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Lower residue decomposition in historically charcoal-enriched soils is related to increased adsorption of organic matter

Bart Kerré*, Bernd Willaert, Erik Smolders

Division of Soil and Water Management, KU Leuven, Kasteelpark Arenberg 20, 3001 Heverlee, Belgium

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ABSTRACT

Previous field observations have shown increased soil carbon (C) sequestration in charcoal amended soils due to an accumulation of non-charcoal derived soil C. This study was set up to compare and analyse mineralization of non-charcoal derived C between soils that were either or not historically enriched in charcoal. Maize straw (^{13}C-enriched) was added to samples of arable soil collected under historical charcoal kilns and corresponding adjacent control soil. The respiration was monitored in laboratory conditions for 227 days. Charcoal in soil significantly lowered total soil respiration (1905 vs. 1984 mg C kg^{-1}). Mineralization of ^{13}C-enriched added maize C (AMC) was unaffected by charcoal in the initial weeks after maize straw addition, however differences became significant at longer incubations yielding a markedly lower mineralized fraction in the charcoal enriched samples after 227 days (70 versus 62%, $P < 0.05$). A two fraction mineralization model revealed no charcoal effect on the labile fraction and its degradation but that the stable fraction of AMC was larger and degraded slower in the presence of charcoal. A soil drying-rewetting event (35 days) increased respiration to the same extent in charcoal-enriched as in adjacent soils. In contrast, the dissolved organic carbon (DOC) in pore water was significantly lower in charcoal-enriched than in adjacent soils. Microbial biomass-C (MBC) determined by fumigation-centrifugation was not significantly different between charcoal-enriched and adjacent soil (309 mg vs. 266 mg MBC kg^{-1}). A soil adsorption experiment with DOC, extracted from a grassland soil, revealed larger DOC sorption with increasing soil charcoal concentration. This study shows that reduced C mineralization of non-charcoal C in charcoal-enriched soil is most likely related to enhanced sorption of more recalcitrant organic matter, rather than to lower MBC.

1. Introduction

Biochar, a type of charcoal, is promoted as a soil amendment to increase soil carbon (C) sequestration and subsequently mitigate climate change (Woolf et al., 2010). Charcoal-C is highly persistent in soil and charring biomass is a way to increase overall persistency of biomass-C in the environment. In addition, biochar added to soils can increase long-term sequestration of non-charcoal C, as shown in soils under historical charcoal kilns in agricultural and forest sites (Borchard et al., 2014; Hernandez-Soriano et al., 2016a; Kerré et al., 2016a).

Increased C sequestration due to biochar can result from higher crop yields, especially in tropical soils where biochar amendment has positive effects on soil pH, water retention capacity and cation exchange capacity (Jeffery et al., 2011). For temperature regions, however, reduced crop-derived C mineralization in presence of charcoal may be more relevant. Short-term studies with fresh biochar reported both negative (reduced C decomposition) and positive priming (i.e. enhanced C decomposition) effects on non-biochar C following biochar amendment to soil (Zimmerman et al., 2011). This demonstrates that the extent and direction of priming effects are dependent on biochar characteristics such as feedstock and pyrolysis conditions, and, more importantly, its residence time in soil (Kerré et al., 2016b; Singh and Cowie, 2014; Zimmerman et al., 2011). Indeed, there is growing consensus that negative priming effects of aged biochar will prevail on the long term, although relevant long-term studies are scarce.

Hernandez-Soriano et al. (2016a) showed that decomposition of maize crop residue can be halved in long-term charcoal-enriched soils relative to corresponding unamended soils. The drawback of that study was that the limited stable C isotope discrimination capacity did not allow to unequivocally estimate the fraction of

* Corresponding author.
E-mail address: bart.kerre@ees.kuleuven.be (B. Kerré).

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maize crop residues in both soils since the charcoal and soil organic matter had small differences in ^{13}C natural abundance. Reduced mineralization of native soil C in charcoal amended soils was also observed by Liang et al. (2010), however this study was conducted on tropical soils. Therefore, unequivocal C degradation studies with and without historical charcoal amendment in temperate soils are, to our knowledge, non-existent. Consequently, thorough understanding of the underlying mechanisms of negative priming effects in charcoal-amended soils are lacking.

Negative priming following biochar amendment is attributed to a decreased bioavailability of added labile C through increased sorption (Kasozi et al., 2010) or enhanced organo-mineral associations (Brodowski et al., 2006; Kerré et al., 2016a; Singh and Cowie, 2014), and reduced microbial activity (Liang et al., 2010). Sorption of organic matter to biochar is promoted through biochar surface oxidation and formation of functional groups with time, referred to as biochar 'ageing' (Cheng et al., 2014; Zimmerman et al., 2011). Leaching of dissolved organic carbon (DOC) might be attenuated in charcoal-enriched soils, with a preferential retention of more recalcitrant DOC components (Eykelbosh et al., 2015; Kalbitz et al., 2005; Maestrini et al., 2015). Apart from sorption-related C stabilization, charcoal has the capacity to promote stabilization of C through a faster incorporation of C into physically protected soil fractions (Hernandez-Soriano et al., 2016a; Kerré et al., 2016b).

The effect of aged charcoal on microbial biomass and activity is unclear. Fresh biochar forms a preferential microhabitat for organisms in soil due to its labile C content, porosity, sorption capacity and change in abiotic factors (e.g. increasing pH) (Luo et al., 2013). A meta-analysis study of Liu et al. (2016) indeed showed an overall positive effect of biochar amendment on microbial biomass carbon (MBC) on the short-term. This is in agreement with the overall short-term biochar-induced positive priming, observed in another recent meta-analysis (Maestrini et al., 2015). Whether this is still valid on the longer term, however, needs further investigation (Lehmann et al., 2011), as charcoal ages over time, as discussed above. Indeed, Liang et al. (2010) observed higher microbial biomass and concurrent negative native soil C priming in soils with aged charcoal. The higher MBC was attributed to charcoal providing a protecting habitat for microorganisms, rather than to an increased C and nutrient availability.

We recently showed that crop-derived C concentration in charcoal-enriched soils can increase up to a factor 1.7 relative to corresponding adjacent soils after several decades of use (Kerré et al., 2016a). The objective of current study was to explore the mechanisms responsible for this increased C sequestration in presence of aged charcoal. Therefore, we used the exact same soil samples from Kerré et al. (2016a), which are obtained from agricultural fields containing historical (>150 year) charcoal production sites. Decomposition of crop residue will be simulated with a highly ^{13}C-enriched maize straw to ensure accurate calculations. The hypothesis is that maize-C respiration will be lower when added to charcoal-enriched soils compared to that in adjacent soils. Additionally, we hypothesize that this reduced C mineralization can be related to changes in microbial biomass, and reduced release of DOC in charcoal-enriched soils with a high DOC-sorption capacity. A soil drying-rewetting cycle was included to identify the role of charcoal on respiration under such conditions.

2. Materials and methods

2.1. Soil sampling

Four different fields were sampled (January 2014) where charcoal-enriched soils were identified under historical charcoal production sites, visible as 'black spots' on the bare arable fields. Those sites were in use in the 18th–19th century before being abandoned, and have approximate diameter of about 10–20 m. On each field, a composite soil samples (eight subsamples, 0–23 cm) was collected from two charcoal-enriched soils and two corresponding adjacent soils. The adjacent soils were sampled within 10 m of the black spots, on the same field, as fully described in Kerré et al. (2016a). This yielded 16 different soil samples (4 fields, 2 spots sampled, either in or adjacent to the spot). All soil samples were air-dried, sieved to 2 mm and stored until experiments. Main soil properties are given in Table 1.

2.2. Long-term incubation experiment

In a first experiment, triplicate subsamples (40 g dry soil) of the 16 soil samples were placed in 300 mL closed glass jars and pre-incubated (25 °C, 60% water-filled pore space (WFPS), darkness) during three weeks. Thereafter, uniformly ^{13}C-labelled maize straw (De Troyer et al., 2011) ($\delta^{13}C = 1940‰$) was added at 5 g dry matter per kg dry soil (equivalent to 2.1 g C kg^{-1} soil) and thoroughly mixed. After mixing, the jars were incubated in the same conditions as during pre-incubation and randomly distributed. Additionally, three empty jars were included to determine background conditions.

Soil respiration (CO_2) and carbon isotopic signature ($\delta^{13}C$) was monitored during 227 days through periodical air sampling and renewal of the headspace. Concentration (ppm) of CO_2 was measured with a LI-COR CO_2 infrared gas analyser (LI-820, Lincoln, Nebraska, USA) and $\delta^{13}C$ through gas chromatography isotope ratio mass spectrometry (GC-IRMS, Thermo Fisher Scientific, Bremen, Germany). At the end of the incubation, all soil samples were air-dried, and subsamples were oven-dried (50 °C) and ball-milled to determine residual organic C content and $\delta^{13}C$, with a Flash EA 1112 HT coupled to isotope ratio mass spectrometry (IRMS, Thermo Fisher Scientific, Bremen, Germany).

The proportion (f) of C derived from the added maize-C (AMC) in the different C pools (i.e. CO_2 or total soil) was calculated using a two-component isotopic mixing model:

$$f = \frac{\delta^{13}C_{pool} - \delta^{13}C_{soil}}{\delta^{13}C_{maize} - \delta^{13}C_{soil}} \quad (1)$$

with $\delta^{13}C_{pool}$ the isotopic composition (in ‰) of C of the measured pool, $\delta^{13}C_{soil}$ the isotopic composition of the original soil (i.e. before addition of the maize straw), and $\delta^{13}C_{maize}$ the isotopic composition of the ^{13}C-labelled AMC (1940‰). The $\delta^{13}C_{pool}$ of the CO_2 was first blank-corrected taking into account the concentration and isotopic signature of the empty jars. Finally, the amount of AMC in each pool was calculated by multiplying f with the total OC in the corresponding pool. The total AMC mineralization (% of AMC added) after a specific incubation time equals the sum of the amounts of AMC respired between day 0 and the corresponding incubation time, as a percentage of AMC added.

The respiration data were converted to residual soil AMC, i.e. residual AMC = 100 − % of AMC mineralized. The evolution of residual AMC was described by a double-exponential model (Zimmerman et al., 2011):

$$AMC_R = AMC_L * e^{-k_L * t} + AMC_S * e^{-k_S * t} \quad (2)$$

where AMC_R = residual AMC fraction in soil (% of AMC added), AMC_L and AMC_S = fraction of labile and stable AMC pool (% of AMC mineralized), respectively, k_L and k_S = the first order decay rate constant for the labile and stable pool (day^{-1}), respectively, and t = incubation time (day). Note that $AMC_L + AMC_S = 100$, i.e. model