Quantifying char-C turnover in soil, and implications for greenhouse balance

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Introduction

- Ø The long-term benefits of artificially-produced char for increasing soil C sequestration and mitigating rising atmospheric CO_2 will depend on its ability to persist in soil.
- Ø Naturally occurring char in soil has been shown to posses turnover time of a few 100 to >1000 years.
- Ø Little research has been undertaken to document turnover time of artificially-produced char.
- Ø The char produced during incomplete combustion (pyrolysis) of biomass waste at temperatures > 200 ºC and under limited oxygen supply can be highly resistant to biological degradation (Baldock and Smernik, 2002, Organic Geochem., **33**:1093-1109).
- Ø Short-term studies incorporating C tracer (e.g. 2 month study by Hamer et al., 2004, Organic Geochem., **35**:823-830) show that char-C does decompose. However, extrapolation from such short periods is highly speculative.
- Ø Longer term studies (at least several years), are required to ascertain char turnover and provide insights into mechanisms of its stabilisation in soil.
- Ø This information can then be used to document C sequestration benefits of added char-C in soil.

Aims

Ø Using the natural C isotopic difference between char-C (C_3-vegetation source) and soil C (C_4-vegetation source), this study aims to:

(a) identify sources of C respired following addition of char in soil

(b) quantify turnover of a range of C_3-char types

(c) monitor stabilisation mechanisms of char-C in soil, with focus on chemical recalcitrance.

Ø Additionally, we provide preliminary estimates of the greenhouse gas balance of application of char to soil.

Approach and methodology

- Ø We have recently initiated a long-term (up to 5 years) laboratory incubation experiment.
- Ø Char produced from feedstocks of contrasting chemical composition (see Table 1), but all originating from C_3-plant sources ($\delta^{13}C$ ~ -21.7 to -28.8‰), were incorporated into soil ($\delta^{13}C$ ~ 14.1‰) obtained from Toorak Research Station in Queensland (21°016′S, 141°784′E) growing Mitchell grass (Astrebla spp.).
- Ø Chars were prepared at two different temperatures (400 °C or 550 °C) and activation levels (activated or non-activated) (see Table 1).
- Ø In addition to variable chemical composition of the feedstocks, temperature and activation treatments can induce further differences in recalcitrance of char; for example, the aromaticity of char increases with increasing production temperature (Baldock and Smernik, 2002, Organic Geochem., **33**: 1093-1109).

Measurements of char turnover processes include:

(a) quantification of char-C and native soil-C-derived CO_2 using the isotopic ^{13}C signature, thereby estimating the priming effect of char addition on soil C

(b) char-C loss from different size fractions (see the fractionation procedure in Fig. 2).

(c) chemical characterisation of decomposing C fractions (^{13}C NMR)

(d) microbial biomass C and associated $\delta^{13}C$ to identify sources of C being metabolised by microbes.

Incubation experiment plan

- Ø Char (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 + char mixture was placed in sealed buckets.
- Ø Three replicates of each treatment in a two-factor (char type × sampling time) design.
- Ø Temp: 22±1 ºC, clay soil, moisture at 52% WHC
- Ø CO_2 trap (2 M NaOH)
- Ø Soil (± char) to be removed 8 times over 5 years (0 d, 9 d, 6 wk, 6 mo, 1 yr, 1.5 yr, 2 yr, 5 yr) for various measurements mentioned above.

Fig. 1: *Sealed buckets used for the char-C turnover experiment. The NaOH solution in the bucket traps the CO_2 released during char decomposition.*

The char-derived C in the respired CO_2 will be 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-char-derived C

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

$\delta^{13}C_4$ = $\delta^{13}C$ signature of C_4-soil

$\delta^{13}C_3$ = $\delta^{13}C$ signature of C_3-char

$$C_3 = F_3 \times C_t$$

(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-char

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

The natural abundance of ^{13}C is expressed, relative to the international VPDB standard as: $\delta^{13}C = 1000 \times (R_{sample}/R_{standard} - 1)$ (‰), where R is the molar ratio $^{13}C/^{12}C$.

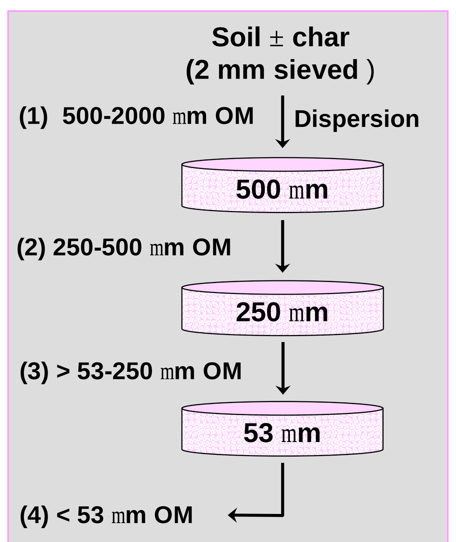


Fig. 2: *Fractionation scheme for separating organic matter (OM) in soil into different size fractions*

The turnover time of char-C can be estimated by fitting kinetic models to the cumulative amount of CO_2-C evolved from char. Some examples of such models are (Alvarez and Alvarez 2000, Soil Science Society of America Journal, **4**:184-189).

Exponential: $C_{min} = C_0(1 - e^{-kt})$

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

Exponential plus linear $C_{min} = C_L(1 - e^{-k_L t}) + C\,t$

Where, C_{min} = mineralised carbon, C_0 = potentially mineralisable carbon pool, k = mineralisation constant, fraction mineralised per time unit, t = time, C_L = labile carbon pool, k_L = labile pool mineralisation constant, C_R = resistant carbon pool, k_R = resistant pool mineralisation constant, C = resistant pool mineralisation rate.

Turnover time T = 1/k ; half-life $t_{1/2}$ = T * ln(2)

Table 1: *Feedstocks used for making char, along with $\delta^{13}C$ signatures of feedstocks and the corresponding char.*

Feedstock type	Temp. (°C)	Activation	Feedstock / Char (% C)	Feedstock / Char (‰ $\delta^{13}C$)
(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 + rice hulls	400	Non-activated	39.3 / 46.8	-24.9 / -25.0
(T9) Poultry manure + rice hulls	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

Initial results

- Ø Carbon content of char increased as temperature increased from 400 to 550 °C for bluegum feedstocks, but not for the poultry and cow manures (Table 1).
- Ø $\delta^{13}C$ of char became depleted by up to -1.2‰, compared to $\delta^{13}C$ of feedstock, except for char from leaves (no change in $\delta^{13}C$) and paper sludge ($\delta^{13}C$ enrichment of -1.9‰) (Table 1).
- Ø The observed $\delta^{13}C$ depletion was greater at high temperature. $\delta^{13}C$ of alkaline paper sludge was higher than the other feedstocks (by -1.3 to 4‰), likely due to the presence of ^{13}C-enriched carbonates (Lichtfouse et al. 2002, Geochemical Transactions, **3**: 48-50). $\delta^{13}C$ value increased further upon charring (Table 1).
- Ø The decomposition rate of organic matter (char and native soil carbon) decreased with increasing incubation time (Fig. 3a).
- Ø The cumulative % of char-C decomposed (C mineralised from char-amended minus control soil) (Fig. 3b) indicates highest level of char-C decomposition in T8. The $\delta^{13}C$ analysis of CO_2-C mineralised will be used to quantify the precise level of char-C decomposed.

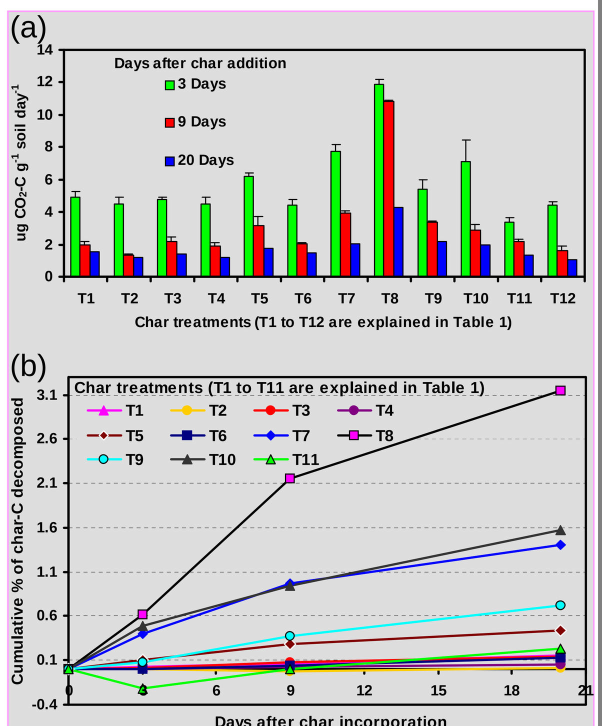


Fig 3: ***(a)*** *The rate of decomposition of char treated soils (& also non-amended control) at different times after char incorporation, and* ***(b)*** *cumulative % of char-C decomposed (minus soil-C) up to 20 days*

Greenhouse balance of paper sludge char application to soil:

- Ø Using char as a soil amendment is said to be a carbon negative process (more CO_2 is removed from the atmosphere than is released). To quantify its "carbon negativity", we calculated the whole of life greenhouse gas (GHG) balance for various chars applied to different crops (char case), and compared this with the current practice (reference case).
- Ø The emissions reduction benefit is calculated as the difference in emissions between the char and reference cases.
- Ø The factors that influence the GHG benefit of char as a soil amendment are:

a) the proportion of biomass C that is retained in char after pyrolysis,

b) the net energy exported from the pyrolysis process,

c) the turnover rate of char-C in soil,

d) the reduction in nitrous oxide emissions from soil,

e) the reduction in fertiliser requirements,

f) the growth increases resulting from char application,

g) the fossil fuel consumption in production, processing, transport and application of char

h) fossil fuel source and biomass use in reference case.

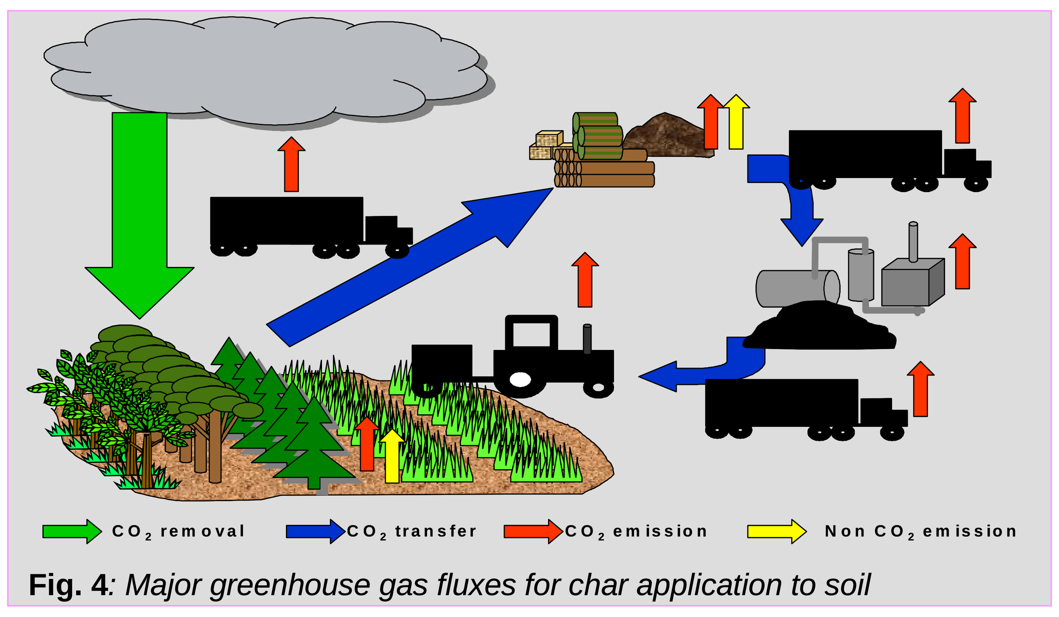
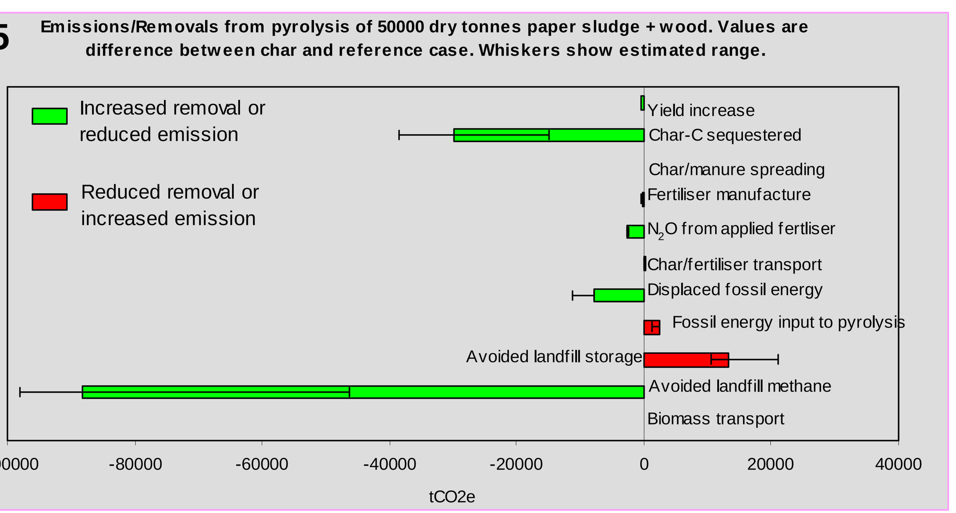


Fig. 4: *Major greenhouse gas fluxes for char application to soil*

- Ø The net emissions reduction for different char scenarios ranged from 35 to128 kt CO_2e per 50 kt (dry) feedstock, equivalent to 0.5-1.6 times the CO_2e in the feedstock.
- Ø The main factors influencing GHG balance of char application, in order of significance, were avoided methane emissions due to avoidance of landfilling, C sequestration in soil, avoided C storage in landfill, displaced fossil fuel emissions for heat generation, reduced N_2O emissions from soil, and fossil fuel input to the pyrolysis process.
- Ø **Fig. 5** shows the GHG balance for paper sludge + wood char application to a broccoli crop, compared with paper sludge + wood that is landfilled and the crop is fertilised conventionally. Net emissions reduction is 109kt CO_2e.

Fig. 5



Conclusions

- Ø The large differences (7.6 to 14.7‰) in $\delta^{13}C$ of soil compared with chars used for the incubation experiment will allow us to quantify turnover of char-C in soil using the mass balance and kinetic equations given above.
- Ø Desk-top calculation indicates char can reduce GHG emissions by up to 1.6 times the CO_2e content of the feedstock.
- Ø The turnover rate of char-C in soil is one of the most significant factors influencing the GHG balance. Thus it is critical to quantify this component.

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