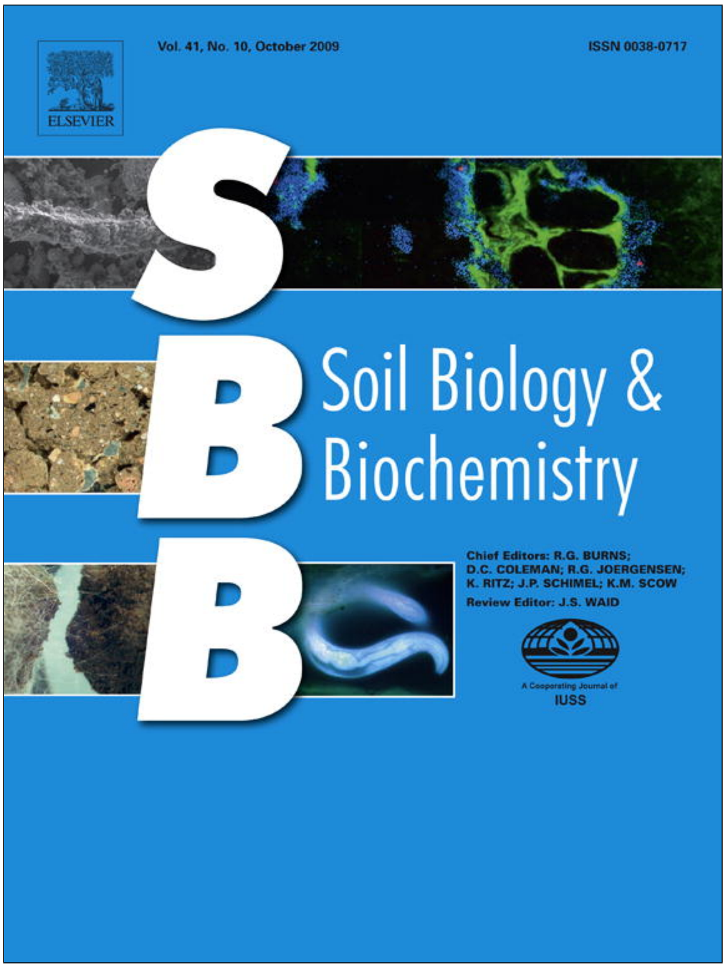

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Soil organic C stabilization and thresholds in C saturation

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ABSTRACT

When building soil organic matter (SOM) contents in agricultural production systems, stabilization of both pre-existing as well as added C is important. A laboratory mineralization experiment was conducted over 374 days to evaluate the effect of pre-existing SOM on soil C mineralization after addition of organic matter (OM) using sugar cane. The SOM gradient used here stretched from 21 to 106 g C kg^{-1} soil and was a result of different periods of continuous cultivation of 5, 20, 35 and 105 years in comparison to a forest soil. The rate of organic C mineralization was found to be dependent on the status of pre-existing soil organic C (SOC). Highly degraded soil which had been under continuous cultivation for 35 years and more showed the highest rate of C mineralization per unit SOC (117.9 mg C g^{-1} C) while forest soil had the lowest amount of C mineralized per unit SOC (73.5 mg C g^{-1} C). Forest soil had the highest amount of increased C mineralization as a result of organic matter (OM) additions (8.0 mg C g^{-1} soil) followed by the highly degraded soil that had been under cultivation for 105 years (5.5 mg C g^{-1} soil). Additional mineralized C as a function of time after forest conversion declined progressively within the first 20 years of continuous soil use. Soil which had been under continuous cultivation for 20 years had the lowest amount of additional mineralized C (4.0 mg C g^{-1} soil). SOM stabilization efficiency in the studied soils appears to be highest with intermediate cultivation history of about 20 years. These soils that have been recently converted to cultivation also appear to have a greater ability to stabilize added OM than the most degraded soils investigated in this study. It is thus advisable to provide intervention strategies to reverse SOM decline for farming communities at an intermediate stage before the soils are highly depleted of SOC.

1. Introduction

Land use will largely determine the potential for soil organic C (SOC) storage and ultimately C sequestration in soil (Bronick and Lal, 2005; Zingore et al., 2005; Solomon et al., 2007). Total ecosystem budgets reflect a long-term equilibrium in C pools and fluxes (Houghton, 2005). In an unmanaged environment, both mineralization and stabilization of C need to be at equilibrium for a sustained ecosystem productivity to be realized. However, this steady state is massively warped when these unmanaged ecosystems are converted to agricultural production which, depending on the management, can initiate a series of soil degradation processes (Macedo et al., 2008). The magnitude and intensity is influenced by the biophysical characteristics of the soil as well as environmental factors such as temperature and rainfall.

Moreover, soil organic matter (SOM) plays an integral part in sustaining soil cation exchange capacity (CEC) and soil aggregation. It also acts as an active sink and source reservoir for plant nutrients (Craswell and Lefroy, 2001; Six et al., 2002a,b; Gulde et al., 2008; Macedo et al., 2008) thus determining productivity of an ecosystem (Sollins et al., 2006). As a result, in soil systems that have low-activity clays, such as highly weathered tropical soils (Sanchez, 1976; Jones et al., 1997; Steiner et al., 2007), the effectiveness of nutrient cycling resulting from OM decomposition define their productivity (Vitousek, 1984; Macedo et al., 2008). Therefore, SOM depletion leads to degradation of the soil system as the nutrient holding capacity weakens threatening the system's sustainable production (Lemenih et al., 2005). In this study we investigated the link between soil degradation status, SOM replenishment and stabilization.

Replenishment of labile SOM pools in degraded soils could easily be attained by appropriate management interventions such as using organic inputs (Lehmann et al., 1998) or short-term fallows (Barrios et al., 1997). Nonetheless, ecosystem deterioration and the

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resultant low SOM status have a direct and/or indirect influence on the decay rate of the added OM, C stabilization and the cycling of nutrients in terrestrial ecosystems. Although increased quantity and frequency of either internal or external C inputs could be considered as a positive step towards increasing SOM, improving C stability in the soil matrix is equally as important. Sollins et al. (2007) emphasized the need for a clear understanding and definition of the underlying mechanisms for SOC stabilization. This can help in providing meaningful predictions of carbon dioxide (CO_2) emissions under changing climatic regimes and steadily increasing demand for both agricultural and forest products.

The ability to stabilize C in the soil varies to a great extent depending on the chemical and physical properties of the mineral matrix as well as the morphology and the chemical structure of SOM (Baldock and Skjemstad, 2000). The presence of multivalent cations in the soil matrix (Kaiser and Guggenberger, 2000) also affects the stabilization of organic C in soil (Baldock and Skjemstad, 2000). In recent advances on the C saturation concept, Six et al. (2002a), Stewart et al. (2007, 2008) and Gulde et al. (2008) reiterate that the physicochemical characteristics inherent to soils put a ceiling on the protective capacity of SOM pools by soil aggregates and clay minerals, which limits increases in SOM even with the addition of organic inputs (e.g. Campbell et al., 1991; Paustian et al., 1997; Solberg et al., 1997; Kimetu et al., 2008). Six et al. (2002a) and Stewart et al. (2007) hypothesized that soils with high OM status have a lower C stabilization efficiency compared with low OM-containing soils. However, this has not yet been demonstrated along a wide gradient of pre-existing SOC. Additionally, in the Pendleton long-term experiments, Oregon, Knoth (2004) observed that C mineralized from added OM was lower when the OM was added to less degraded soils with greater amounts of SOM. Therefore, the effects of pre-existing SOM quantity and quality on stabilization of added OM appear to be still unresolved. We thus sought to investigate how the status of pre-existing SOM influences the stabilization of the added OM hypothesizing that a threshold of soil C saturation can be identified beyond which soil C stabilization by OM additions progresses very slowly.

The main objective of this study was to evaluate the effect of pre-existing SOC on soil C mineralization in response to OM additions and identify thresholds of soil C saturation beyond which C stabilization progresses very slowly. The following hypotheses were tested in this study: (i) soils with low levels of SOC show low C mineralization in response to OM additions than soils with high SOC; (ii) if pre-existing SOC influences the stabilization of added OM, there is a threshold in soil C saturation with decreasing SOC and increasing soil degradation beyond which soil C mineralization increases.

2. Materials and methods

2.1. Experimental set up

An incubation trial was conducted to evaluate the influence of pre-existing SOM status on the stabilization of added OM in a controlled environment. Constant temperature laboratory soil incubations at 30 °C (Sanchez et al., 2001) were set up to monitor CO_2 evolution in order to evaluate the effects of OM additions on C mineralization. One hundred grams of soil were used for the set of untreated soil while for the treated soil; 98 g of soil were mixed with 2 g of sugar cane (total $C = 420$ mg g^{-1}, total $N = 10$ mg g^{-1}, C/N ratio of 42) ground to fine powder. Thus, a total of about 0.8 g C and 0.02 g N were added to each incubation vessel. Three replicates were used per treatment including a set of three empty mason jars (blanks).

The soil was sampled from the South Nandi district of western Kenya which is predominantly a heavy textured Ultisol with 74% clay + silt and 26% sand. The SOM contents of these soils range from about 20 mg g^{-1} to 100 mg g^{-1} as a result of different lengths of continuous maize cropping, stretching from recent forest conversions (five years) to conversions done in the late 19th century (over 100 years) (Kinyangi et al., 2006; Solomon et al., 2007; Kimetu et al., 2008). Forest soil was included as a reference point for soil degradation. More details on site characteristics are given in Table 1. Soil moisture content was adjusted to field capacity (determined to be 30%–40% w/w; which was maintained throughout the incubation period) after which the unit was incubated in 1-L mason jars for slightly over one year.

2.2. Soil respiration measurement

Carbon dioxide released from soil was trapped using soda lime (Edwards, 1982) whereby about 0.5–2.0 g of soda lime (Mallinckrodt Baker, Paris, KY, highest absorption capacity 26%) was put in 30-mL Qorpak vials, dried for 24 h at 105 °C then exposed in 1-L mason jars containing soil as well as in the empty jars (blanks) which were tightly closed. After each CO_2 trapping, the vials containing soda lime were retrieved and dried for 24 h at 105 °C after which the dry weight was determined. The amount of CO_2 absorbed by the soda lime is proportional to the weight increase (pre-exposure dry weight subtracted from post-exposure dry weight) of soda lime during the exposure period (Grogan, 1998). The amount of mineralized C was quantified gravimetrically using the following equation: Mineralized C (mg) $= [1.69 \times (\text{weight gain}) \times 12/44]$; whereby 1.69 is a pre-determined correction factor for weight loss during soda lime drying of water formed during the reaction of CO_2 with soda lime (Edwards, 1982; Grogan, 1998). Values obtained from blanks were subtracted from the treatment values so as to account for the CO_2 absorption during soda lime handling. Soda lime was changed after seven days for the first sampling, after two weeks for the second and third samplings, then after every four weeks in subsequent samplings.

2.3. Statistical modeling

Biogeochemical degradation of both added and pre-existing OM was modeled using non-linear regression. Model equation and curve fitting were calculated in Sigma Plot for Windows, Version 9.0 (SPSS Inc. 2004). Carbon mineralization was fitted using a four parameter double exponential rise curve:

$$y = a[1 - \exp(-bx)] + c[1 - \exp(-dx)]$$

where a and c represent the size of labile and recalcitrant C fractions, respectively, while b and d represent the corresponding mineralization rates for the labile and recalcitrant C fractions, and x is the mineralization time in days.

Table 1
Site characteristics (means and standard errors ($n = 3$)).

Time of continuous cultivation (years)	Initial soil indicators				
	SOC (g kg^{-1})	CEC_{pot} ($mmol_c$ kg^{-1})	CEC_{eff} ($mmol_c$ kg^{-1})	pH_{water} (1:2.5)	BS (%)
0	105.0 ± 0.0	nd	331 ± 0.0	6.2 ± 0.1	nd
5	59.9 ± 2.3	320 ± 9	235 ± 13	6.3 ± 0.1	99.6 ± 0.0
20	32.6 ± 1.6	170 ± 3	47 ± 5	5.2 ± 0.1	70.2 ± 0.0
35	21.7 ± 1.4	187 ± 18	91 ± 5	5.5 ± 0.0	96.3 ± 0.3
105	21.1 ± 1.1	262 ± 3	116 ± 0.1	5.9 ± 0.0	98.1 ± 0.1

Source: Modified from Kimetu et al. (2008); nd = no data.
CEC_{pot}: cation exchange capacity determined at a pH of 7.
CEC_{eff}: cation exchange capacity determined at the pH of the soil.
BS: base saturation is the fraction of cation exchange sites that are occupied by Ca, Mg, K, and Na at CEC_{eff}.

The statistical differences between experimental treatments and between soil degradation stages at each point of measurement and cumulative C mineralization were determined through Analysis of Variance (General ANOVA procedure, GenStat version 10.1, Rothamsted Research Station, 2007) using a completely randomized design with three replicates. Mean separation was computed using least significant difference (LSD) at $P < 0.05$.

3. Results

The rate of organic C mineralization depended on the length of time of continuous soil use (Fig. 1). Highly degraded soil that had been under continuous cultivation for more than 35 years showed the highest rate of C mineralization per unit SOC, while forest soil had the lowest amount of C mineralized per unit SOC. Cumulative SOC mineralization over slightly above one year increased from forest with 73.5 mg g^{-1} C to 5 years of cultivation with 82.8 mg g^{-1} C, and more significantly after 20, 35 and 105 years with 100.5, 117.9, and 104.4 mg g^{-1} C, respectively (Table 2).

Although C mineralization depended on the pre-existing soil organic C status (Fig. 1), an addition of OM stimulated C mineralization in all soils (Fig. 2). Thus, significantly higher ($P < 0.05$) C mineralization was observed when OM was added as compared with soil to which no OM was added. This was the case both per unit mass of soil (Fig. 2) and per unit SOC (data not shown). Especially for the amended soils, the rate of C mineralization decreased with time of incubation indicating that less C was mineralized as time of incubation progressed. An initially high C mineralization rate was observed which slowed after the first 50 days of incubation and in some instances (conversion of 20 years and older with added OM) attained a plateau after about 300 days. Soil with the highest SOC had the highest rate of C mineralization per unit soil mass (Fig. 2). Rates of C mineralization in the unamended soils were relatively constant after the first 14 days of incubation throughout the incubation period regardless of the status of the pre-existing SOC.

The rate of labile C mineralization in soils with OM added was lowest in soil that had been under continuous cultivation for 20 years (Table 3). The same observation was evident whether determined per unit soil mass (Table 3a) or per unit SOC (Table 3b).

Total C mineralized as a result of added OM differed significantly ($P < 0.05$) depending on the status of the pre-existing SOC (Table 2). Forest soil depicted the highest apparent C mineralized from OM additions (8.0 mg C g^{-1} soil, difference between C mineralization with and without OM addition; Table 2) during the one year incubation period followed by the highly degraded soil (5.5 mg C g^{-1} soil). Soils that had been under continuous cultivation for 20 years had the lowest amount of applied C mineralized (4.0 mg C g^{-1} soil). A progressive increase of mineralized C with continuous soil use brought apparent applied C mineralization in the highly degraded soil as high as 5.5 mg C g^{-1} soil.

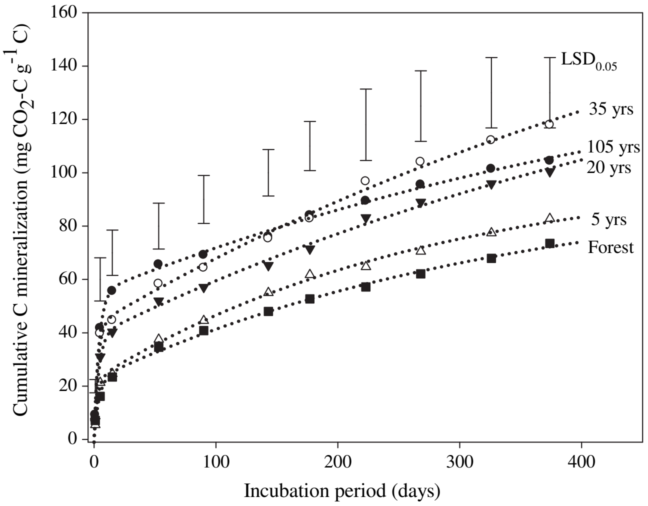

Fig. 1. Cumulative C mineralization per unit soil organic C in unamended soil with varying cultivation histories over a more than one year incubation period ($n = 3$ and error bars are LSD at $P < 0.05$).

Table 2
Total CO_2-C mineralization over 374 days as a function of time under cultivation and OM additions; values in the same column followed by the same letter are not significantly different at $P < 0.05$ ($n = 3$).

Time (years)	Without OM addition	Without OM addition	With OM addition
	(mg CO_2–C g^{-1} C)	(mg CO_2–C g^{-1} soil)	(mg CO_2–C g^{-1} soil)
0	73.5^{c}	7.8^{a}	15.8^{a}
5	82.8^{bc}	4.9^{b}	10.3^{b}
20	100.5^{ab}	3.8^{c}	7.8^{c}
35	117.9^{a}	3.0^{cd}	8.1^{c}
105	104.4^{ab}	2.4^{d}	7.9^{c}

4. Discussion

Carbon mineralization as a result of OM inputs increased to a greater extent in soils with high pre-existing SOC. For example, the largest amount of C (accounting for about 88% of the added OM) was mineralized in the forest soil during the incubation period. This observation can be attributed to (a) the presence of a relatively higher level of active microbial biomass in the soil (Li et al., 2004; Goberna et al., 2006) and (b) the possible attainment of the C protection limit of this soil (C saturation point) (Stewart et al., 2007, 2008; Gulde et al., 2008). Six et al. (2002a) and Stewart et al. (2007) point out that the physicochemical characteristics inherent to soils can put a ceiling on the protective capacity of stable SOM pools associated with soil aggregates and clay minerals, which limit increases in SOM even with increased external or internal inputs. This proposed C limit may have led to reduced protection of the added OM which was hence mineralized to a large extent. This could indicate reduced stabilization efficiency in soils containing already large amounts of SOC. This concurs with Hassink (1996) who observed that the degree of saturation of the protective capacity of a soil predicts the decomposition and stabilization rate of added OM.

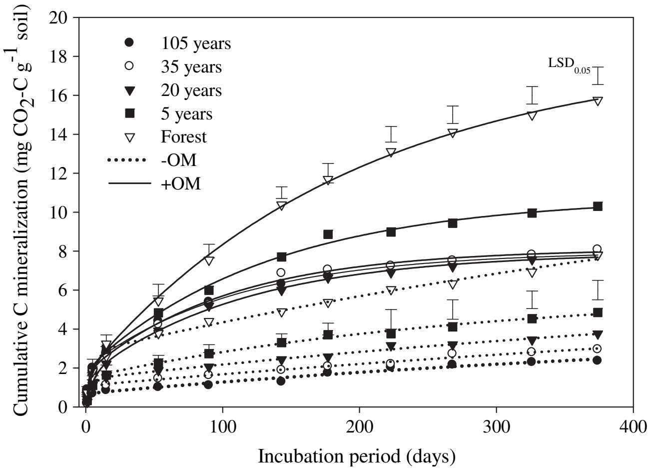

Fig. 2. Cumulative C mineralization in soils with differing cultivation histories with (+OM) and without (−OM) added OM over a more than one year incubation period ($n = 3$ and error bars are LSD at $P < 0.05$).

Table 3
Non-linear regression for C mineralization after OM addition (amended soil only) across a chronosequence of continuous soil use. Model: Four parameter double exponential rise: $y = a[1 - \exp(-bx)] + c[1 - \exp(-dx)]$.

Parameter	Time of continuous soil use (years)				
	0	5	20	35	105
a. per unit soil					
a	1.73	1.908	1.5477	1.7378	1.9915
b	0.2797	0.4026	0.2037	0.4479	0.4924
c	16.51	8.87	6.3797	6.3831	6.0025
d	0.0051	0.0075	0.0087	0.0098	0.0091
P value	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
r^2	0.9988	0.9969	0.9987	0.9968	0.9994
b. per unit soil organic carbon					
a	13.2	27.06	39.34	44.96	65.47
b	0.3	0.435	0.169	0.495	0.4912
c	146.7	144.16	139.52	197.4	197.32
d	0.0052	0.0068	0.0078	0.0099	0.0091
p value	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
r^2	0.9989	0.998	0.9991	0.9985	0.9994

The possible attainment of a C saturation point in these soils was also shown in our earlier study (Kimetu et al., 2008). Adding OM in the amount of 18 t C ha^{-1} with widely varying quality over three cropping seasons did not result in a significant increase in SOC in the high C-containing soils. This has also been shown in several other studies that have been carried out in high C-containing soils (Campbell et al., 1991; Paustian et al., 1997; Solberg et al., 1997). Several suggestions have been put forward to further explain this C protection limit for different soils. These include the silt + clay content (Hassink, 1996, 1997; Stewart et al., 2007), soil structure (Pulleman and Marinissen, 2004), and the biochemical complexity of organic compounds (Baldock and Skjemstad, 2000). On the other hand, the amount of C mineralized after adding OM in the highly degraded soil was also relatively high compared to the moderately degraded soils (20-year cultivation history). This high C mineralization in the soils with the longest cultivation history (hence lowest SOC contents) might be an indication of reduced physical protection of organic compounds in the soil (Del Galdo et al., 2003; Degryze et al., 2004; Grandy and Robertson, 2006). An explanation may be a high rate of aggregate turnover (Six et al., 1998) caused by continuous soil tillage which exposes both the pre-existing and added C to microbial degradation.

Soils with a 20-year cultivation history had the lowest C mineralization rate which may indicate a higher C stabilization rate. Once forest soils are converted to agricultural production, disruption of soil aggregation may cause exposure of the SOC to microbial degradation leading to a rapid decline of SOC within the first 15–20 years of continuous soil use.

According to Lützow et al. (2006), the two main factors that control soil C storage are input (quantity and quality) and decomposition rate. Taking into account the observations in the current study, we propose that an additional key factor was the status of the pre-existing SOC which controls decomposition rates of added OM and hence C storage in the soil. As argued by Six et al. (2002a) and Stewart et al. (2007, 2008), the further a soil is from its saturation point, the more efficient it is in sequestering and storing C, whereas, a soil approaching its saturation point will be less efficient in sequestering added C and will accrue added C at a slower rate (Hassink and Whitmore, 1997; Stewart et al., 2007). If a soil has already reached its C saturation point, any further C additions are more likely to be immediately degraded by soil microbes. Hence, soils with high pre-existing OM contents are likely to limit further C storage especially if the C saturation point has already been attained. Therefore as observed in the current study, the soils with low pre-existing OM could accrue and stabilize added OM more readily than the higher SOC-containing soils.

5. Conclusions

Depending on the C saturation limit of a soil, soils with high soil organic C have high rates of labile C mineralization possibly due to limited protection of organic matter by minerals. Mineralization rates from soil depleted in SOC were lower than in high C-containing soils. The least additional mineralization as a response to adding OM was observed in soil which had been under continuous cultivation for 20–35 years. This appears to be a cut-off point whereby stabilization of any added OM does not increase further. OM additions appear to be most efficient for increasing SOC in soils with intermediate cultivation history that are not as saturated with SOC as soils that have been recently converted to cultivation but have greater ability to stabilize added OM than the most degraded soils investigated here. Further studies should investigate whether the quality of added OM has an influence on the C stabilization dynamics discussed here.

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