



Organic carbon dynamics in soils with pyrogenic organic matter that received plant residue additions over seven years



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ABSTRACT

The effect of repeated application of plant residues on mineralization of different organic carbon (OC) pools in a pyrogenic organic matter (PyOM) amended soil was determined using an incubation study conducted over 7.1 years. At five occasions during this period, sugarcane residues (C₄) were mixed with the soil (C₄) with or without PyOM (C₃) amendments. Organic C mineralized during the incubation period or remaining in different physical soil fractions after 7.1 years was partitioned into PyOM carbon (PyOM-C) and native soil organic matter C (nSOM-C) or sugarcane C plus nSOM-C (SC-C + nSOM-C). When compared to the control, total cumulative OC (comprising both nSOM-C and PyOM-C) mineralized in the presence of PyOM was 40% higher after the first 2.5 years, but equal by 6.2 years and 3% lower by the end of the incubation period. The cumulative nSOM mineralization after 7.1 years was 2.57 mg CO₂–C g^{–1} soil with PyOM compared to 3.16 mg CO₂–C g^{–1} soil without PyOM addition ($p = 0.13$; $n = 3$). More than 60% of the added PyOM-C was present in the free-light fraction by the end of the 7.1 years. In total, 93% of the added PyOM-C remained in soil compared to 25–28% of SC-C + nSOM-C. Sugarcane residues increased the remaining PyOM-C in the occluded-light fraction by 3% ($p < 0.05$) and in the organo-mineral fraction by 4% ($p < 0.1$), suggesting a possible preferential use of SC-C or accumulation of metabolites of decomposed PyOM. However, the addition of sugarcane had no significant effect on overall mineralization of PyOM. The presence of PyOM accelerated the mineralization of SC-C + nSOM-C by 9% ($p < 0.001$). This is probably due to enhanced mineralization of sugarcane residues rather than native SOM. Although PyOM was likely to accelerate mineralization of added plant residues throughout a 7-year period, PyOM did not increase cumulative nSOM mineralization when plant residues were absent ($p > 0.05$), so PyOM may reduce nSOM mineralization in the long term.

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1. Introduction

Pyrogenic carbon (PyC) is produced from vegetation fires (Czimeczik and Masiello, 2007) and is thought to constitute a significant portion of soil organic C (SOC) (Preston and Schmidt, 2006; Knicker, 2011). The substantial accumulation of PyC in soil, despite estimates of relatively small amounts of PyC produced during fires (Forbes et al., 2006), may be explained by the fact that mineralization of PyC is very slow and it remains in soil for longer periods of

time than uncharred OC (Baldock and Smernik, 2002; Kuzyakov et al., 2014). In some cases, pyrogenic organic matter (PyOM) improves soil fertility and other soil properties (see Biederman and Harpole, 2013 for a recent review). Therefore, it has been suggested that biomass could intentionally be converted into PyOM (typically called biochar in this context) and applied to agricultural soils as a mechanism to sequester atmospheric CO₂ and reduce global warming (Lehmann, 2007; Whitman et al., 2010; Woolf et al., 2010).

Sometimes PyOM can accelerate native soil organic matter (nSOM) mineralization, an effect referred to as positive priming (Wardle et al., 2008; Luo et al., 2011). This could partially offset the net C accrual by PyC (Woolf and Lehmann, 2012). Other studies, however, report decreased net mineralization of nSOM, often after

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an initial increase (Zimmerman et al., 2011; Whitman et al., 2014a, 2014b). The mechanisms for these divergent results are not yet clear (Whitman et al., 2015). Moreover, the addition of relatively easily-mineralizable plant residues to PyOM-containing soil may also alter the mineralization rates of PyC, the added residue and existing nSOM (Keith et al., 2011; Whitman et al., 2014a). In agricultural and forest soils, such residues repeatedly enter the soil in the form of root exudates and crop or foliage residues. To date, however, no information exists on how OC mineralization would change with repeated application of plant residues to PyOM-amended soils (Whitman et al., 2015).

Repeated addition of plant residues may affect the mineralization of either or all of the three organic matter forms: the PyOM, the existing nSOM, and the residue itself. First, PyOM mineralization itself differs whether or not relatively easily mineralizable plant residues are added (Hamer et al., 2004). Repeated residue additions may either reduce PyOM mineralization due the microorganisms' preference for organic matter that is easily mineralizable, or increase PyOM mineralization due to co-metabolism (Willmann and Fakoussa, 1997). Since mineralization of PyOM that was in the soil for centuries did not increase after plant residue additions (Liang et al., 2010), but fresh PyOM mineralized to a greater extent (Hamer et al., 2004), we expect that any increase in PyOM mineralization during the first plant residue addition will give way to a decrease in PyOM mineralization during subsequent additions.

Second, PyOM-induced changes in nSOM mineralization appear to follow a distinct temporal pattern (Woolf and Lehmann, 2012), likely affecting both nSOM and any added residues. While more often than not, increased mineralization of nSOM has been observed in an initial phase over a period of weeks or a few months after PyOM additions, decreased mineralization of nSOM has been documented thereafter (Keith et al., 2011; Zimmerman et al., 2011). Increased mineralization of nSOM in the initial period after PyOM addition is hypothesized to be caused by the stimulation of microbial activity and mineralization of easily metabolizable C present on PyOM surfaces or by changes in pH and nutrients (Whitman et al., 2014a). This stimulation of mineralization would be expected to be short-lived and likely not operate on residues that are applied several years after the PyOM entered the soil. A reduction in mineralization of repeatedly added residues may be expected as a result interactions of nSOM or added residues with PyOM surfaces that have been reported recently for one-time additions (Whitman et al., 2014b).

Therefore, the objective of this study was to determine the effects of repeated soil application of plant residues on carbon dioxide emissions and on cumulative OC amounts in physically separated OC fractions after one-time PyOM addition in an incubation study conducted over a 7-year period. We hypothesized that (i) repeated application of abundant plant residues will reduce PyOM mineralization, and (ii) one-time PyOM addition will decrease mineralization of nSOM and repeatedly added plant residues.

2. Materials and methods

2.1. Soil type and organic additions

The soil was an aniso-hyperthermic kaolinitic Typic Haplustox, sandy clay loam, which developed from alluvial sediments originating in the Andes under a mean annual temperature of 26 °C and precipitation of 2200 mm. It was taken from an experiment at the Matazol farm in the Llanos Orientales of Colombia (N 04°10'15.2", W 72°36'12.9") (Major et al., 2010a). The native C₄ vegetation dominated the region for a long period of time, giving rise to soil $\delta^{13}\text{C}$ value of -12.89‰ , and OC content of 20 mg g⁻¹ (Table 1).

Table 1
Properties of the soil, PyOM and sugarcane materials used in the experiment.

		PyOM	Soil	Sugarcane
pH	(H ₂ O)	10.1	nd	nd
pH	(KCl)	8.9	3.9	nd
Total C	(mg g ⁻¹)	717	20	415
$\delta^{13}\text{C}$	(‰)	-28.86	-12.89	-11.90
Total N	(mg g ⁻¹)	2.6	1.3	10.8
C/N	(w/w)	280	15	38
H/C	(mol/mol)	0.26	nd	nd
Ash	(% w/w)	8	nd	nd
Ca ^a	(mg g ⁻¹)	2.93	0.19	nd
K ^a	(mg g ⁻¹)	3.30	0.03	nd
Mg ^a	($\mu\text{g g}^{-1}$)	291	57	nd
P ^a	($\mu\text{g g}^{-1}$)	259	13	nd
CEC ^b	(mmol _c kg ⁻¹)	235	110	nd

nd: not determined.

^a Available nutrient contents extracted with Mehlich 3.

^b Determined at pH 7.

The PyOM was made from prunings of old mango (*Mangifera indica* L.) trees using a mound kiln with pyrolysis temperatures between 400 °C and 600 °C and carbonization times of approximately 48 h (Major et al., 2010a). The PyOM was crushed by hand using a metallic disk pestle, to pass through a 5-mm sieve, and mixed well. The PyOM had a $\delta^{13}\text{C}$ value of -28.86‰ , and OC of 717 mg g⁻¹ (Table 1).

The plant residue was derived from sugarcane (*Saccharum officinarum* L.) plants grown in a greenhouse and fertilized with a nutrient solution. After harvesting, the plants were separated into leaves and stems, cut, and oven-dried at 45 °C for 48 h. Only the leaves were ground to <2 mm and used for the incubation (and referred to here as 'plant residue'). The sugarcane residues had a $\delta^{13}\text{C}$ value of -11.90‰ , and OC of 415 mg g⁻¹ (Table 1).

2.2. Long term incubation experiment

Four treatments with and without added plant residues were arranged in a randomized complete block design with three replicates: (1) 2 g PyOM mixed with 98 g soil (PyOM); (2) 2 g sugarcane mixed with 98 g soil (SC); (3) 2 g sugarcane and 2 g PyOM mixed with 96 g soil (PyOM + SC); and (4) a control treatment with only 100 g soil (NON). Blank jars were included, as well, to account for any leakages. The PyOM and sugarcane were added to the air-dried soil before the experiment and mixed well. The long term incubation experiment spanned 7.1 years (2596 days). At four times during the incubation (at day 921, 1523, 2010, 2257), an additional 2 g sugarcane was mixed with the soil in SC and PyOM + SC treatments, and will be referred to as five different phases of the incubation. Similar mixing of the soil was done to the two treatments where no sugarcane was added. The samples were kept in 0.95-L wide-mouth, airtight Mason jars, and incubated at a constant temperature of 30 °C. Soil moisture content was adjusted to 55% of water holding capacity at the beginning of the incubation and maintained over the incubation period by watering to weight at regular intervals.

For measurements of C mineralization, evolved CO₂ was trapped by the soda lime and the amount of mineralized C was quantified gravimetrically (Edwards, 1982; Grogan, 1998). The amount of CO₂ absorbed by the soda lime is proportional to its dry-weight increase and evolved CO₂ can be calculated using a conversion factor of [1.69 (weight gain) 12/44] (Grogan, 1998). About 0.2–1.0 g soda lime (Mallinckrodt Baker, Paris, Kentucky, highest absorption capacity 26%) were added to 30-mL Qorpak vials, dried for 24 h at 105 °C before and after each CO₂ trapping. During the incubation period, CO₂ trapped in soda lime was sampled 57 times. Sampling intervals were shorter immediately after each sugarcane addition (day 1 and

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