The mean turnover time of biochar in soil varies depending on biomass source and pyrolysis temperature

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Abstract
The rate of turnover (decomposition) of biochar carbon (C) is the major determinant of its value in long-term C sequestration in soil. However, little research has been undertaken to quantify the mean turnover time of biochar applied to soil and its effect on 'native' soil C. In order to precisely quantify the magnitude and rate at which biochar C is decomposed in soil and released as CO_2, we have initiated a long-term incubation experiment using a novel method based on measuring the inherent differences in $\delta^{13}C$ signature between biochar and soil. Briefly, biochars from a range of C_3-biomass sources (bluegum wood and leaves, paper sludge, poultry manure on rice hull, and cow manure) produced at different temperatures (400ºC or 550ºC) and activation level (activated or non-activated), were applied to a clay-rich soil (Vertisol) from a C_4-pasture (*Astrebla* spp.) field. Soil-respired CO_2-C and microbial-C and their associated $\delta^{13}C$ values have been measured over 2.3 years to date, and are continuing. Results show decomposition of biochar C varied depending on biomass source and pyrolysis temperature and only 0.3% to 6.0% of the applied biochar C was decomposed in the first 2.3 years of incubation. Biochar application enhanced decomposition of 'native' soil C; this priming effect on soil C was higher in soil amended with leaf or poultry manure biochars than wood biochars. Microbial biomass C was not affected by the biochar treatments, except for the low-temperature poultry manure biochar treatment which significantly increased microbial biomass C as compared to the control. Our estimates of mean turnover time of biochar-C, determined by fitting the two-pool kinetic model to the cumulative CO_2-C evolved under ideal conditions in the laboratory, ranged from approximately 100 to 1300 years between biochar types. The low-temperature (400°C) manure biochars decomposed substantially more quickly than the high-temperature (550°C) biochars.

Key Words
Biochar carbon turnover, soil carbon turnover, natural ^{13}C abundance, microbial biomass, priming

Introduction
There is growing interest in the use of biochar (black C) as a soil amendment, with potential to increase soil C, improve soil properties, reduce greenhouse gas (GHG) emissions, and enhance agricultural productivity. Because the pyrolysis process produces biochar that can provide long-term C sequestration in soil, and also generates renewable bioenergy, it is said to be a "carbon negative" process (removing more CO_2 from the atmosphere than is emitted). Desktop calculations of whole of life GHG balance of biochar production and utilisation for a range of biochar scenarios, compared with conventional practices, have shown that biochar C turnover rate is one of the major factors affecting the GHG mitigation value of its application to soil (Cowie, unpublished).

Review of the literature has indicated that very little is known about turnover rate of naturally-produced or manufactured biochar (e.g. Schmidt and Noack, 2000; Lehman *et al*., 2006). The biochar remaining in soil following fire events in natural and managed ecosystems (black C) is considered an inert pool of soil C (i.e. highly resistant to biological degradation), which could accumulate over the course of centuries or millennia. Because of its long residence time, black C is considered to play a vital role in long-term sequestration of C in soil (Skjemstad *et al*., 2001; Preston and Schmidt, 2006). It is likely that manufactured biochar will have similarly slow turnover time when applied to soil. However, contradictory degradation rates of both (natural and manufactured) biochar types have been reported in the literature (Bird *et al*., 1999; Hamer *et al*., 2004; Kuzyakov *et al*., 2009). The recalcitrance of biochar against biological degradation also is likely to depend on pyrolysis temperature. For example, the aromaticity of biochar has been shown to increase with increasing production temperature (Baldock and Smernik, 2002). Clearly, research is needed to accurately quantify mean turnover time and understand stabilisation mechanisms of biochar C in soil. For the present study, biochars from a range of C_3-vegetation sources ($\delta^{13}C$ ~ -22 to -29 ‰) were incorporated into a clay-

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rich soil (Vertisol) collected from a paddock under C_4-vegetation (Mitchell grass, *Astrebla* spp., with $\delta^{13}C$ ~ -14 ‰) and are being incubated for up to 5 years. In this paper, we report the results obtained in the first 2.3 years of incubation.

Methods

Soil and biochar material and their preparation for incubation

Soil for this study was collected from a paddock (top 10 cm depth) at Toorak Research Station (TRS) in Julia Creek (Queensland) (21°016′S, 141°784′E). The soil is classified as a Vertisol and contains 0.42% organic C and -14.1‰ $\delta^{13}C$ signature (Table 1). Biochars from a range of C_3-biomass sources (blue gum wood and leaves, paper sludge, poultry manure on rice hull, and cow manure) were prepared at different temperatures (400ºC or 550ºC) and activation level (activated or non-activated) (Table 1) by Best Energies, Australia.

Table 1. Biochar treatments (T1 to T12) along with total carbon content (%) and $\delta^{13}C$ signature (‰) of the biomass, the corresponding biochar and the soil used in the experiment.

Biomass source	Pyrolysis temperature (°C)	Activation treatment	Biomass / Biochar (% total C)	Biomass / Biochar (‰ $\delta^{13}C$)
(T1) Blue gum wood	400	Activated	47.9 / 73.2	-27.6 / -28.5
(T2) Blue gum wood	550	Activated	47.9 / 83.9	-27.6 / -28.8
(T3) Blue gum wood	400	Non-activated	47.9 / 72.8	-27.6 / -28.4
(T4) Blue gum wood	550	Non-activated	47.9 / 83.3	-27.6 / -28.8
(T5) Blue gum leaves	400	Activated	50.1 / 67.8	-28.2 / -28.2
(T6) Blue gum leaves	550	Activated	50.1 / 74.1	-28.2 / -28.2
(T7) Paper sludge	550	Activated	33.5 / 32.0	-23.6 / -21.7
(T8) Poultry manure	400	Non-activated	39.3 / 46.8	-24.9 / -25.0
(T9) Poultry manure	550	Activated	39.3 / 46.0	-24.9 / -25.1
(T10) Cow manure	400	Non-activated	20.0 / 21.5	-27.4 / -27.5
(T11) Cow manure	550	Activated	20.0 / 18.8	-27.4 / -27.9
(T12) Non-amended soil			0.42	-14.1

Incubation experiment

The soil (650 g, air-dried, 2 mm sieved) from a paddock under C_4-vegetation, adjusted to ~ 70% of water holding capacity using a dilute inorganic N solution, and inoculated with 1.4 g of a microbial-rich <2mm moist soil, was placed in plastic containers in triplicate. Ten days after preconditioning of the moist soil to ensure development of microbial populations, different biochar materials (ground to <2 mm) were homogenously mixed with the soil to a concentration of 8.2 g biochar per kg of soil (oven-dried basis), corresponding to 10.2 t biochar per ha to a depth of 10 cm (bulk density 1.25 t m^{-3}). A control treatment of soil without biochar was also included. Just before refilling the containers, 2 ml of nutrient solution (containing N, P, K, Ca, Mg, S, Cu, Zn, Mo, Co, Na) in appropriate concentrations was sprayed onto biochar-amended and non-amended soils and then uniformly mixed. Following amendments, containers were placed in 5-L sealed buckets containing (i) 100 mL of water to maintain a water-saturated atmosphere, and (ii) 30 mL of 2 M NaOH to trap microbial-respired CO_2. The sealed buckets were then placed in a dark room and incubated at 22±1°C.

Analyses

Soil-respired CO_2 is being monitored by periodically removing NaOH from sealed containers and then measuring trapped CO_2 by titration with HCl. The CO_2 trapped in NaOH is precipitated with $SrCl_2$ aqueous solution as $SrCO_3$ for $\delta^{13}C$ analysis using an IRMS (Harris *et al*., 1997). The biochar-derived and soil-derived C is determined from a ^{13}C mass balance equation (Rochette *et al*., 1999; Schweizer *et al*., 1999).

The mean turnover time of decomposing biochars was determined by fitting the two-pool model to the cumulative biochar-derived CO_2-C evolved. To determine soil microbial biomass C, moist soil samples (23–24g) were fumigated for 10 d in with chloroform containing amylene (0.006% v/v) as a stabiliser, followed by extraction with 80 ml of 0.5 M K_2SO_4. The corresponding non-fumigated soil samples were also extracted

with 0.5 M K_2SO_4 in the same way on the day of fumigation. Organic C in the filtered 0.5 M K_2SO_4 extracts was determined by the dichromate digestion method of Vance *et al*. (1987).

Results

- Carbon content of biochar increased as pyrolysis temperature increased from 400°C to 550°C for bluegum biomass, but not for the poultry and cow manures (Table 1).
- The $\delta^{13}C$ of biochar was depleted by up to -1.2‰, compared to $\delta^{13}C$ of biomass, except for biochars from leaves (no change in $\delta^{13}C$) and paper sludge ($\delta^{13}C$ enrichment of -1.9‰) (Table 1).
- The $\delta^{13}C$ of paper sludge biochar was higher by 3.3 to 7.1‰ compared with the other biochars probably due to the presence of ^{13}C-enriched carbonate (Table 1).
- The rate of C mineralisation from biochar-amended and control soils decreased with time (Figure 1).

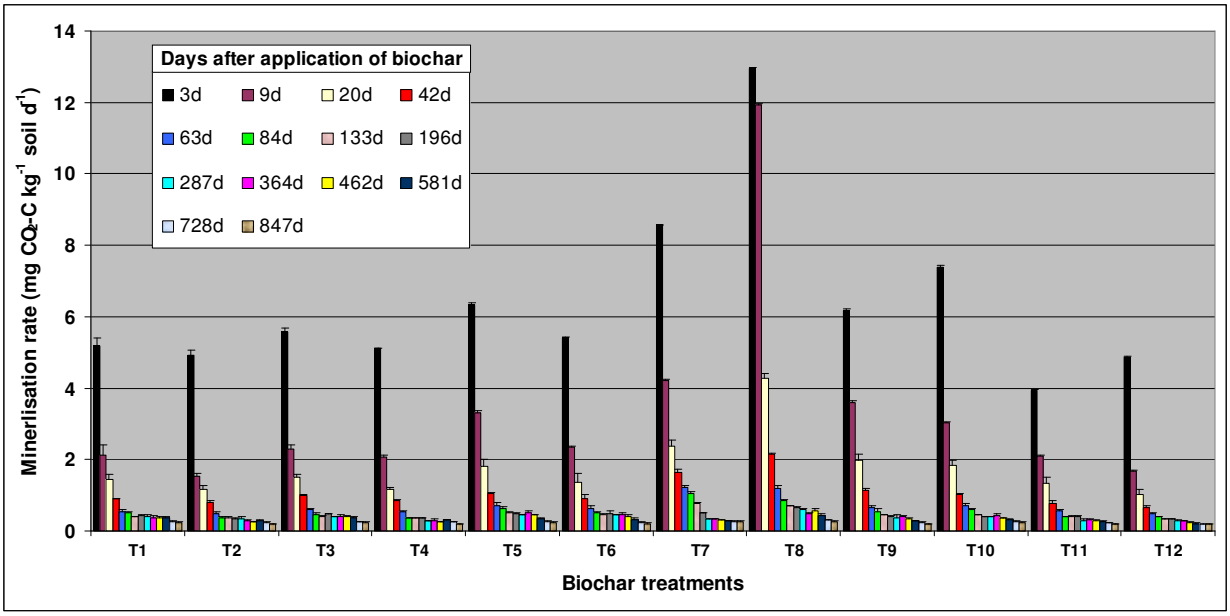

Figure 1. The rate of mineralisation of carbon in biochar-amended and non-amended (control) soils at different times of incubation (3d to 847d, see legends). Details of treatments, T1 to T12, are presented in Table 1. The bars show 1 standard error of means of three replicates.

- In the first 2.3 years of incubation, decomposition of biochar C in soil ranged from 0.3% to 6% of biochar C applied, depending on biochar type (data not shown).
- On cumulative basis over 2.3 years, biochar application enhanced decomposition of 'native' soil C; this positive priming effect on soil C was higher in soil amended with leaf or poultry manure biochars than wood biochars (data not shown).
- Microbial biomass C was not affected by the biochar treatments, except for the low-temperature leaf and poultry manure biochar treatments, which significant ($P < 0.05$) increased soil microbial biomass C as compared to the control (Figure 2).
- Our estimates of mean turnover time of C in biochars, determined by fitting the two-pool kinetic model to the cumulative CO_2-C evolved under controlled and optimal conditions of soil moisture and temperature in a laboratory, ranged from approximately 100 to 1300 years, with poultry manure showing fastest turnover and wood biochar the longest residence time (data not shown).

Conclusion

This study has found that the rate of decomposition of biochar varies with biomass source and pyrolysis temperature. While some biochars (e.g. wood biochars synthesised at 550°C) are highly stable in soil environment with mean turnover time >1000 years, other biochars can also survive in soil for >100 years. In general, biochars that decomposed faster also increased microbial biomass and turnover of native soil C more than other biochars. Turnover times in the field are likely to be slower than measured in this laboratory study, which intentionally employed conditions of moisture and temperature ideal for decomposition. The stability of biochar C and its influence on native soil C should be further tested under a range conditions likely to be experienced in the field.

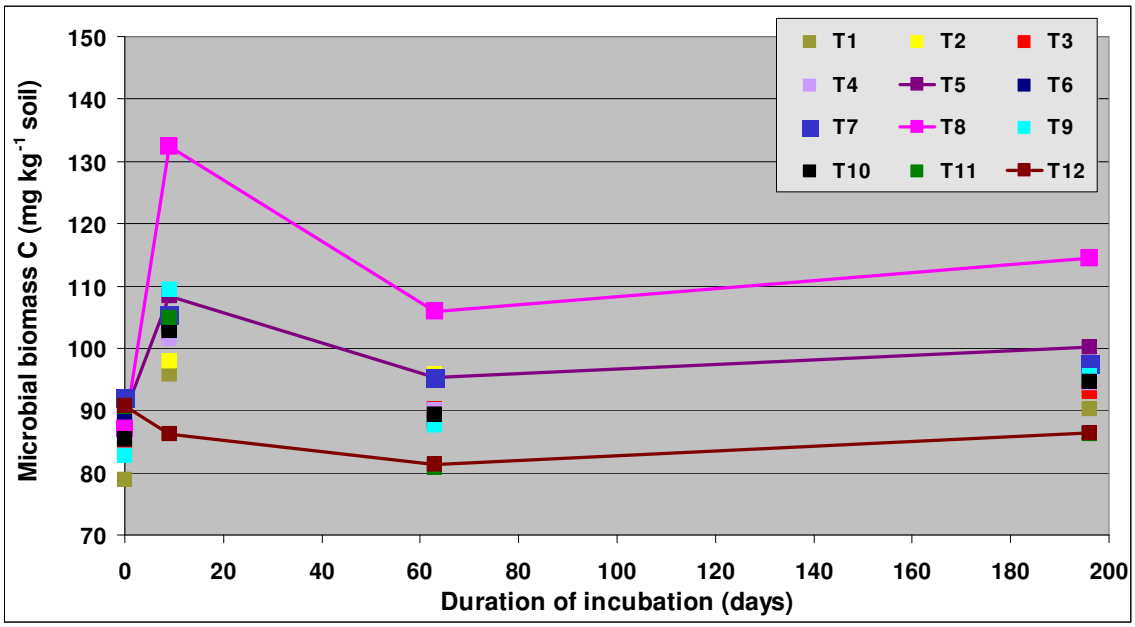

Figure 2. Biochars influence on microbial biomass C during 196 days of incubation. The treatment numbers shown in legend are explained in Table 1. Averaged over 196 days, microbial biomass C in biochar-amended soils shown by symbol plus solid line is significantly higher at $P < 0.05$, as compared to control (T12).

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