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1 Effects of ageing and successive slash-and-burn practice on the chemical
2 composition of charcoal and yields of stable carbon

3 Selvalakshmi Selvaraj ^{a, b}, José M de la Rosa ^c, Zhijun Huang ^{a, b}, Futao Guo ^a,
4 Xiangqing Ma ^{a, b*}

5
6 Affiliation and address of the authors:

7 Selvaraj Selvalakshmi

8 a College of forestry, Fujian Agriculture and Forestry University, Shangxiadian road, Cangshan district, Fuzhou, 350002,
9 China.

10 b Chinese fir Engineering Technology Research Center of the State Forestry Administration, Fuzhou 350002, People's
11 Republic of China. e-mail: selvaphd09@gmail.com

12
13 José M de la Rosa

14 c Instituto de Recursos Naturales y Agrobiología de Sevilla, Consejo Superior de Investigaciones Científicas (IRNAS-CSIC),
15 Reina Mercedes Av. 10, 41012, Seville, Spain. e-mail: jmrosa@irnase.csic.es

16
17 Huang Zhijun

18 a College of forestry, Fujian Agriculture and Forestry University, Shangxiadian road, Cangshan district, Fuzhou, 350002, China.
19 e-mail: fjhuangzj@126.com

20

21

22

23   Futao Guo

24   a College of forestry, Fujian Agriculture and Forestry University, Shangxiadian road, Cangshan district, Fuzhou, 350002, China.

25   e-mail: guofutao@126.com

26

27   Xiangqing Ma *

28   a College of forestry, Fujian Agriculture and Forestry University, Shangxiadian road, Cangshan district, Fuzhou, 350002, China.

29   Telephone: 0591-83789645; Fax: 0591-83780261.

30   b Chinese fir Engineering Technology Research Center of the State Forestry Administration, Fuzhou 350002, People's

31   Republic of China.

32

33   *Corresponding author- e-mail: lxymxq@126.com; Telephone: 0591-83789645; Fax: 0591-83780261.

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Abstract

Chinese fir (*Cunninghamia lanceolata*) plantations cover over 12 Mha in the southeast provinces of China. The traditional conditioning of fields of this conifer involves the slash-and-burn practice. As a result of this practice, pyrogenic carbon (PyC) is produced by the incomplete combustion of organic matter; this includes a continuum of materials ranging from partially charred biomass and charcoal to soot. Owing to the structure and composition of PyC, it has traditionally been considered to have high chemical recalcitrance and resistance to degradation. Thus, PyC produced during slash-and-burn cultivation practices may profoundly alter the terrestrial carbon (C) cycle and soil chemical composition. Hence, this study aims to investigate the quantitative and qualitative composition of charcoal from the oldest Chinese fir plantation in China. Charcoal was sampled in soils from plots of different stand ages after one to four slash-and-burn rotations. This approach permitted an assessment of the effects of ageing and consecutive slash-and-burn rotations on the chemical composition of charcoal and the estimation of the stocks of stable C. The chemical composition of the PyC fraction was examined via elemental (CHN) and ^{13}C nuclear magnetic resonance spectroscopy (^{13}C NMR) analyses. These revealed some signs of degradation, such as a decrease in relative abundance of aryl-C and an increase in H/C_{at} values over time. The stocks of charcoal and yield of stable C in soil slightly increased with the number of fires, reaching a maximum of 1164 kg of PyC per hectare after four prescribed burns. Nevertheless, charcoal stocks decreased sharply with increasing stand age after each slash-and-burn event. In fact, over 25%

of the charcoal stock was lost during the period from 12- to 21-years after the first slash-and-burn, and 85% was lost in the 97-year old stand. Our results together indicate that there has been a substantial loss of charcoal in soils following slash-and-burn rotations, on a time scale of decades associated with gentler slopes. Our results question the long-term persistence of charcoal in soils and highlight the necessity for periodic slash-and-burn rotation to maintain PyC stocks.

Keywords:

Chinese fir; pyrogenic carbon; C stocks; Solid state ^{13}C Nuclear Magnetic Resonance Spectroscopy; aryl-C

1. Introduction

China has the largest area of planted forests worldwide, with 36% (69 million ha) of the country's forests being represented by plantations (Chinese Ministry of Forestry, 2014). Chinese fir (*Cunninghamia lanceolata*) is an endemic, evergreen coniferous species cultivated as a commercial tree for its timber quality and fast growth. In recent years, the area under Chinese fir plantation rapidly increased covering over 12 Mha in the southeast provinces of China, accounting for about 80% of the total area where natural forests were converted to monoculture and mixed plantations (Bi et al., 2007; Chen et al., 2016).

In ancient times, natural broadleaved forests were not subjected to frequent prescribed burns; rather the conditioning of the fields of Chinese fir plantations involved the slash-and-burn practice. This practice resulted in the accumulation of

PyOM, commonly called charcoal, at the soil surface. Incomplete combustion during fires in plantations transforms part of the biomass into charcoal, also referred to as pyrogenic carbon (Schneider et al., 2011). Pyrogenic Carbon (PyC) comprises a continuum of materials from partially charred biomass and charcoal to soot (Schmidt and Noack, 2000). The pyrogenic process, in general confers the charred materials, a longer mean residence time in the environment as compared to their unburned precursors (Santin et al., 2016; De la Rosa et al., 2008). Thus, PyC produced during slash-and-burn cultivation practices may profoundly alter the terrestrial carbon (C) cycle. Chapin et al. (2002) reported that up to 40% of the terrestrial C cycle was affected by fires associated with natural or agricultural practices. It has been observed that the fires transform about 3% of the initial biomass to PyC (Forbes et al., 2006), and the latest estimates indicate that ~50% of the PyC produced by vegetation fires potentially sequester carbon over centuries. Nevertheless, PyC is exposed to degradation factors such as microbes, soil erosion, and transport through the breaking of soil aggregates (Kuziyakov et al., 2014; Berhe et al., 2007; Wang et al., 2013). Moreover, in order to satisfy the high demand for Chinese fir, logs have been harvested after a short rotation period of ~20–25 years since the late 1990s. Thus, contemporary fir plantations are dominated by young (~6 years) and middle-aged (~15 years) trees. Therefore, it is also essential to identify how the rotation period is affected by the slash-and-burn cultivation practice, which has a direct impact on charcoal stocks and its properties.

The potential significance of charcoal and other forms of PyC in C sequestration and soil properties has been clearly stated in several published reports (Lehmann, 2007; Cheng et al., 2008; Luo et al., 2016; De la Rosa and Knicker, 2011; Santin et al., 2016). Literature review provides a better understanding of the general properties and stability of charcoal under different conditions. Zackrisson et al. (1996) found no significant decline in charcoal levels over a 350-year post-fire chronosequence and also recorded large variability in charcoal stocks between sites. Anthropogenic charcoal in Amazonian black earths can be thousands of years old, as can charcoal in European chernozemic soils (1160–5040 years) (Schmidt, 2002) and coastal temperate rain forests (up to 12,000 years) (Gavin, 2003). Hammes et al. (2008) demonstrated that after grassland fires on the Russian Steppe in 1900, stocks of soil PyC declined by only 25% over the next century, and the turnover time was 293 years. Singh et al. (2012) concluded that the mean residence time (MRT) of PyC ranged in the order of centuries, similar to the MRT of slow-cycling pyrogenic organic matter (PyOM) (500–600 years) described by Knicker et al. (2013).

Until now, a few studies have investigated the long-term (i.e. decadal) fate of PyC in soils, and the results have been ambiguous, partly due to the different methodologies used in the characterisation and quantification of PyC (Schneider et al., 2011). Minor changes in the carbon pool have dominant effects on forest C dynamics. Therefore, there is an urgent need to examine the effect of successive prescribed burning on the abundance of charcoal in soils to achieve a general inventory of the stable pools of carbon and employ appropriate soil management.

Additionally, in the present work, the study area (Nanping) constituting the oldest documented plantation (planted in 1919) of Chinese fir in China (first rotation), which permitted us to cover a long period of time. In this study, PyC is used as a general term to describe the solid residues of incomplete combustion of biomass (including charcoal or char). We are conscious that this is only a fraction of the continuum of black carbon materials generated during pyrolysis (Schmidt and Noack, 2000). Nevertheless, studies on the chemical composition and stocks of PyC left in the soil after stubble burning are very scarce. Thus, the present study estimates the stocks, properties, and chemical composition of charcoal from different stand ages and rotations of Chinese fir plantations.

2. Materials and methods

2.1. Study area

The study area was located in a small watershed in Wangtai Town, Nanping City, Fujian Province, China (Fig. 1). The region has a sub-tropical monsoon climate, with a mean annual temperature of 19.3 °C and a relative humidity of 83% (Guo et al., 2014). The mean annual precipitation is 1699 mm, with most precipitation occurring from March to August. The mean annual evapotranspiration is 1413 mm. The altitude of the study area ranges from 150 to 250 m and ~30° slope. The soil is red earth derived from granite (Guo et al., 2005), equivalent to Hapludult based on United States Department of Agriculture (USDA) soil taxonomy (Soil Survey Staff, 2014). The soil texture of the sample site ranged from sandy clay to clay loam. The soil profile was well developed with charcoal deposition in the organic layer, due to

slash-and-burn management practices. The thickness of the A horizon ranged from ~10 to 20 cm, while that of the B horizon was characterized by the accumulation of clay and iron oxides. Soil density ranged from 1.10 to 1.26 g cm⁻³.

2.2. Chronosequence approach

Mature timbers of Chinese fir plantations are harvested at the age of 25-30 years. Before the saplings are planted, the area is cleared and the bark and other plant residues are subjected to slash-and-burn. The sampling campaign was performed in the year 2015. A total of 10 different sites were sampled. They consisted of first rotation stands of 12-, 21-, 40- and 97-years-old (slash-and-burned once); second rotation stands of 12-, 21- and 31-years-old (slash-and-burned twice); third rotation stands of 13- and 21-years-old (slash-and-burned three times); and fourth rotation stands of 10-years-old (slash-and-burned four times). Selection of the sites covered by 12-year old (first and second rotation), 13-year old (third rotation), and 10-year old (fourth rotation) stands was performed to permit the comparison of charcoals with similar periods of time since the last burn and from one to four cycles of slash-and-burn. The average time elapsed between each slash-and-burn cycle was 20 to 25 years.

2.3. Soil sampling

For each site, five subplots (20 x 20 m) with southeastern slopes were established, and three pits were systematically dug diagonally for each subplot. Soil samples were collected (0–20 cm depth) from each of the three sampling pits and mixed thoroughly to form a single composite sample per plot, resulting in a total of

50 samples, and stored in sealed bags. Buffer zones (4 m wide) were included in each direction to avoid edge effects. To minimize the effect of the slope position on soil characteristics, subplots were selected at a mid-slope position. Ohlson et al. (2009) determined that sampling to a depth of 20 cm in these environments is sufficient to estimate the majority of soil charcoal stocks. Two core soil samples were collected to determine soil bulk density (BD) at 0–20 cm depth using metal soil cores (200 cm³). Bulk density cores were dried at 105 °C until a constant dry weight was reached. Coarse fragments (stones, rocks, and roots) were removed manually, and their masses were subtracted from the total weight (bulk density = mass at 105 °C/V_{core} - V_{coarse fragments}).

2.4. Charcoal analysis

Soil samples were air-dried and homogenized. Subsequently, five sets of 400 g dry soil were separated from each plot and passed through 1 mm, 0.5 mm, and 0.25 mm sieves. All charcoal particles were removed manually from the sieves. For the fraction of charcoal ≤ 0.25 mm, the remaining material was placed in a petridish and the charcoal was removed manually using tweezers with the aid of an optical microscope (SMZ18, Nikon Instruments Ltd., Hong Kong). The charcoal concentration was determined in g kg⁻¹ soil (dry weight).

2.5. Elemental analysis

Carbon (C), hydrogen (H) and nitrogen (N) content were determined by using a CHNS Elementar Analyzer (Vario Elementar Analysensysteme, Hanau, Germany).

2.6. Solid-state ¹³C nuclear magnetic resonance spectroscopy

The solid-state ^{13}C cross polarization magic angle spinning (CP-MAS) nuclear magnetic resonance (NMR) spectra were acquired on a Bruker Advance III HD spectrometer (Bruker Instruments Inc., Germany) operating at a ^{13}C resonance frequency of 100.66 MHz. 100 mg of charcoal were packed into a 4 mm (outside diameter) Zr rotor. The contact time used was 3 ms and the acquisition time 20.35 ms. Free induction decay was acquired using a sweep width of 50 kHz. Line broadening for FID processing was done at 75 Hz with over 5,000 scans was accumulated for each sample.

The ^{13}C chemical shifts were calibrated relative to tetramethylsilane (0 ppm) with glycine (COOH at 176.08 ppm). The spectra were quantified by subdividing them into the following chemical shift regions: alkyl C (0-45 ppm); N-alkyl/methoxyl C (45-60 ppm); O-alkyl C (60-90 ppm); aromatic C (90-140 ppm); phenolic carbons (140-160 ppm); carboxyl/amide C (160-185 ppm); carbonyl C (185-250 ppm). The ^{13}C intensity distribution was determined by integrating signal intensity over the above-mentioned chemical shift regions using the MestReNova 10 software (Santiago de Compostela, Spain).

The charcoal fractions from each rotation were analysed to calculate the abundance of charcoal, stocks of PyC, and stable C per hectare for the soils from different chronosequence stands by averaging the three replicates for each sample plot. All statistical analyses were performed with SPSS 17.0 software.

3. Results and discussion

3.1. Chemical composition of charcoals

3.1.1. Elemental composition

Table 1 shows the elemental composition (C, N, H) of the charcoal particles and their atomic ratios (atomic ratio of carbon and nitrogen [$C:N_{at}$] and atomic ratio of hydrogen and carbon [$H:C_{at}$]). The N contents of charcoals were very homogeneous; they ranged from 4.6 g kg^{-1} to 5.7 g kg^{-1} , which is typical for PyC samples derived from wood biomass. Carbon contents were lower than those reported for PyC obtained at severe pyrolysis conditions; they ranged from $273.3 \pm 0.1 \text{ g kg}^{-1}$ (fourth rotations of slash-and-burn; 10-year old trees) to $421.5 \pm 0.6 \text{ g kg}^{-1}$ (first rotation of slash-and-burn; 12-year old trees). The contents of C, H, and N were lower for wildfire charcoal produced from boreal forests, possibly reflecting the differences in precursor material (Hart and Luckai, 2014). Due to prescribed burning, the quantities of C and N in PyC were considerably lower than those reported for many other plantation studies (Krishnaraj et al., 2016; Ohlson et al., 2009). Eckmeier et al. (2007) observed an increase of 1.3 g C kg^{-1} in the 1 cm soil layer in a temperate deciduous forest immediately after slash-and-burn. Similar results were reported by DeLuca and Zouhar (2000) in ponderosa pine forests as a result of selection harvest and prescribed burns. Atomic ratios provide an indication of the aromaticity of charred material (Wiedemeier et al., 2015), where material that is more charred generally has a smaller H:C ratio (Baldock et al., 2002). High $H:C_{at}$ values (in all the cases $H:C_{at}$ are ≥ 0.80) in this study are indicative of the mild condensation degree of aromatic structures forming the PyC. Moreover, the results were higher than those reported by

Nocentini et al. (2010) and Wiechmann et al. (2015), suggesting that the charcoal in our study area may be less charred. Certini (2005) described that in burning conditions typical of prescribed fire, burning efficiency and intensity are generally low. On comparing charcoal samples from plots with an increasing number of slash-and-burn rotations, but covered by plantations of similar age, a decrease in C content and a slight increase in the H:C_{at} ratio was observed [12–10-years old: C decayed from 421.5 ± 0.6 to 273.3 ± 0.1 , H:C_{at} increased from 0.81 to 1.02 (first to fourth rotation); 21-years: C declined from 407.7 ± 1.0 to 342.6 ± 0.1 , H:C_{at} increased from 0.80 to 0.99 (first to third rotation)]. A similar trend is observed for charcoals with the same number of slash-and-burn rotations (see first and second rotation) but with increasing stand age. From the above results, it is clear that the chemical composition of charcoal is altered to material with lower C content and condensation degree with increasing residence time in the soil. This demonstrates the decomposition of charcoal as the age of the stand (age in the soil) increases. In addition, increasing the number of slash-and-burn rotations over the same area does not modify the previous trend. In fact, charcoal from the plots with four slash-and-burn rotations showed the lowest H:C_{at} and C content.

3.1.2. ¹³C Nuclear Magnetic Resonance Spectroscopy of charcoal samples

The ¹³C NMR and relative intensity distribution for each chemical shift region of charcoal samples are shown in Figure 2 and Table 2, respectively. All the ¹³C NMR spectra were very similar, in all the cases aryl-C represents the main fraction (region 90–140 ppm), which is indicated by the intense and broad signal centred at

around 128–129 ppm. Aryl-C comprised from 51.3 to 58.5% (third rotation; 21- and 12-years-old stands respectively). The dominance of aryl-C in charcoal has also been reported by other authors (Hilscher and Knicker, 2011; De la Rosa and Knicker, 2011). In contrast, the signals characteristic of alkyl-C (0–45 ppm) and O-alkyl C (45–60 ppm) were very small. This is due to the dehydration and dehydroxylation reactions, which transform O-alkyl C into aromatic structures during the carbonization process (Knicker et al., 2008). The O-alkyl C spectral region in PyC has been consistently shown to be the first region to lose intensity during decomposition, while the alkyl C, aromatic C, and carbonyl C regions decompose more slowly (Skjemstad et al., 1997). The small peaks at 54 ppm visible in most of the charcoals correspond to C from methoxyl-lignin structures, whereas the weak signals at 10–15 ppm and 170–175 ppm derive from hemicelluloses. The signal of alkyl-C (0–45 ppm) results from the presence of remaining polymethylene structures such as waxes, cutins, lipids, suberins, and resins. The peak at 27 ppm is typically attributed to relatively resistant alkyl structures.

The spectra of charcoals taken from soils under Chinese fir trees show peak shoulders at 142 ppm, which are typical for O-aryl-C derived from lignin compounds. The signal intensities of O-alkyl-C (60–90 ppm), aryl-C (90–140 ppm) and O-aryl-C (140–160 ppm) decreased as the number of rotations increased in the ~12 year-old stands. The intensity of the region corresponding to O-aryl-C (140–160 ppm) ranged from 15.7 to 20.4%. All charcoals exhibited similar percentages (8.5–11.1%) in the region assigned to the carboxyl/amide C group (160–185 ppm),

and no trend was found.

In the first rotation, the percentage of O-aryl regions (140–160 ppm) increased from the 12- to 97-year old stands, which can be attributed to O-substituted (OH) aromatic carbons (phenolic groups). Zhiquan et al. (2005), for example, report that these chemicals (phenols, organic acids, tannin components, ketones and aldehydes) accumulate in the soil when stumps start to decompose in plantations (especially at higher stand age; 97-year old stand in the present study). It has also been reported that phenols, ketones and aldehydes act as allelochemicals, releasing toxic compounds in soils and resulting declines in productivity of replanted Chinese fir plantations (Chen et al., 2014; Huang et al., 2000). In the carboxyl C region (160–185 ppm), the main peak at ~190 ppm, ascribable to carboxyl, amide, and ester C, was highly detected in 21-year old stands (all three rotations). Similar to carboxyl C, the carbonyl C (185–250 ppm) contribution was higher in the 21-year old stands. The exclusive presence of these alkyl structures in the fourth rotation stand lacks any trend related to the relative abundance of charcoal, which may be attributed to the inhomogeneity of different slash-and-burn events.

In summary, the ^{13}C NMR spectra of all the charcoal samples were very similar regardless of the number of slash-and-burn rotations or the age of the fir tree plantation. In the case of samples from sites with only one slash-and-burn rotation, increasing the age (from 12- to 97-years) resulted in a relative decrease in aryl-C (from 57.8% to 53.8%). The peaks at 71–75 ppm, which derive from ether bonds, are clearly identified in the charcoals taken from the youngest plantations (trees of 10 to

12-years of age). Both results offer an evidence for some signs of charcoal degradation with time.

3.2. Assessment of stocks of pyrogenic C in soils subjected to slash-and-burn rotations in Chinese fir plantations

Table 3 shows the abundance of charcoal (g kg^{-1}) and the C content of the charcoal, as well as an estimation of stocks of charcoal and stable C per hectare for the soils from different chronosequence stands over four rotations (slash-and-burn practice) in Chinese fir plantations.

The abundance of charcoal in soils slightly increased with the number of rotations (slash-and-burn events), but decreased with the age of the plantations (and age since the last rotation). The sample of 10-year old stand (fourth rotation) exhibited a charcoal abundance of $0.69 \pm 0.20 \text{ g kg}^{-1}$ soil, which contrasted with the low figure of the sample 97-year old stand (first rotation; $0.07 \pm 0.01 \text{ g kg}^{-1}$ soil). The C content of charcoal samples decreased with increasing age of Chinese fir stands following the last slash-and-burn rotation, which means that the degradation of C contained in the charcoal increased with time. In addition, when comparing plantations of similar age, but with increasing number of slash-and-burn rotations, the decrease in C content of charcoal was more evident. This result suggested that, in addition to the microbial and physical degradation, part of the existing PyC could be consumed by the subsequent prescribed burns. This has also been highlighted as a possible major abiotic mechanism of PyC loss in soils (Preston and Schmidt, 2006;

Czimczik and Masiello, 2007; Kane et al., 2010). Santin et al. (2013) measured losses of existing PyC of up to 15% in an experimental boreal forest fire.

We calculated the stocks of charcoal and stable C (C contained in charcoal) to a fixed soil depth of 20 cm (Table 3). These stocks were adjusted by correcting the data for differences in bulk density. It is well known that PyC comprises a continuum of materials with different properties, and each PyC quantification method is optimized to detect a particular fraction (Hammes et al., 2008). Thus, in most cases, the direct comparison of stocks of PyC with those reported by other authors is completely meaningless. Alternatively, a study of the trends would offer valuable information concerning the dynamics of the pools of PyC and suggest proper soil management practices. Comparison of data from soils in plantations of similar age displayed a positive correlation between estimated stocks of charcoal in soils and the number of slash-and-burn periods, with a maximum of 1164 kg ha⁻¹ (four slash-and-burn rotations). By contrast, a negative correlation was observed in the stocks of charcoal and yield of stable C with increasing time after each slash-and-burn event. In the case of the plot with only one slash-and-burn rotation, over 25% of charcoal stocks and 28% of stable C were lost in nine years (period from 12 to 21 years). The loss in rates of charcoal stocks and stable C seemed to be reduced after 21 years. Nonetheless, loss of charcoal stocks accounted for more than 85% of stable C during the period from 12 to 97-years.

Nguyen et al. (2008) examined PyC degradation in a chronosequence of cultivated soils after clearance by forest fire. The first phase of 30 years was

characterised by a rapid loss of PyC of up to 70%. The second phase had slower rates of PyC degradation. In concurrence with the report of Nguyen et al. (2008), an exponential decay of PyC in A horizons of Umbrisols in grasslands of Southern Brazil was observed (Knicker et al., 2008). Since PyC is not necessarily persistent in all cases, substantial degradation of charcoal occurred in the Nanping soils owing to intensive management systems, following slash-and-burn rotations on a time scale of decades associated with gentler slopes, and may also involve conscious burial of these materials due to erosion leading to the question of their long-term persistence in the soil, which is well supported by several studies (Cheng et al., 2010; Glaser et al., 2002; Lehmann, 2007). Rumpel et al. (2006) reported similar findings for tropical soils where besides *in situ* degradation, preferential erosion of PyC on steep slopes with slash-and-burn agriculture played a major role in charcoal degradation.

4. Conclusions

The abundance and composition of charcoal was analysed in Hapludult soils from the oldest Chinese fir plantations that involve traditional slash-and-burn practice. This permitted us to study the evolution of charcoal composition and the stocks of stable C in soils with up to four slash-and-burn periods and plantations ranging in age from 12- to 97-years. Elemental analyses proved that the chemical composition of charcoal is modified with increasing time in the soil. Aged charcoals have a lower C content and condensation degree. The ^{13}C NMR spectra of all the charcoal samples were very similar and were dominated by aryl-C. However, they

showed a relative decrease in aryl-C and the loss of specific peaks (ether bonds) with increasing age, which suggests decomposition of charcoal with increased residence in the soil. The repetition of slash-and-burn events increased the input of PyC and the stocks of stable C. However, the yields of stable C and charcoal declined with increasing time since the last slash-and-burn event. A loss over 25% of the charcoal stocks was estimated for a period of nine years.

Prescribed burning alters the soil food web structure by burning the litter layer thereby limiting nutrient cycling and influencing soil C quantity, soil respiration and the microbial consortium in frequently burned ecosystems. These activities also cause soil disruption leading to changes in soil properties that are important for soil conservation and plant reestablishment. Hence, the low persistence of charcoal reported for soils following slash-and-burn rotations in the sloping fields of Fujian Province implies the need for periodic slash-and-burn rotation to maintain the stocks of stable C. Future research needs to focus on providing more insights into the circumstances under which PyC may have longer persistence in soils as recommended by Steiner et al. (2009). Finally, an evaluation of the effectiveness and economic viability of charcoal as a soil amendment under field conditions is needed.

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548

549 **Figure Captions:**

550

551 **Figure 1:** Location of the area of study and Wangtai town.

552 **Figure 2:** Solid-state ^{13}C NMR spectra of charcoal samples from the soils under
553 Chinese fir plantation with one time slash-and-burn rotation (12-, 21-, 40- and
554 97-year old plantations); two times slash-and-burn rotations (12-, 21- and 31-year
555 old plantations); three times slash-and-burn rotations (13- and 21-year old
556 plantations) and four times slash-and-burn rotations (10-year old plantation).

557

Table 1. Elemental composition of charcoal sampled for each rotation (slash-and-burn practice) and age of Chinese fir trees. Data are mean $\pm$ standard deviation.

Rotation (slash-and-burn cycle)	Time since last rotation (years)	Nitrogen (g kg ⁻¹)	Carbon (g kg ⁻¹)	Hydrogen (g kg ⁻¹)	C:N_{at}	H:C_{at}
First rotation	12	5.3 $\pm$ 0.1	421.5 $\pm$ 0.6	28.6 $\pm$ 0.2	93.2	0.81
	21	4.7 $\pm$ 0.1	407.7 $\pm$ 1.0	27.3 $\pm$ 0.2	100.5	0.80
	40	4.6 $\pm$ 0.2	376.3 $\pm$ 0.4	26.9 $\pm$ 0.1	95.6	0.86
	97	4.4 $\pm$ 0.1	361.9 $\pm$ 0.2	26.1 $\pm$ 0.3	95.9	0.86
Second rotation	12	5.3 $\pm$ 0.2	384.6 $\pm$ 0.1	28.5 $\pm$ 0.3	85.4	0.89
	21	5.7 $\pm$ 0.1	369.8 $\pm$ 0.0	27.5 $\pm$ 0.1	76.3	0.89
	31	5.5 $\pm$ 0.1	350.1 $\pm$ 0.2	26.2 $\pm$ 0.1	74.2	0.90
Third rotation	13	5.0 $\pm$ 0.0	316.9 $\pm$ 0.1	23.9 $\pm$ 0.1	73.7	0.91
	21	5.2 $\pm$ 0.1	342.6 $\pm$ 0.1	28.2 $\pm$ 0.1	77.5	0.99
Fourth rotation	10	4.8 $\pm$ 0.1	273.3 $\pm$ 0.1	23.2 $\pm$ 0.3	67.1	1.02

562

563

Table 2. Assessment (%) of the different C types as seen by ^{13}C NMR spectroscopy integration regions of charcoal samples.

Rotation/Stand age	185-250	160-185	140-160	90-140	60-90	45-60	0-45 (ppm)
First rotation							
12-year old	6.1	8.5	15.7	57.8	5.1	1.7	5.2
21-year old	8.3	11.1	17.0	57.8	2.9	0.4	2.5
40-year old	9.6	10.4	17.8	56.2	1.6	0.7	3.8
97-year old	8.4	10.6	19.0	53.8	3.0	1.5	3.8
Second rotation							
12-year old	7.6	9.2	17.6	52.1	7.0	2.4	4.3
21-year old	7.2	10.1	18.8	52.4	3.2	1.7	6.6
31-year old	5.7	8.0	15.8	52.1	6.6	2.9	8.9
Third rotation							
13-year old	5.5	8.3	19.3	58.5	3.5	1.1	4.0
21-year old	8.0	9.9	18.8	51.3	3.8	1.9	6.4
Fourth rotation							
10-year old	3.8	9.7	20.4	56.1	2.7	1.9	5.4

564

565

Table 3. Estimation of charcoal content and yields of stable C of soils subject to successive slash-and-burn rotations

Rotation/Stand age	Abundance of charcoal in soils $\pm$ standard deviation ^{a)}	Estimated contents ^{b)}	
		Charcoal in soil (kg ha ⁻¹)	Yield of stable C in soil (g PyC ha ⁻¹)
First rotation			
12-year old	0.37 $\pm$ 0.09	657	277
21-year old	0.28 $\pm$ 0.03	487	199
40-year old	0.26 $\pm$ 0.08	440	165
97-year old	0.07 $\pm$ 0.01	114	41
Second rotation			
12-year old	0.51 $\pm$ 0.03	905	348
21-year old	0.30 $\pm$ 0.07	475	176
31-year old	0.14 $\pm$ 0.01	234	82
Third rotation			
13-year old	0.55 $\pm$ 0.03	918	295
21-year old	0.51 $\pm$ 0.06	851	292
Fourth rotation			
10-year old	0.69 $\pm$ 0.20	1164	318

- 570 a) Charcoal particles were carefully separated by manual sieving;
- 571 b) Estimation for a depth 0-20 cm taking into account the soil density of each sample.
- 572
- 573
- 574

HIGHLIGHTS

- Chemical composition of charcoal is modified with increasing time in the soil.
- Aged charcoals have a lower C content and condensation degree.
- The ^{13}C NMR spectra of all the charcoal samples are dominated by aryl-C .
- Charcoal stocks and yield of stable C increased with the number of fires.

Figure 1

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Figure 2

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