Quantifying biochar carbon stability in soil using natural ^{13}C-isotope approach

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Introduction

➢ The long-term benefits of artificially-produced char (biochar) for increasing soil C and mitigating rising atmospheric CO_2 will depend on its ability to persist in soil.

➢ Natural char in soil has been shown to possess turnover time of several hundred to >1000 yrs.

➢ Little research has been undertaken to document turnover time of biochar (Kuzyakov et al. 2009; Soil Biol. Biochem. **41**:210-219)

➢ The biochar produced during incomplete combustion of biomass waste at temperatures > 200 ºC and under limited oxygen supply (pyrolysis) can be highly resistant to biological degradation (Baldock and Smernik 2002, Organic Geochem. **33**:1093-1109).

➢ Short-term studies (e.g. 2-mo study by Hamer et al. 2004, Organic Geochem. **35**:823-830) only track decomposition of labile components in biochar. Extrapolation from such studies to obtain reliable estimates of biochar-C turnover rates is highly speculative.

➢ Longer term studies (at least several years) are required to ascertain biochar-C turnover (stability) and to provide insights into mechanisms of its stabilisation in soil.

➢ This information will assist in documenting net emission mitigation benefits of biochar.

Aims

➢ Using the natural ^{13}C difference between biochar-C (C_3-vegetation source) and soil C (C_4-vegetation source), this study aims to:

(a) Quantify turnover time of a range of biochars;

(b) Quantify the influence of biochar on the turnover of 'native' soil C;

(c) Monitor stabilisation mechanisms of biochar-C in soil over time; and

(d) Identify sources of C that microbes use during decomposition of biochar in soil

Methodology

➢ Eleven biochars (δ^{13}C ~ -21.7 to -28.8 ‰) produced from contrasting C_3-biomass sources (Table 1) were incorporated into soil (δ^{13}C ~ 14.1 ‰) under C_4 Mitchell grass (*Astrebla* spp.).

➢ This large difference (7.6 to 14.7‰) in δ^{13}C between soil C and biochar-C is ideal for separating sources of decomposing C in soil.

➢ Biochars were prepared at two temperatures (400°C or 550°C) and two activation levels (activated or non-activated) (Table 1).

➢ In addition to wide variations due to biomass type, pyrolysis temperature and activation treatments may induce further differences in biochar properties; e.g. the aromaticity of biochar increases with increasing production temperature (Baldock and Smernik 2002, Organic Geochem. **33**:1093-1109).

Conclusions

➢ This study shows that the rate of decomposition of biochar-C varies with biomass source and pyrolysis temperature.

➢ While some biochars (e.g. 550°C wood biochar) are highly stable in soil with mean turnover time >1000 years, other, less stable, biochars can also remain in soil for >100 years.

➢ Given the relatively short duration of our experiment (2.3 years to-date), biochar turnover time may be even longer than estimated here.

➢ In general, biochars that decomposed faster also increased microbial biomass and turnover of 'native' soil C more than other biochars.

➢ Turnover rates in the field are also likely to be slower than measured in this lab study, which intentionally employed conditions of moisture and temperature ideal for decomposition.

➢ The stability of biochar C and its influence on soil C should be further tested under a range conditions likely to be experienced in the field.

Incubation experiment plan

➢ Biochar (2 mm sieved) was mixed with soil (2 mm sieved, 0.42% C) at 10 t ha^{-1} to 10 cm depth (BD = 1.3 t/ m^3). Nutrients (N, P, K, Ca, Mg, S, Cu, Zn, Mo, Co, Na) were also added. Soil + biochar mixture was placed in sealed buckets.

➢Three replicates of each treatment in a two-factor (biochar type × sampling time) design.

➢ Temp: 22±1 ºC, clay soil, moisture at 60% WHC

➢ CO_2 trap (2 M NaOH)

➢ Soil (± char) to be removed 8 times over 5 years (0 d, 9 d, 6 wk, 6 mo, 1 yr, 2 yr, 3 yr, 5 yr) for analyses (microbial biomass, isotopic and spectroscopic analysis of size fractions).

Sealed buckets used for the biochar-C turnover experiment. The NaOH solution in the bucket traps the CO_2 released during biochar decomposition.

Biochar-C in the respired CO_2 is being determined using a mass balance approach:

$$F_3 = (\delta^{13}C_t - \delta^{13}C_4) / (\delta^{13}C_3 - \delta^{13}C_4)$$

F_3 = Fraction of C_3-biochar-derived C

$\delta^{13}C_t$ = δ^{13}C signature of total respired CO_2 from biochar-amended soil

$\delta^{13}C_3$ = δ^{13}C signature of C_3-biochar and $\delta^{13}C_4$ = δ^{13}C signature of C_4-soil

$$C_3 = F_3 \times C_t$$

(where $C_t = C_3 + C_4$ is the CO_2-C from char-amended soil)

C_3 = Amount of CO_2-C derived from C_3-biochar

C_4 = Amount of CO_2-C derived from C_4-soil

The turnover time of biochar-C can be estimated by fitting the two-pool kinetic model to the cumulative amount of CO_2-C evolved from biochar.

Doubled exponential: $C_{min} = C_L(1 - e^{-k_L t}) + C_R(1 - e^{-k_R t})$

Where, C_{min} = mineralised carbon, t = time, C_L = labile carbon pool, k_L = labile pool mineralisation constant, C_R = resistant carbon pool, k_R = resistant pool mineralisation constant,

Mean residence (turnover) time $T = 1/k$; half-life $t_{1/2} = T * \ln(2)$

Results

➢ The δ^{13}C of biochar was depleted by up to -1.2‰, compared to δ^{13}C of biomass, except for biochar from leaves (no change in δ^{13}C) and paper sludge (1.9‰ increase in δ^{13}C) (Table 1).

➢ The δ^{13}C of paper sludge biochar was higher by 3.3 to 7.1‰ compared with the other biochars possibly due to the presence of ^{13}C-enriched carbonate (Table 1).

➢ The rate of C release from biochar-amended and control soils decreased with time (Fig. 2a).

➢ In the first 2.3 years, about 0.3% to 6% of added biochar C was decomposed, depending on biochar type (data not shown).

➢ Soil microbial biomass was not affected by biochar, except for the 400°C leaf and poultry manure biochar treatments (data not shown).

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

Biomass type	Temp. (°C)	Activation	Biomass / Biochar (% C)	Biomass / Biochar (‰ δ^{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

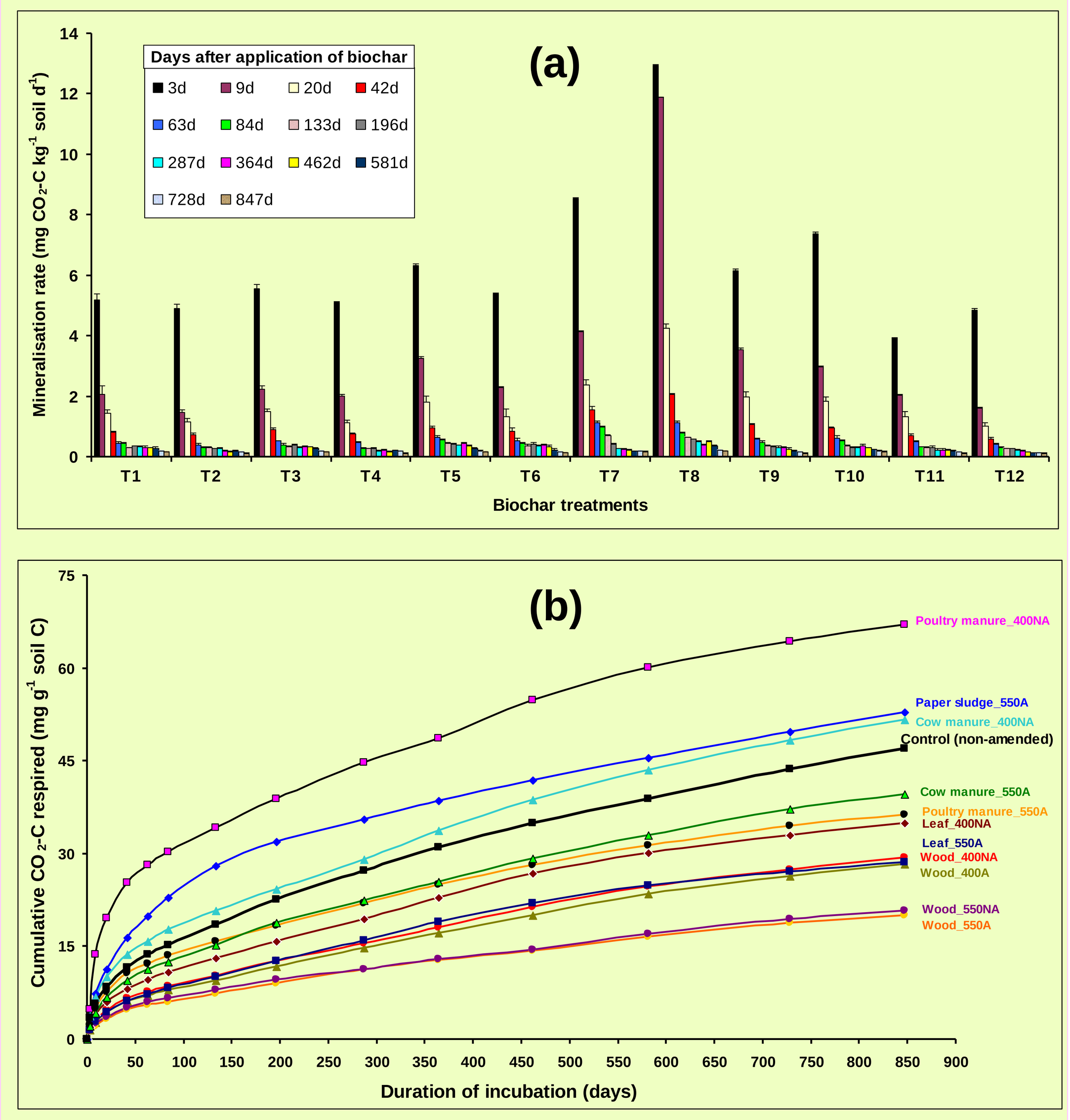

Fig 3: (a) The rate of C mineralisation from biochar amended and non-amended soils at different times of incubation, and (b) cumulative CO_2-C respired per unit of initial total C in biochar-amended or non-amended soil.

➢ The fraction of C mineralised per unit of initial soil+biochar-C was lower for most biochar-amended soils (cf. control), except for the low-temp. (400°C) poultry manure and cow manure biochars (Fig. 2b).

➢ Decomposition of 'native' soil C was enhanced by biochar; the leaf and poultry manure biochars showed the greatest positive priming effect on soil C (data not shown).

➢ Our estimates of mean residence time of biochar-C under optimal conditions of soil moisture and temperature (22°C), ranged from *ca*. 100 to 1300 years, with the low-temp. manure biochars showing the fastest turnover and the high-temp. wood biochar the longest residence time (Fig. 3).

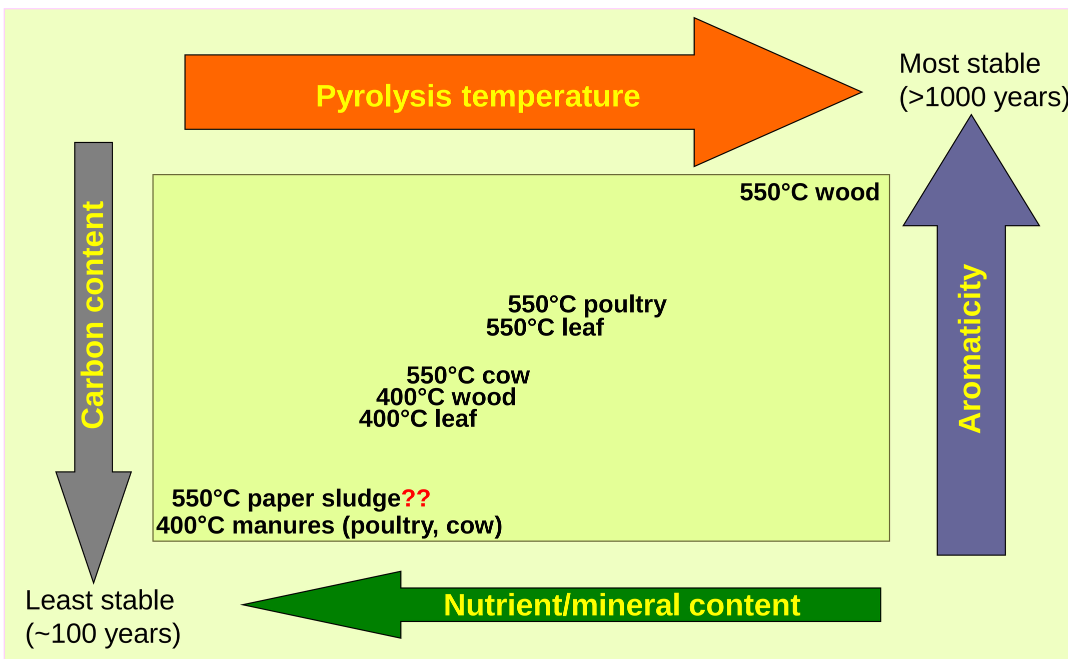

Fig 3: A schematic representation of the influence of biochar properties and pyrolysis temperature, with arrow sizes indicating the approximate magnitude of the influence, on mean turnover time of biochar carbon estimated in the present study.

Acknowledgements

We thank Adriana Downie of Pacific Pyrolysis for providing biochar samples. Dr Evelyn Krull of CSIRO L&W provided the schematic for precise presentation of our turnover estimates. We also appreciate technical support of Dr Kamaljeet Kaur and David Giles of Industry and Investment NSW.