple (one-component) model was observed [21]. Parallel to fitting our data to a simple (one-component) exponential model, in application of Equations (7a) and (7b), we also evaluated the double (two-component) exponential C decomposition model. Parameters generated by such model are shown in Table 5 below.

Table 5. Biphase (two-component) exponential models of C decomposition of organic materials applied to Ruzibazi soil.

Organic material	k _r	k _s	t _{0.5} (r)	t _{0.5} (s)	% Rapid
<i>Calliandra calothyrsus</i>	0.029	0.002	24	347	55
<i>Gliricidia sepium</i>	0.029	0.002	24	347	55
<i>Pisum sativum</i>	0.053	0.012	13	58	78

Compared to the two other organic materials under investigation, the double (two-component) exponential model indicates that *Pisum sativum L.* residues are characterized by a higher proportion of rapid fraction (78 %) and subsequently higher decomposition rate constant (k_r = 0.053 day⁻¹) and lower half-lives [t_{0.5}(r) = 13 days and t_{0.5}(s) = 58 days]. Despite its lower N content (1.37 %) and high C/N (33), pea (*Pisum sativum L.*) residues decomposed faster than *Calliandra calothyrsus Meisn* (% N = 3.80; C/N = 12) and *Gliricidia sepium (Jacq.) Walp* (% N = 2.93; C/N = 15.4), which were characterized by higher N contents and lower C/N ratios. The lignin content is apparently the controlling factor of the decomposability of the soil applied organic materials.

3. CONCLUSION

Organic C mineralization as measured by CO₂ evolution is used as an indicator of the persistence or decomposability of organic materials applied to soil. This methodology was used to compare the decomposability of leaves from two agroforestry legume species (*Calliandra calothyrsus Meisn* and *Gliricidia sepium (Jacq.) Walp*) and pea (*Pisum sativum L.*) residues collected after crop harvest. At the completion of the incubation study, percent C mineralization followed the order: *Pisum sativum L.* (77.3 %) > *Calliandra calothyrsus Meisn* (60.8 %) > *Gliricidia sepium (Jacq.) Walp* (56.7 %). This trend does neither follow the N content nor the C/N ratios of the organic materials tested. Instead, this study shows that lignin content is the controlling factor of their decomposability. As a matter of fact, lignin content followed an opposite trend to percent C decomposition: *Pisum sativum L.* (0 %) < *Calliandra calothyrsus Meisn* (4.16 %) < *Gliricidia sepium (Jacq.) Walp* (6.33 %). Carbon mineralization data were fitted to simple (one-component) and biphase (two-component) exponential models. The latter model was considered biochemically more realistic, because organic materials are composed of various biochemical structures with presumably different decomposability potentials. *Pisum sativum L.* showed higher percent rapid fractions (78 %), higher decomposition rate constants (k_r = 0.053 day⁻¹; k_s = 0.012 day⁻¹) and lower half-lives [t_{0.5}(r) = 13 days; t_{0.5}(s) = 58 days] than the two agroforestry legume species (*Calliandra calothyrsus Meisn* and *Gliricidia sepium (Jacq.) Walp*). The higher lignin content of the latter species is a limiting factor of their decomposability. The results revealed pea (*Pisum sativum L.*) residues as the most efficient in carbon mineralization.

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