

CARBON SEQUESTRATION IN BIOCHAR AMENDED SOILS

Article Id: AL201928

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Warming of the climate system is unequivocal, as is now evident from observations of increases in global average air and ocean temperatures. Eleven years from 1995-2006 rank among the twelve warmest years in the instrumental record of global surface temperature (since 1850). The 100-year linear trend (1906-2005) of 0.74 [0.56 to 0.92] °C is larger than the corresponding trend of 0.6 [0.4 to 0.8] °C (1901-2000) and over the 21st century average temperature of earth surface is likely to go up by an additional of 1.8- 4°C (IPCC, 2007). This temperature increase can be attributed to the altered energy balance of the climate system resulting from changes in atmospheric concentrations of the greenhouse gases (GHGs) (Fig. 1).

The dynamics of terrestrial ecosystems depend on interactions between a number of biogeochemical cycles, particularly the carbon cycle, nutrient cycles, and the hydrological cycle, all of which may be modified by human actions. Terrestrial ecological systems, in which carbon is retained in live biomass, decomposing organic matter, and soil, play an important role in the global carbon cycle. The combined anthropogenic radiative forcing is estimated to be +1.6 [-1.0, +0.8] W m⁻², indicating that, since 1750, it is extremely likely that humans have exerted a substantial warming influence on climate.

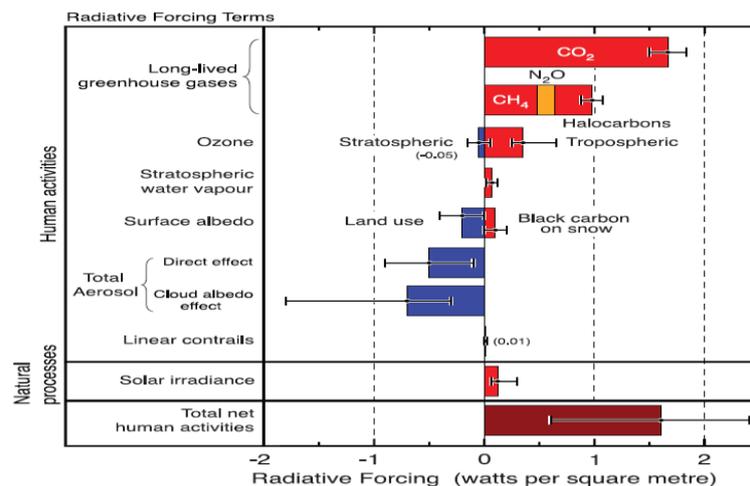


Fig.1-Summary of the principal components of the radiative forcing of climate change (IPCC, 2007)

Climate change has not come alone; it has brought with it a number of threats to the environment, ecosystem and entire mankind. Some of these include the reduction in the terrestrial and arctic snow cover (Post *et al.*, 2009), rise in sea level (IPCC, 2007), decline in crop yield, reduction in ecosystem services (Walker *et al.*, 2009), increase in frequency of extreme events (e.g. the hurricane Katrina in 2007) especially drought (e.g. monsoon failure in India in 2009), change in biodiversity (IPCC, 2007) because of pole-ward shift of principal biomes, and increase in global hunger and food insecurity. There is a strong link between food insecurity, soil degradation, and climate change (Fig.2), because of a strong positive feedback among the underpinning processes.

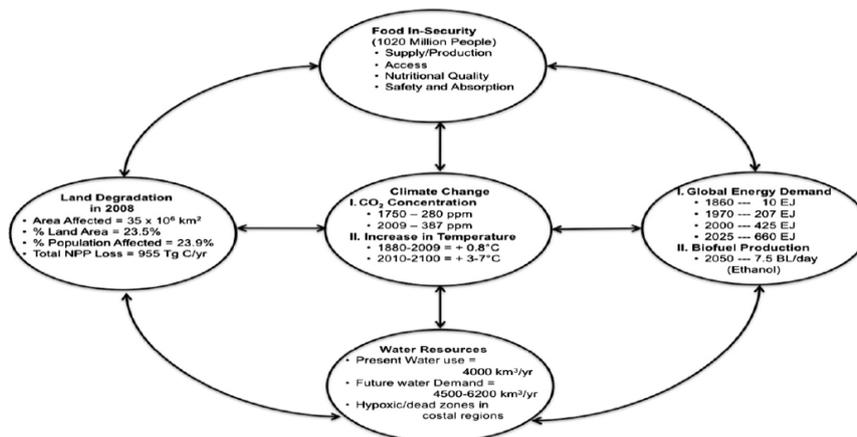


Fig.2- Inter-twinning global scale challenges related to climate change

The twin crisis of climate change and food insecurity can be addressed by restoring soil organic carbon pool through carbon sequestration in agro-ecosystems, especially in agricultural soils. The global potential of C sequestration in soils of agro-ecosystems is about 2.1 billion tons C/yr (Lal, 2010). If the SOC pool in world soils can be increased by 10% (+250 billion tons) over the 21st century, it implies a drawdown of about 110 ppm of atmospheric CO₂ (1 billion tons of soil C = 0.47 ppm of atmospheric CO₂).

Carbon sequestration

Carbon sequestration is the capture and secure storage of carbon that would, otherwise, be emitted or remain in the atmosphere. Carbon sequestration in the agriculture sector refers to the capacity of agriculture lands and forests to remove carbon dioxide from the atmosphere. Carbon dioxide is absorbed by trees, plants and crops through photosynthesis and stored as carbon in biomass in tree trunks, branches, foliage and roots and soils (EPA, 2008) (Fig.3).

Forests and stable grasslands are referred to as carbon sinks because they can store large amounts of carbon in their vegetation and root systems for long periods of time. Soils are the largest terrestrial sink for carbon on the planet. The ability of agriculture lands to store or sequester carbon depends on several factors, including climate, soil type, type of crop or vegetation cover and management practices.

Soil application of biochar, charcoal created by low-temperature pyrolysis of biomass under anaerobic conditions, is now a day's considered as an option to increase the SOC pool (Roberts et al., 2010). The potential of biochar application for SOC sequestration may be 1 billion tons C/yr or more (Sohi et al., 2010).

Biochar

Biochar is the carbon-rich product obtained when biomass, such as wood, manure or leaves, is heated in a closed container with little or no available air. In more technical terms, biochar is produced by so-called thermal decomposition of organic material under limited supply of oxygen (O₂), and at relatively low temperatures (<700°C). These charred organic matters are applied to soil in a deliberate manner, with the intent to improve soil properties.

Conceptually, biochar is the “charcoal (biomass that has been pyrolysed in a zero or low oxygen environment) for which, owing to its inherent properties, scientific consensus exists that application to soil at a specific site is expected to sustainably sequester carbon and concurrently improve soil functions (under current and future management), while avoiding short- and long-term detrimental effects to the wider environment as well as human and animal health” (Verheijen et al., 2010).

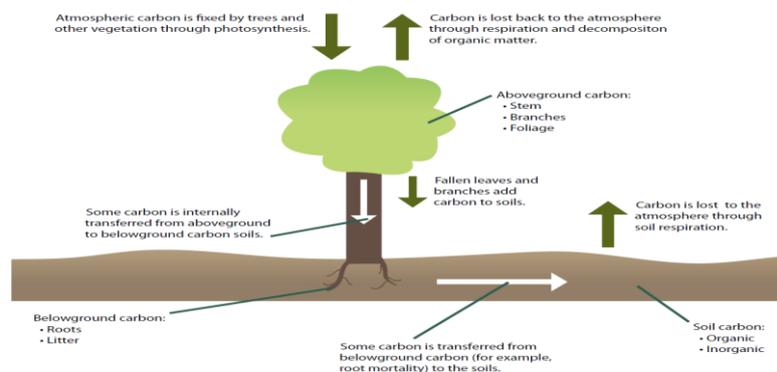


Fig.3- Processes of carbon gain and loss for trees and soils

There are a number of options for carbon sequestration in agro-ecosystems (Fig.4) (Lal, 2011).

Land application of biochar is not a new concept. It traces its roots to observations made by 19th century naturalists. In the recent past, terra preta soils in the Amazonian Basin have been linked to the ability to sequester carbon, as well as improve agricultural production. These terra preta soils have received large amounts of charred

materials, the residues from biomass burning (Sombroek *et al.* 2003).

Biochar Stability and Stabilization

The stability of biochar is of fundamental importance in the framework of biochar use for environmental management. There are

two reasons why stability is important; first, stability determines how

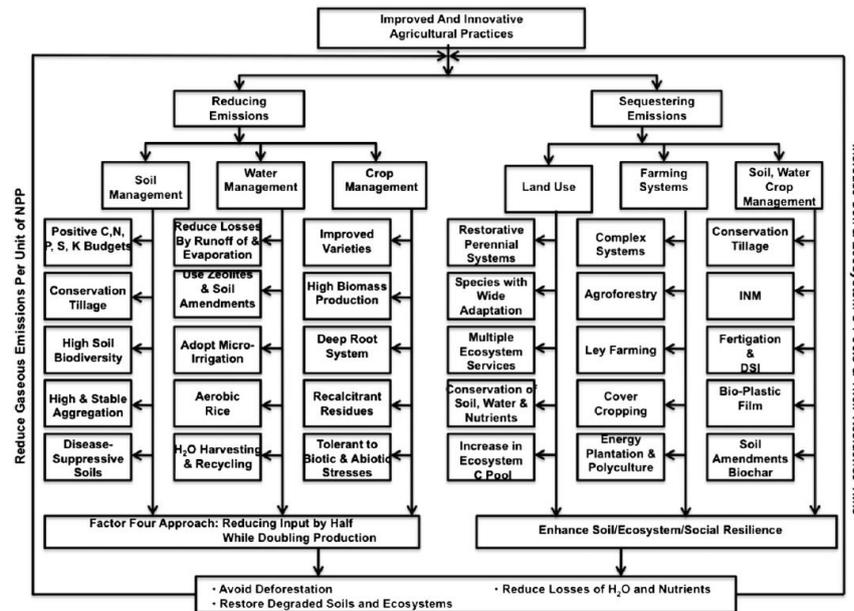
Fig.4- Technological options to reducing emissions and sequestering emissions from agricultural ecosystems

long C applied to soil as biochar will remain sequestered in soil and how long it may influence emissions of greenhouse gas from the pedosphere and contribute to the mitigation of climate change. Second, stability will determine how long biochar can provide benefits to soil and water quality.

Conversion of biomass to biochar followed by application of biochar to the soil increases the residence time of carbon (C) in the soil relative to the application of the same biomass directly to the soil, and therefore can be considered over particular timescales to result in a net withdrawal of atmospheric CO₂ (Lehmann, 2007).

Mean Residence Time

Biochar found in high proportions in the so-called ‘Terra Preta’ soils of the Amazon region have been radiocarbon dated and found to originate from 500 up to 7000 years BP (Liang *et al.*, 2008). They provide a visually compelling proof for the longevity of biochar. By matching annual production of char by savannah fires to measured char stocks for various



soils in Northern Australian woodlands, mean residence times of 718 to 9259 years were obtained. But, the most likely and conservative scenarios suggested mean residence times of 1300 to 2600 years under the dry-land conditions of Northern Australia (Lehmann *et al.*, 2008).

Biochar Stability Framework

The available scientific evidence clearly demonstrates that biochar is the most stable form of organic matter that can be added to soil. However, some types of biochar can be mineralized to a significant extent in the short term and all types of biochar eventually decompose, with a complex interplay of stabilization, destabilization and transport processes that change over time. It is therefore important to quantify the extent of short-term decomposition both for the calculation of C credits as well as for its effects on soil.

The generally slow decay of biochar poses challenges to quantifying its longevity. Decomposition rates of plant litter have often been established experimentally by adding litter to soil and measuring its disappearance. Since the turnover time of litter ranges between weeks and years, the organizational and financial commitment to such efforts is feasible. In contrast, direct measures of turnover times for biochar may require centuries to millennia, and are therefore not experimentally accessible by such an approach.

Schematically, this challenge can be depicted for a hypothetical data set in Figure 5 (Lehmann *et al.* 2006). The calculated MRT increases if data are available for longer periods of time. If data were only available for two years, the MRT obtained by a double-exponential model is merely 57 years.

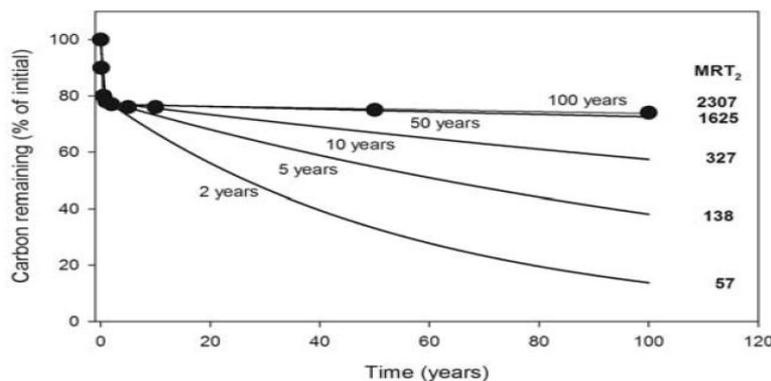


Fig.5- Double-exponential model ($C_{\text{remaining}} = C_1 e^{-k_1 t} + C_2 e^{-k_2 t}$, with 1 and 2 being a labile and stable pool, respectively) fitted to hypothetical data of biochar decay after 0.1, 0.5, 2, 5, 10, 50 or 100 years, assuming data availability for either the first 2, 5, 10, 50 or 100

years. MRT_2 is the mean residence time of the stable pool 2, calculated from the rate k_2 , and is given in years.

Mechanisms of Biochar Stability and Stabilization

The principal mechanisms operating in soils through which biochar entering the soil is stabilized and significantly increase its residence time in soil are intrinsic recalcitrance, spatial separation of decomposers and substrate, and formation of interactions between mineral surfaces. The relatively stable nature of organic matter protected within aggregates or through the formation of organo-mineral interactions may also be of relevance to the stability and longevity of biochar in soil.

Recalcitrance

The conversion of organic matter to biochar by pyrolysis significantly increases the recalcitrance of C in the biomass. The composition changes through a complete destruction of cellulose and lignin and the appearance of aromatic structures (Paris and Zickler, 2005) with furan-like compounds. These changes in the composition of organic bonds by pyrolysis have a significant effect on the stability of biochar.

Carbon Stability in Soils

To assess the biochemical stability of black carbon (BC) in soils, a chronosequence of ancient BC rich anthrosols (Terra Preta de Indio) and their adjacent soils were taken from four sites namely Hatahara (HAT), Lago Grande (LG), Acutuba (ACU) and Dona Stella (DS) (central Amazon, Brazil) in a study carried out by Liang and co-workers (2008). The properties and age of the soils are given in table 1.

Table 1-Properties of BC-rich Anthrosols and adjacent soils in the central Amazon

Site	Type	Depth (cm)	Age (years BP)	pH		Organic C ($mg\ g^{-1}$)	Total N ($mg\ g^{-1}$)	C/N ratio	Sand (%)	Silt	Clay
				1:2.5 (H ₂ O)	1:2.5 (KCl)						
HAT	Anthrosol	43–69	500–1000	6.4	5.5	22.0	1.0	23	51.3	21.7	27.0
	Adjacent soil	0–10		4.6	3.8						
LG	Anthrosol	0–16	900–1100	5.9	4.9	31.5	1.8	18	47.9	29.6	22.6
	Adjacent soil	0–8		4.2	3.5						
ACU	Anthrosol	48–83	2500–3000	5.6	4.2	15.7	1.0	16	81.9	7.7	10.4
	Adjacent soil	0–30		4.7	3.9						
DS	Anthrosol	Buried (190–210)	6700–7000	5.0	4.1	16.5	1.1	15	96.8	2.9	0.3
	Adjacent soil	0–12		3.9	2.6						

Table 2-The turnover time of total SOC

Sites	Type	Turnover time(years)	BC fraction(% of totalC)	Aromatic Carbon (%)
Hatahara	Anthrosol	50	79.4	41.5
	Adjacent soil	18	20.2	23.6
Acutuba	Anthrosol	52	73.1	32.6
	Adjacent soil	20	44.3	26.3
Dona Stella	Anthrosol	44	75.1	35.5
	Adjacent soil	9	10.6	21.3

This higher stability of organic carbon in anthrosols can be attributed to the presence of significantly higher BC fraction with more aromatic-C forms (Table 2).

Effect of Temperature on Biochar Stability

Baldock and Smernick (2002) showed that thermal alteration decreases bioavailability of wood. In their experiment *Pinus resinosa* sapwood were heated at different temperatures (70, 150, 200, 250, 300 and 350°C) and incubated separately in a sand medium to which nutrient solution and microbial inoculum derived from decomposing *Pinus resinosa* wood were added (Fig. 6).

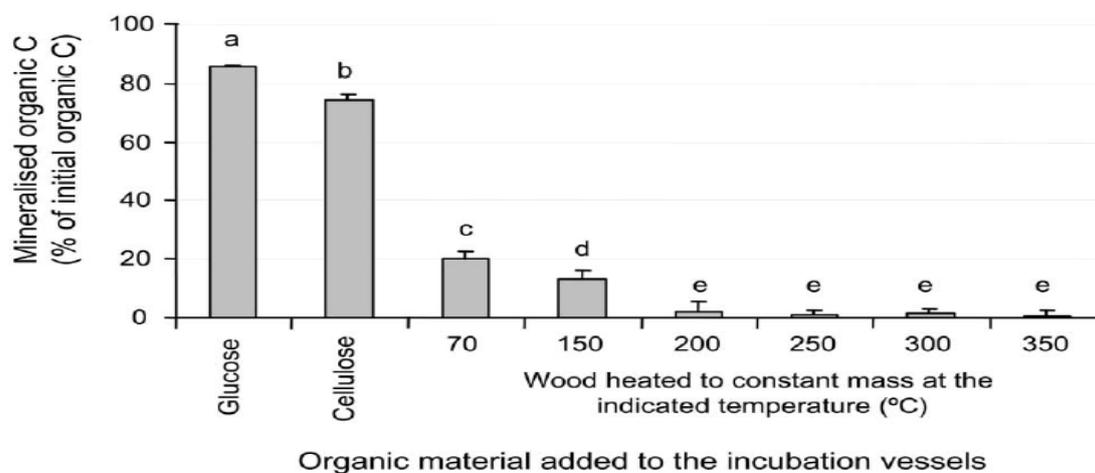


Fig. 6 -Mineralisation of organic carbon contained in glucose, cellulose, and *Pinus resinosa* sapwood heated to thermal equilibrium at increasing temperatures

This higher stability of thermally altered woods can be attributed to increase the aromaticity as indicated by progressive decrease in H/C and O/C ratios (Table 3) and conversion of O-alkyl to aryl and O-aryl groups with increasing temperature (Fig.7).

Table 3- Molar elemental ratios calculated for *Pinus resinosa* sapwood heated to the indicated temperatures

Heating temperature (°C)	Molar elemental ratios (<i>n</i> = 3)	
	H/C	O/C
70	1.52 ^a (0.02)	0.72 ^a (0.01)
150	1.45 ^a (0.03)	0.70 ^a (0.02)
200	1.02 ^b (0.02)	0.61 ^b (0.00)
250	0.51 ^{cd} (0.03)	0.44 ^c (0.01)
300	0.46 ^d (0.02)	0.40 ^d (0.00)
350	0.54 ^c (0.03)	0.32 ^e (0.01)
ANOVA <i>P</i> -value	< 0.0001	< 0.0001

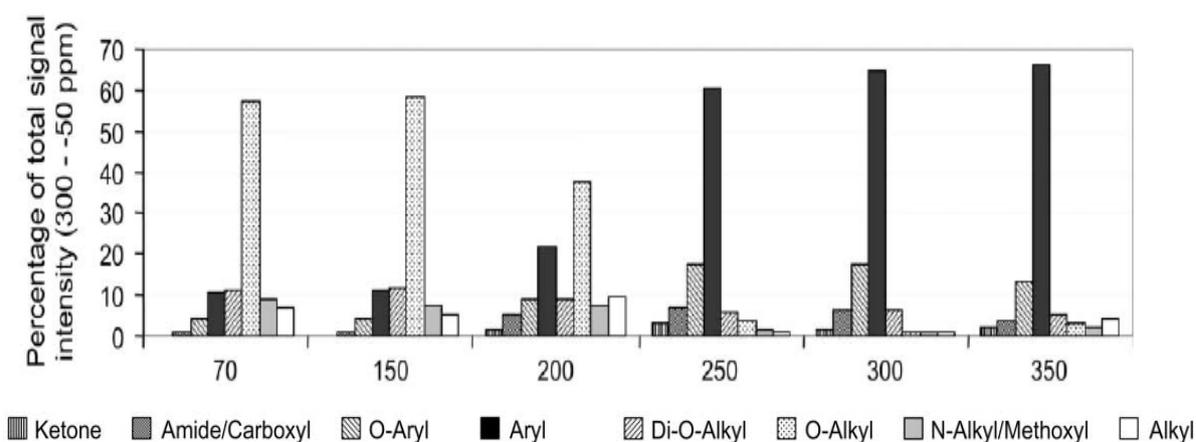


Fig. 7- Distribution of total ¹³C NMR signal intensity into chemical shift regions

Another study by Bruun and co-workers (2010) also supported the fact that increasing production temperature increases the stability of biochar (Fig. 8).

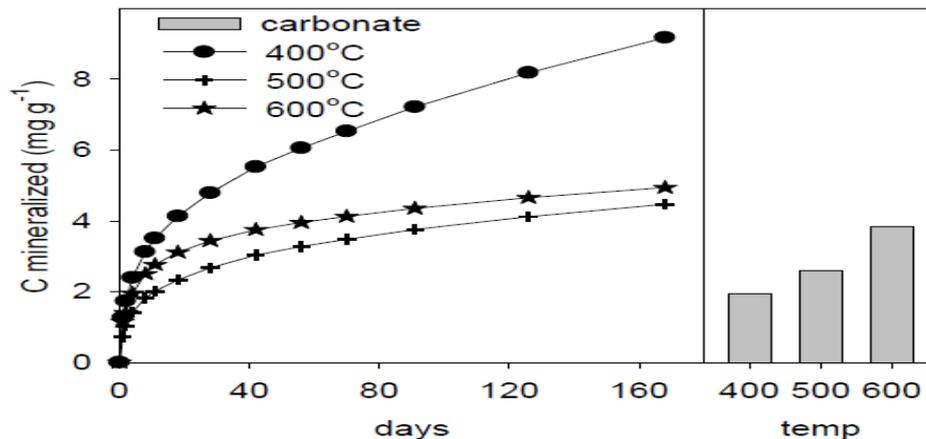


Fig. 8-Mineralization of C and C in carbonates of biochars produced at 400°C, 500°C and 600°C

They studied the mineralization of ¹⁴C labelled biochar produced at different temperatures in the range from 400°C to 600°C, and incubated in different soils at the same water potential. Mineralization decreased considerably as production temperature increased from 400 to 500°C, reduced at 600°C (Fig. 8).

Influence of biochar on native organic carbon

Biochar can promote rapid loss of forest humus and below ground carbon during the first decade after its formation (Wardle *et al.*, 2008). In their experiment, mesh bags filled with pure humus collected from the forest, pure charcoal created in the laboratory, or a 50:50 mixture of humus plus charcoal were left in the field and harvested over 10 years. It was found that over the 10-year period, loss of mass and C from the bags containing mixtures of charcoal and humus was substantially greater than what was expected on the basis of the components considered separately (Fig.9A & C).

Substrate (i.e., glucose)-induced respiration (SIR), a relative measure of active microbial biomass, was always significantly greater in the mixture bags than the value predicted on the basis of the charcoal and humus components considered separately (Fig. 9B).

On the contrary, to the above finding, Bruun *et al.* (2010) reported slower mineralization of SOM with more biochar added (Fig. 10). However, the effect of biochar on plant litter decomposition was very small (Table 4).

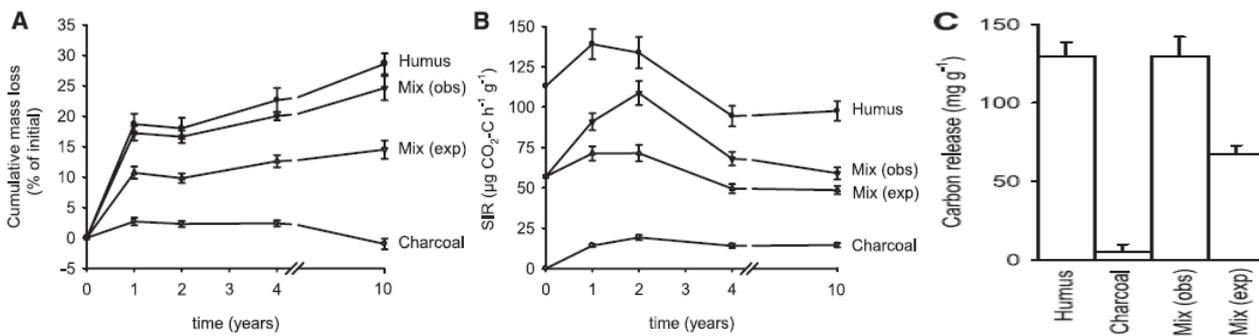


Fig. 9- Changes in litterbag properties over a 10-year period: (A) Total mass loss; (B) SIR;

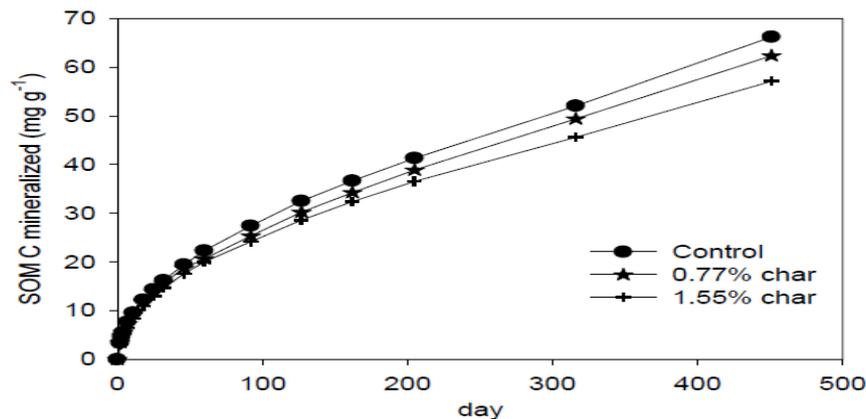


Fig.10- Mineralization of SOM C from a control soil and soils amended with different amounts of biochar

Table 4-Mineralization of plant litter with and without addition of biochar

Amount of Biochar applied (%)	Litter C mineralized (%)
0	48±0.2
0.15	45±1.6

The reason for decreased mineralization of SOM and litter upon addition of biochar can be manifold. First, the addition of biochar may change water availability by absorption. Secondly, microorganisms degrading biochar may immobilize N and impose N limitation on SOM decomposition.

Carbon sequestration potential of biochar

Biochar is recalcitrant nature, so the release of the biochar-C is a very slow process, resulting in a long-term removal of C from the atmosphere. In addition, pyrolysis of biomass generates a bio-oil and a syngas, which can be used to replace fossil fuels e.g. by using the bio-oil as fuel in power plants and the gas to provide heat for the pyrolysis process. Combining these three pyrolysis outputs renders the whole process not only carbon neutral, which is very often the vision for bioenergy solutions, but actually carbon-negative (Bruun *et al.*, 2011) (Fig. 11).

Mitigation of carbon emissions is obtained not only from biochar soil application, but also from substitution of fossil fuel by the produced bio-oil. The quantity of fossil fuel replaced depends on a range of parameters such as the efficiency of the technology used to convert bio-oil into the desired energy form, the kind of fossil fuel it substitutes, and the handling and transportation of biomass and bio-oil.

In the assessment of the different biochars' sequestration potentials, the stability and quantity of produced biochar are the two main parameters to assess. As discussed, the stability can be increased by raising the pyrolysis temperature, but this will be at the expense of the quantity produced (Fig. 11).

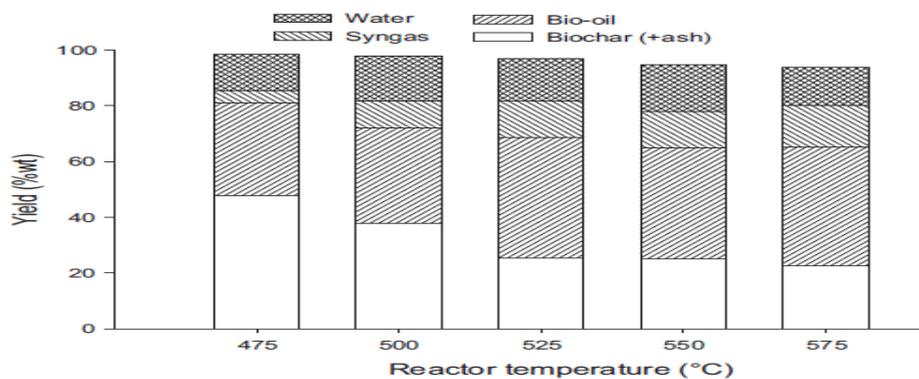


Fig. 11- Mass balance of pyrolysis products as a function of increasing reactor temperature

This inverse relation makes it possible to determine the pyrolysis temperature that gives the highest C sequestration. Based on the assumption that all biochar carbohydrates will be mineralized to CO₂ within a relatively short timeframe, the original feedstock sequestration potentials is calculated and shown in Table 5.

Table 5-Overall mitigation of carbon emissions in relation to initial straw-C, when combining biochar-C sequestration and bio-oil fossil fuel C substitution

Temperature (°C)	Yield ^a (g C kg ⁻¹ C)	Stability ^b (% of wt)	Yield ^c (g kg ⁻¹)	Substitute (g kg ⁻¹)	Substitute (g C kg ⁻¹)	Biochar ^d (g C kg ⁻¹ C)	Bio-oil (g C kg ⁻¹ C)	Total (g C kg ⁻¹ C)
475	550	65.6	463	190	161	360	410	770
500	464	82.7	505	207	176	380	450	830
525	329	92.4	584	239	204	300	520	820
550	316	95	570	234	199	300	500	800
575	291	97	560	230	195	280	500	780

Assumptions- Heating value of bio-oil: 16.4 MJ kg⁻¹, Heating value of fuel oil: 40 MJ kg⁻¹, C content of fuel oil: 85% (w/w), C content of wheat straw: 39.4% (w/w)

a- Feedstock-C that ends up in biochar, b- Total biochar cellulosic-C þ hemicellulosic-C percentage subtracted from 100%, c- Yield of bio-oil per kg feedstock, d- Biochar-C sequestration per kg feedstock-C pyrolyzed. Calculated as biochar ‘Yield’ multiplied by ‘Stability’

Biochar is highly stable against microbial decomposition and applying this to farmland has the potential to mitigate GHG emissions. However, CO₂ is emitted throughout the biochar life cycle (Fig.12), including pyrolysis, transportation, and farmland application.

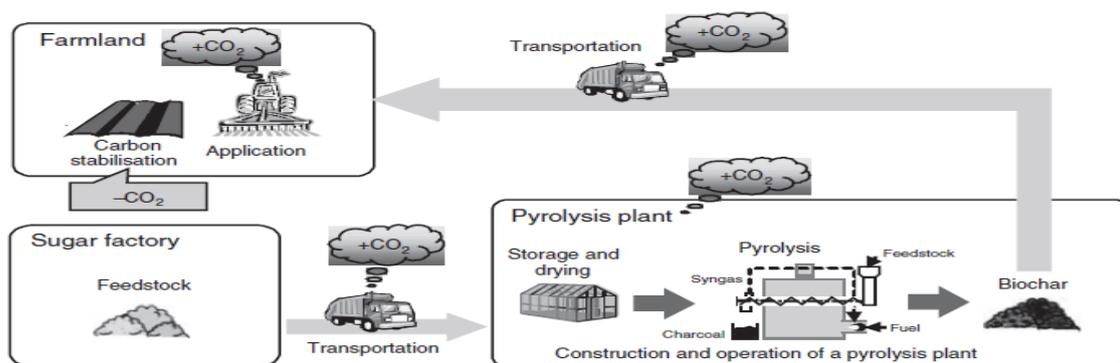


Fig.12- Biochar life cycle (e.g. sugarcane bagasse)

Therefore, estimating the net carbon sequestration potential by considering these CO₂ emissions is important. Kameyama *et al.* (2010) carried out a study on Miyako island (Japan) to estimate the net carbon sequestration potential of farmland application of bagasse charcoal produced by the pilot plant. To this end, the operational properties of the carbonisation device were examined, and CO₂ emissions and carbon stabilised as charcoal within the life cycle of bagasse charcoal were calculated. Furthermore, the CO₂ mitigation potential was estimated on the basis of inventory data from the pilot plant.

Conclusions

- Stability of biochar-C increases with production temperature making it more suitable for the purpose of carbon sequestration in soil.
- To derive the maximum possible benefit of carbon sequestration by soil application, both yield and stability of the biochar should be optimized.
- Carbon sequestration by biochar is likely to be less in soils relatively higher in native-C than in soils relatively lower in native-C due to stimulation of native carbon loss by biochar application.
- Biochar technology can be a promising approach for soil carbon sequestration when the capacity of biochar-C to remain sequestered in soil is combined with the capacity of bio-oil to reduce CO₂ emission by substituting fossil fuel use.

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