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【Note】

Relationship between fixed carbon and organic carbon of bamboo charcoal

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Abstract: Inorganic carbon content (inorganic C) of bamboo charcoals prepared at temperatures of 300-800°C and collected from different producers and kiln types in Japan were measured. The organic carbon content (organic C) was then calculated from the difference in total carbon content (total C) and inorganic C. This calculation was facilitated with reference to Appendix 4 of the UN's Intergovernmental Panel on Climate Change (IPCC) "2019 Refinement to [its] 2006 Guidelines for National Greenhouse Gas Inventories". Regardless of preparation temperature, producer, or kiln, there was little inorganic C in the charcoals, and no large difference in the values for organic C and total C. We obtained a significant equation from the relationship between organic C and the fixed carbon content (FC) estimated by proximate analysis. This regression equation may be useful to correct FC to organic C for bamboo charcoal.

Keywords: bamboo charcoal, proximate analysis, fixed carbon, organic carbon, inorganic carbon

1. Introduction

Global warming related to greenhouse gas emissions brings much attention to the processes of removing CO_2 from the atmosphere -i.e., methods for carbon dioxide removal (CDR). Biochar is one of these methods, where atmospheric CO_2 is absorbed by plants and trees as they grow. In this method, the biomass is converted, in an oxygen-limited environment, into charcoal-like material -biochar- which can be applied to soils as an agent for soil improvement[1]. The recalcitrant carbon in biochar is recognized as storing carbon, away from the atmosphere, for decades to centuries.

For the purpose of estimating the change produced in mineral soils' carbon stocks by burying biochar in cropland and grassland soils, the UN's Intergovernmental Panel on Climate Change (IPCC) defined a methodology as a formula for calculation. In the equation, published in Appendix 4 of the IPCC's "2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories[2]", one of the variables is organic carbon content (organic C) of biochar from various feedstocks. This variable is ordinally estimated as a difference between total carbon (total C) and inorganic carbon (inorganic C)[3]. The other variables are the amount of biochar carbon remaining after 100 years (F_{perm}), and the mass of biochar incorporated into mineral soil.

Concerning organic C for bamboo charcoal, Nagumo *et al.*[4] have measured a total of 15 bamboo charcoals using a dichromate oxidation method. They obtained an average value of 424 mg/g (42.4%) for 30-minute reaction, noting that the residual charcoal after oxidation still contained recalcitrant carbon. Therefore, the result show that the method with short

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reaction time was not suitable for estimating the carbon stock in bamboo charcoal.

By contrast, we have prepared charcoal from the moso bamboo cultivar *Phyllostachys pubescens* at temperatures of 300-800°C, and then collected a total of 13 commercial bamboo charcoals from different producers in Japan who use different kiln types[5]. We next measured the chemical characteristics by proximate and elemental analysis. In particular, we estimated the charcoals' fixed carbon content (FC), considering it an indicator of biochar's carbon sequestration potential. However, although it would have a close relation to organic C, FC is not suitable for use directly in the equation derived by the IPCC guidelines.

In this study, we measured inorganic C using the bamboo charcoals already selected for our previous study[5]. We then calculated organic C using inorganic C, and newly clarified a relationship between FC and organic C. We additionally examined the charcoals' time dependence in organic C using a dichromate oxidation method, and we will discuss the recalcitrant carbon of charcoal production at different temperatures.

2. Materials and Method

2.1 Bamboo charcoals

We used moso bamboo charcoals prepared at temperatures of 300-800°C, and a total of 13 commercial bamboo charcoals. Preparation procedures for the charcoals at different temperatures, and evidence collected from the commercial bamboo charcoals, have been described in our previous report[5]. In addition, the report describes the charcoals' precise chemical characteristics.

2.2 Dichromate oxidation method for determining organic carbon content

We measured organic carbon content by oxidation (organic $C_{oxidation}$) according to the literature, using a mixture of $K_2Cr_2O_7$ and H_2SO_4[6].

We carefully placed 10 mg of oven-dried charcoal powder (fractions 53 μm sieve on and 100 μm sieve pass) in a 100 ml conical flask, and then added 10 ml of 0.4N $K_2Cr_2O_7$ - H_2SO_4 mixture. The flask was next heated with condenser refluxed at 200°C using a hotplate (Yamato Scientific co., ltd, MG600H) for 15-420 min. After the reaction, we further added 10 ml of deionized water, and cooled the mixture to room temperature. We then titrated the excess $Cr_2O_7^{2-}$ in the mixture with a 0.2N $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ - H_2SO_4 mixture. We tested at least three replicates in this experiment.

We calculated organic Coxidation using equation (1) as follows.

$$\text{Organic } C_{oxidation}\ (\%) = ((B - T) \times F \times 60) / W \quad (1)$$

Here, B is the volume of blank solution (ml); T is the titration volume (ml); F is the correction coefficient for the 0.2N $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ - H_2SO_4 mixture; W is the weight of the charcoal sample (mg).

2.3 Determination of inorganic carbon content

We measured inorganic carbon content (inorganic C) by treating 0.3-0.5 g of dried powder (< 180 μm sieve) with 1N HCl solution in an enclosed reactor (Amicon ultrafiltration cell, model 8050) according to ASTM D4373[7]. Carbon dioxide gas was evolved during the reaction between the acid and the charcoal's carbonate fraction. Since the pressure in the closed reactor is proportional to the mass of reagent-grade $CaCO_3$, we measured the resulting pressure in the reactor using a pressure gauge with a maximum range of 5 kPa. The relationship between the mass of $CaCO_3$ and its corresponding pressure was used as a calibration curve. Calculating inorganic C based on the calibration curve, we used the ratio of C to $CaCO_3$.

2.4 Calculation of organic carbon according to guidelines

We calculated the organic carbon content (organic C_{ipcc}) using equation (2).

Organic C_{ipcc} (%) = total C - inorganic C (2)

Here, total C is the mass of elemental carbon by elemental analysis (%). In this study, we used the values from Tables 3[5] and 5[5] of our previous report.

3. Results and Discussion

3.1 Organic carbon content (organic $C_{oxidation}$) of bamboo charcoal determined by dichromate oxidation method

Carbon being the principal element of charcoal, total C measured by dry combustion method and FC by proximate analysis have often been used to determine the quality of charcoal. In this experiment, we measured organic $C_{oxidation}$ of bamboo charcoals by dichromate oxidation method.

Time-dependent changes in the ratio of organic $C_{oxidation}$ to total C (organic $C_{oxidation}$ / total C) are shown in Figure 1. The values for total C of charcoals at 600°C and 800°C were 85.4% and 89.4%, respectively (see Table 1). For the 800°C charcoal, the ratio increased quickly, up to 0.9, as the reaction time increased to 180 min. After that, there was no great change in the ratio, and the value was 0.92 at 420 min. On the other hand, the organic $C_{oxidation}$ / total C of charcoal prepared at

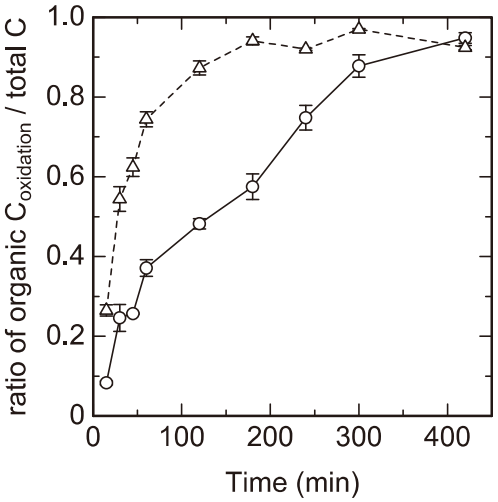

Fig. 1 Time-courses of change in ratio of organic $C_{oxidation}$ to total C
Legend: ○ : 600°C; △ : 800°C
Error bars indicate ranges of standard deviation

600°C increased slowly, reaching 0.95 after 420 min. It is clear that most of the carbon at both temperatures was oxidized by dichromate, and the speed of oxidization was different depending on the heat-treatment temperature (HTT).

Table 1 shows the organic $C_{oxidation}$ / total C at 30 min and 420 min of oxidation for the charcoals at different HTTs. We found no great difference in ratio at 420 min of oxidation, as all values were between 0.92 and 1.01. This means most of the carbon was oxidized, regardless of the HTT, after

Table 1 Chemical characteristics and ratio of organic $C_{oxidation}$ to total C in charcoals at different temperatures

HTT*1	FC*2	total C*3	organic $C_{oxidation}$ / total C*4			
			30 min		420 min	
(°C)	(%)	(%)	average	SD*5	average	SD*5
300	59.9	69.8	0.82	0.02	0.95	0.01
400	75.2	78.7	0.81	0.05	0.95	0.03
500	84.9	81.2	0.56	0.09	0.98	0.03
600	89.7	85.4	0.31	0.04	0.95	0.03
700	90.5	85.7	0.27	0.05	1.01	0.00
800	93.5	89.4	0.52	0.03	0.92	0.01

*1 heat-treatment temperature

*2 fixed carbon is the value in Table 3[5]

*3 total C is the value of elemental C in Table 3[5]

*4 ratio of organic $C_{oxidation}$ to total C

*5 standard deviation

sufficient reaction time. Meanwhile, the ratio at 30 min oxidation shows that the speed of oxidation was different: the ratio decreased from 0.82 to 0.27 as the temperature increased from 300°C to 700°C, and beyond this temperature the value increased to 0.52.

With regard to the observed speed of oxidation in bamboo charcoals, Satonaka[8] reported a similar change in the organic $C_{oxidation}$ / total C for wood charcoals prepared from mizunara (*Quercus crispula* Blume) at 300-1100°C. The ratio after 150 min oxidation decreased from 0.56 to 0.10 as the temperature increased from 300°C to 600°C, and above 700°C the value increased to 0.30. In general, it is known that aromatic linked structures in charcoal are formed and developed when the temperature increases[9]. Since the relatively stable structures would resist the dichromate oxidation in a short reaction time, the ratio -organic $C_{oxidation}$ / total C- decreases. It is also known that at temperatures over 600°C, the surface area of charcoal increases[10]. The mass of surface area would affect the reaction frequency between the substances of charcoal and the oxidation reagents. At temperatures of 800°C, being above 700°C, in our study and Satonaka's, the increased ratio of organic $C_{oxidation}$ / total C was probably an effect of the large amount surface area, although a close relationship between the dichromate oxidation and the surface area of charcoal must be clarified in a future study.

3.2 Organic carbon content (organic C_{ipcc}) of bamboo charcoals according to IPCC guidelines

Table 2 shows inorganic C and organic C_{ipcc} of bamboo charcoals prepared at 300-800°C. There are lower values for inorganic C in the charcoals, although the increasing temperature increased these values. As a result, there was no great difference in the values for the total C and organic C_{ipcc} at each temperature (compare Tables 1 and 2). Meanwhile, the value of organic $C_{oxidation}$ after 420 min was almost the same as that of total C (Table 1). Since the dichromate oxidation method required long reaction time and heavy metal solution, the measurements of inorganic C and total C seemed to be a method to easily and rapidly evaluate the organic C in charcoal.

Table 3 shows FC, total C, inorganic C and organic

Table 2 Inorganic C and organic C_{ipcc} of charcoals at different temperatures

HTT*1 (°C)	inorganic C (%)	organic C_{ipcc}*2 (%)
300	0.09	69.7
400	0.11	78.6
500	0.17	81.1
600	0.39	85.0
700	0.48	85.3
800	0.58	88.8

*1 heat-treatment temperature

*2 organic C_{ipcc} = total C - inorganic C

Table 3 Chemical characteristics and organic C_{ipcc} of commercial bamboo charcoals

No.	FC*1 (%)	total C*2 (%)	inorganic C (%)	organic C_{ipcc}*3 (%)
1	90.7	86.8	0.21	86.6
2	81.4	81.4	0.16	81.2
3	93.8	89.0	0.20	88.8
4	76.9	82.3	0.11	82.2
5	94.7	90.3	0.13	90.2
6	90.9	87.6	0.21	87.4
7	71.3	74.0	0.12	73.9
8	89.7	83.3	0.17	83.1
9	85.1	83.3	0.12	83.2
10	87.7	82.9	0.20	82.7
11	78.6	80.1	0.12	80.0
12	78.3	75.5	0.20	75.3
13	93.0	87.2	0.15	87.1
average	85.5	83.4	0.16	83.2
SD*4	7.5	4.9	0.04	4.9
CV*5	0.09	0.06	0.24	0.06
maximum	94.7	90.3	0.21	90.2
minimum	71.3	74.0	0.11	73.9
△*6	23.4	16.3	0.10	16.3
median	87.7	83.3	0.16	83.1

*1 fixed carbon is the value in Table 5[5]

*2 total C is the value of elemental C in Table 5[5]

*3 organic C_{ipcc} = total C - inorganic C

*4 standard deviation

*5 coefficient of Variation

*6 maximum - minimum

C_{ipcc} for the commercial bamboo charcoals. The FC and total C are the values shown in our previous report[5]. As shown in the table, all of the charcoals showed little inorganic C, where the average was 0.16% and the maximum and minimum values were 0.21 and 0.11%, respectively. We thus found no great difference in either total C or organic C_{ipcc}.

The relationship between FC and organic C_{ipcc} is shown in Figure 2. The symbols used in the figure indicate the types of charcoal. These bamboo charcoals -prepared at different temperatures and collected in Japan- are respectively marked with a double circle (◎) and a filled circle (●). A positive relationship -i.e., Organic C_{ipcc} (%) = 0.52 × FC (%) + 38.38 (coefficient of determination: 0.97)- was clear among the charcoals at different temperatures. In addition, the 13 plots for the commercial charcoals fell on a line through regression analysis. It is clear that the equation could be used to correct FC to organic C_{ipcc}.

In Appendix 4 of the IPCC's guidelines[2], the amount of biochar carbon that would persist for 100 years (F_{perm}) was derived at different pyrolysis temperatures: low (350-450°C), medium (450-600°C) and high (more than 600°C). We therefore divided the commercial bamboo charcoals into these three categories (see Figure 2), summarizing the averages for FC and organic C_{ipcc} in Table 4.

As shown in Figure 2, four charcoals (4, 7, 11, and 12) were found in the low temperature range. The averages of FC and organic C_{ipcc} were 76.3% and 77.8%, respectively (Table 4). We found no great difference between these values. Meanwhile in the high temperature range, there were five charcoals (1, 3, 5, 6, and 13) showing averages of 92.5% and 88.2%, respectively for FC and organic C_{ipcc} -the value for organic C_{ipcc} was about 4% less than that for FC. The reason for this difference can be explained by the measuring method for FC[5].

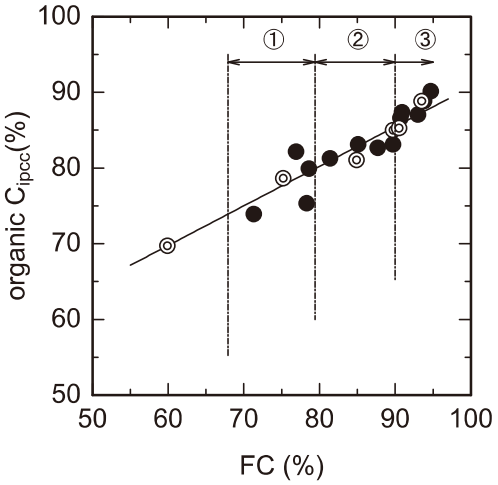

Fig. 2 Relationship between fixed carbon (FC) and organic carbon (C_{ipcc})
Legend: ◎ : bamboo charcoals prepared at 300-800°C; ● : commercial bamboo charcoals
Labeled regions mark the range of FC in bamboo charcoal at ① 350-450°C, ② 450-600°C, and ③ above 600°C

The values for F_{perm} in Table 4 were also the standard values for calculating the change in carbon stocks of mineral soils associated with biochar amendment, used regardless of the feedstock or production processes of biochar. In addition, the variation at each temperature range

Table 4 Average and SD of fixed carbon (FC) and organic C_{ipcc} for commercial bamboo charcoals at three categories

Temperature	No.	FC (%)		organic C_{ipcc} (%)		F_{perm}*2
		average	SD*1	average	SD*1	
Low (350-450°C)	4, 7, 11, 12	76.3	3.4	77.8	3.9	0.65 ± 15%
Medium (450-600°C)	2, 8, 9, 10	86.0	3.6	82.6	0.9	0.80 ± 11%
High (> 600°C)	1, 3, 5, 6, 13	92.5	2.0	88.2	1.6	0.89 ± 13%

*1 standard deviation

*2 amount of biochar carbon remaining after 100 years described in the Appendix 4 of IPCC guidelines[2]; mean value ± 95% bootstrap confidence limit expressed as a percentage of the mean

was wide. Therefore, future studies should derive the F_{perm} values for bamboo charcoal incorporated into soils in Japan.

4. Conclusion

We measured inorganic C of bamboo charcoals prepared at temperatures of 300-800°C, as collected from different producers and kiln types in Japan. We then calculated the organic C_{ipcc} from the difference between inorganic C and total C as estimated by elemental analysis. We found little inorganic C in those charcoals, at values below 0.6%. Therefore, no great difference was found between the values for organic C_{ipcc} and total C.

We obtained a significant equation, Organic C_{ipcc} (%) = 0.52 × FC (%) + 38.38, in the relationship between FC as estimated by proximate analysis and organic C_{ipcc}. This will be useful to correct FC to organic C_{ipcc} for bamboo charcoal.

During short-time oxidation, bamboo charcoals' organic $C_{oxidation}$ is affected by mass of stable aromatic linked structures and the formed surface area. Meanwhile, sufficient reaction time mostly oxidized the carbon in charcoal, and organic $C_{oxidation}$ reached the same level as total C.

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References

1) IPCC (2018) Global Warming of 1.5°C, Intergovernmental Panel on Climate Change, pp.342-346
2) https://www.ipcc-nggip.iges.or.jp/public/2019rf/pdf/4_Volume4/19R_V4_Ch02_Ap4_Biochar.pdf (2019) Intergovernmental Panel on Climate Change, pp.1-2
3) https://www.biochar-international.org/wp-content/uploads/2018/04/IBI_Biochar_Standards _V2.1_Final.pdf (2019) International Biochar Initiative, p.13
4) Nagumo T, Ando M, Mori C (2014) *Japanese Journal of Soil Science and Plant Nutrition*, **85** (1), 37-42
5) Kurimoto Y, Kajimoto T, Ozawa F, Inoue Y, Shibata A (2019) *Wood Carbonization Research*, **16** (1), 3-12
6) Japanese Society of Soil Plant Nutrition (1986) Soil Standard Method of Analyses and Measurements, Hakuyuusya, Tokyo, pp.86-94
7) ASTM D4373-14 (2019) ASTM International, West Conshohocken, PA, USA
8) Satonaka S (1963) *Research Bulletin of the Hokkaido University Forests*, **22** (2), 609-814
9) Kai T, Yamamoto S, Ishihara S (2000) *Resources Processing*, **47** (3), 132-139
10) Kurimoto Y, Kano K, Sawabe O (2004) *Mokuzai Gakkaishi*, **50** (2),106-115

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【ノート】

タケ炭の固定炭素と有機態炭素の関係

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概要：モウソウチクを原料として300-800℃の温度で調製したタケ炭とともに，生産者や炭化方法の異なった市販タケ炭を用いて無機態炭素の測定を行った。その後、気候変動に関する政府間パネル（IPCC）「2006年IPCC国別温室効果ガスインベントリガイドラインの2019年改良」の付属書4に示された有機態炭素を求めるため、全炭素と無機態炭素の差から有機態炭素を算出した。

供試したタケ炭の無機態炭素は、炭化温度や生産者、炭化方法に係わらず少ない値であったことから、元素分析で求めた全炭素と有機態炭素の間に大きな違いはなかった。また、工業分析で求めた固定炭素と有機態炭素の間に有意な回帰式が得られた。この関係式はタケ炭の有機態炭素をタケ炭の固定炭素を用いて見積る際に有用であると考えられた。

キーワード：タケ炭, 工業分析, 固定炭素, 有機態炭素, 無機態炭素