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The Possibility of Use Research Methods of Soil Organic Matter for Assess the Biochar Properties.

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ABSTRACT

To characterize the biochar prepared in different pyrolysis modes of various woody and herbaceous materials (10 samples) used the method of stepwise oxidation of soil organic matter (SOM) and methods extraction of SOM fractions (by the hot water and mixture Na₄P₂O₇-NaOH). Results showed that the content of more oxidizable organic matter (OM) in biochar samples depends on the mode of pyrolysis and source of plant material. There is a strong positive correlation between the content of more oxidizable OM and the content of labile OM fractions in biochar samples. The content of OM of the inert to oxidation in biochar samples obtained at pyrolysis temperatures about 400-600C approximately constant and does not depend on the initial material. Using the method of SOM estimation for characteristics of biochar is promising, since this information can be used in existing models and concepts of the dynamics of OM in soils.

Keywords: biochar, soil fertility, carbon sequestration, labile organic matter, stable organic matter, inert organic matter.

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INTRODUCTION

Currently (Presently), is growing (is increasing, increases) the interest in the use of biochar produced by pyrolysis of different origin plant residues as a promising component for soil application. The application of biochar allows to solve two major problems of our time: the prolonged (long-term) improvement of soil fertility [1-3] and the sequestration of atmospheric carbon [4-6]. According to R. Lal [7] and Y. Kuzyakov et al. [8] the carbon content in biochar in the stable to oxidation form can be stored in the soil from a few hundred to thousands of years. In the prospect (In the long term), application of biochar to the soil provides to withdraw up to 50% of the carbon of plant residues from the biological cycle. However, the stability of biochars in soils to a largely depended on the type of plant residues and conditions of pyrolysis [9]. In parallel with inert components (benzo polycarboxylic acid) a significant part of the carbon in the pyrolysis products of the organic materials can be represented by humic substances, glycolipids, phospholipids and other compounds [10], which are characterized by different resistance to microbial degradation. The adding (the application) these substances with biochar to the soil can change (can alter) the active (labile) OM content in the soils.

In soil science accumulated numerous assesment methods of stability (lability) of SOM and approaches to evaluation of its chemical and biochemical stability, which are discussed in detail in the review paper [11]. Wherein will be the advantage of using these methods as compared to other which are focused on obtaining technical characteristics of the pyrolysis product of the plant residues? It is obvious that the use of these methods allows us to adapt the information to the existing models and concepts of the dynamics of OM in soils. This approach will allow in perspective to determine the place of biochar in the total OM pool of different soils under different conditions of their use.

The aim of this research is to study the possibility of use the research methods of SOM for assess the biochar properties for obtain the information allowing to predict their behavior in soils.

MATERIALS AND METHODS

Materials

Biochar samples prepared from various woody and herbaceous material was kindly provided by Dr. M.R. Bayan (Department of Agriculture and Environmental Sciences. Lincoln University in Missouri. USA). Biochar samples were obtained by Dr. M.R. Bayan developed by him pyrolysis technologies. These samples was crushed and sieved through $\varnothing 0.25$ mm ($\varnothing 0.10$ mm for determination of total carbon and nitrogen content).

Table 1: The biochar characteristics and the total carbon, nitrogen and ash content.

Biochar ID	Biomass	Temperature of pyrolysis	Total content (%)			Ash (%)
			C	N	C/N	
1	Pine	400-600 °C	84.4	0.167	506	2.7
2	Cedar	400-600 °C	86.3	0.292	295	1.0
3	Oak	400-600 °C	78.2	0.400	195	2.8
4	Miscanthus	400-600 °C	77.6	0.564	138	10.9
5	Willow	400-600 °C	79.6	0.278	286	6.8
6	Corn stover	400-600 °C	66.3	0.863	77	19.9
7	Switchgrass	400-600 °C	71.2	0.658	108	13.9
8	Willow	< 400 °C	77.3	0.228	339	2.7
9	Corn stover	< 400 °C	57.2	0.902	63	13.5
10	Switchgrass	< 400 °C	63.1	0.470	134	8.3

Total carbon and nitrogen content were performed with a vario MICRO cube (Fa Elementar). The ash content was determined by calcination at 1000 °C [12]. The total carbon content in biochar samples varies from 57.2% to 86.3% (the variation coefficient is 12.7%), the total nitrogen content from 0.167% to 0.902% (the variation coefficient is 53.9%). Also varies the ratio the total carbon to total nitrogen content, which is an order of magnitude higher than in the poorest by nitrogen of plant residues. General characteristics of this sampling

can be evaluated as sufficiently homogeneous on total carbon content, but very different on the qualitative composition of the biochar OM and the content of mineral elements in them.

General analytical methods

To characterize the labile fraction of biochar samples was used the extraction method of OM with hot water [13]. To assess the humic substances content in the biochar samples was used the method of accelerated determination of organic carbon content extracted with a mixture of $\text{Na}_4\text{P}_2\text{O}_7$ -NaOH [14]. This method is a simple approach to the extraction of humic substances and in contrast to traditional methods of chemical extraction of humic substances from soils, such as Dabin method, Schnitzer method, IHSS (International Humic Substance Society, Univ. of California, Los Angeles) [12] excludes procedures successive treatments with acids and alkalis.

For the common characteristics of stability of the all (entire) pool of biochar OM was used the stepwise oxidation method - modified Walkley- Black method [15] put forward by (which was proposed by) K.Y. Chan et al. [16]. This method used to study the SOM and involves the performance the soil oxidation with potassium dichromate at various concentrations of sulfuric acid with determining the amount of OM subjected to oxidative degradation on the remainder of the unreacted $\text{K}_2\text{Cr}_2\text{O}_7$. This approach suppose the extraction 4 pool of SOM by oxidizing ability: fraction 1 (12 N H_2SO_4) – the organic carbon content oxidizable by 0,167 mol L^{-1} $\text{K}_2\text{Cr}_2\text{O}_7$ with concentration 12 N H_2SO_4 ; fraction 2 (18 N – 12 N H_2SO_4) – the difference between the organic carbon content oxidizable by 18 N and 12 N H_2SO_4 ; fraction 3 (24 N – 18 N H_2SO_4) – the difference between the organic carbon content oxidizable by 24 N and 18 N H_2SO_4 and fraction 4 (TOC – 24 N H_2SO_4) – the difference between the total organic carbon (TOC) determined by dry combustion and organic carbon oxidizable by 24 NH_2SO_4 (the final is equivalent the carbon content determined by the original Walkley - Black method). The application of this method to assess the oxidizability of biochar requires modifications related to the physical properties of these samples. To determine the titration endpoint of the remainder potassium dichromate by Mohr salt was used the automatic potentiometric titrator ATP-2 with software Titrate-5. The potentiometric titrator provides the automatically performance (carrying out) a redox titration with a pair of electrodes (platinum- silver chloride) because visual titration in the presence of biochar samples is not possible.

RESULTS

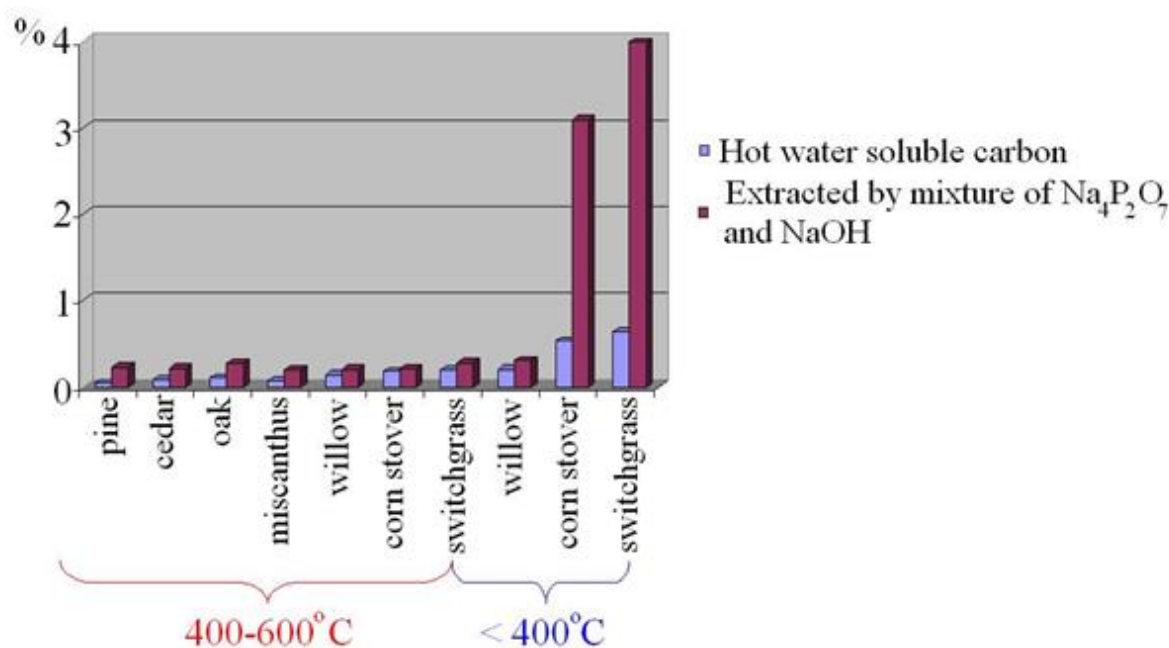


Figure 1: The carbon content in the OM fractions (% of total weight) extracted with hot water and mixture $\text{Na}_4\text{P}_2\text{O}_7$ -NaOH from biochar samples

Figure 1 presents results of the determination of carbon content extractable from biochar samples by the hot water and mixture $\text{Na}_4\text{P}_2\text{O}_7\text{-NaOH}$. The graph shows that the fraction content in the biochar samples extractable by hot water vary greatly. The maximum content of labile OM is typical for corn stover and switchgrass produced at low temperature of pyrolysis ($< 400^\circ\text{C}$). The low content of water-soluble fraction is observed in biochar samples produced by pyrolysis at temperatures $400\text{-}600^\circ\text{C}$. The same regularity observed for the alkali-soluble OM.

According to M. Korschens et al [17] the carbon extracted by hot water evaluated as an indicator of the readily degradable carbon content in the soil. According to the hot water extractable carbon content possible to draw a conclusion about the degree of availability of soils by the active OM. Consequently, the application to the soil the biochar of different biomass composition will affect on the content of the active pool SOM, as a result will cause to different effects on soil biota and plants.

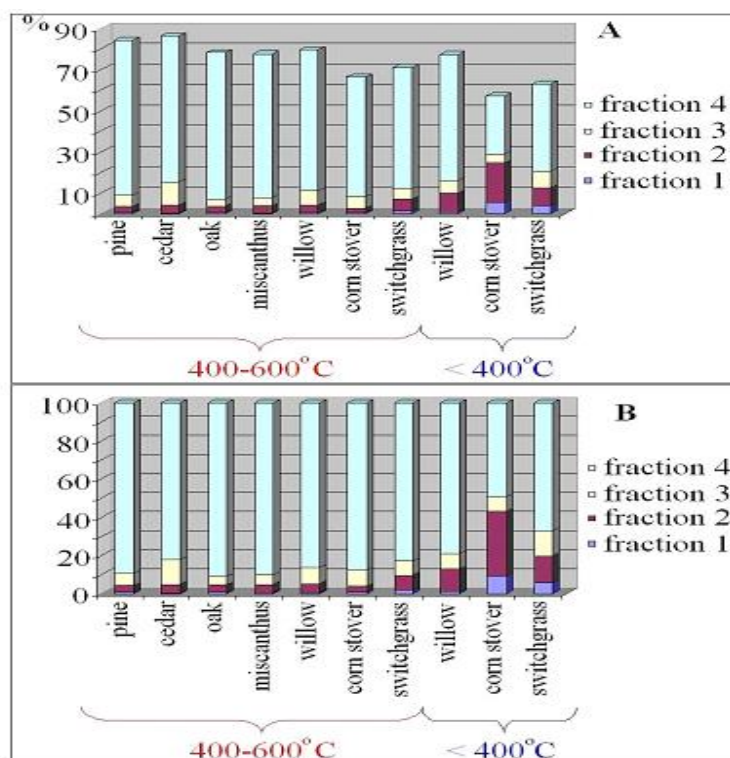


Figure 2: OM fraction content in biochar samples (A- in% by biochar weight, B – in % to the total carbon content), estimated by oxidizing ability according to Chan method (Chan et al., 2001)

Figure 2 shows the results of the carbon content determination of the pool of biochar OM the evaluated by the ability to oxidize according to Chan, calculated in % by biochar weight (Fig. 2A) and in % to the total carbon content (Fig.2B). The results presented in% of the total carbon content are more informative because biochar samples differ greatly in ash content.

The graphs show that the OM content the inert to oxidation with potash bichromate in the presence of $24\text{N H}_2\text{SO}_4$ (fraction 4 by Chan) in biochars obtained by pyrolysis in the temperature range $400\text{-}600^\circ\text{C}$ are uniform and vary from 82 to 90 % with variation coefficient only 4% (fig.2B). The inert OM content significantly lower in biochar samples obtained at low temperature pyrolysis ($< 400^\circ\text{C}$) from corn stover, switchgrass and willow. The application of the Chan method to assess the biochar properties shows that the high pyrolysis temperature of different plants biomass provides the production of the final product with approximately the same content of the inert OM.

The content of the more oxidizable OM (fraction 1 and 2 by Chan) in samples obtained by the pyrolysis at temperatures $<400^\circ\text{C}$ from corn stover, switchgrass and willow significantly higher than biochar obtained at

the temperature of pyrolysis 400-600°C. The content of fraction 1 and 2 in samples obtained at high temperature of pyrolysis vary widely. The results show a high dependence the content of active fractions of OM from the type of plant biomass and the pyrolysis temperature. This conclusion is agreement with the data obtained at the biochar estimation on the content of OM fractions extractable by hot water and mixture $\text{Na}_4\text{P}_2\text{O}_7\text{-NaOH}$. Table 2 presents the correlation matrix of the carbon fractions content subjected to various oxidation by Chan, the content of OM fractions extractable by hot water and mixture $\text{Na}_4\text{P}_2\text{O}_7\text{-NaOH}$.

Table 2: The correlation matrix of carbon content in the fractions (in % of total carbon) extracted by different methods from biochar*

		The OM fractions extracted by oxidizing ability according to Chan				Hot water-extractable carbon	Extracted by mixture of $\text{Na}_4\text{P}_2\text{O}_7\text{-NaOH}$
		Fraction 1	Fraction 2	Fraction 3	Fraction 4		
The OM fractions extracted by oxidizing ability according to Chan	Fraction 1	1,00	0,95 (p=0,00)	0,19 (p=0,59)	-0,96 (p=0,00)	0,92 (p=0,00)	0,92 (p=0,00)
	Fraction 2		1,00	0,11 (p=0,76)	-0,97 (p=0,00)	0,81 (p=0,01)	0,78 (p=0,01)
	Fraction 3			1,00	-0,35 (p=0,33)	0,43 (p=0,79)	0,42 (p=0,77)
	Fraction 4				1,00	-0,89 (p=0,00)	-0,87 (p=0,00)
Hot water- extractable carbon						1,00	0,98 (p=0,00)
Extracted mixture of $\text{Na}_4\text{P}_2\text{O}_7\text{-NaOH}$							1,00

* Highlighted in red are statistically significant Pearson correlation coefficients (at a significance level $p < 0,05$).

Commending correlation relations may be noted that there is a statistically significant correlation between the content of organic carbon extracted with hot water and mixture of $\text{Na}_4\text{P}_2\text{O}_7\text{-NaOH}$. As well observed a close statistically significant correlation between the content of the fractions 1 and 2.

DISCUSSION

Figure 3 shows one of classifications of SOM according to E. Strosser [11]. The scheme presents that only a small portion of the total SOM refers to an inert substance (under which understand insoluble after the acid and alkali treatment, the non-hydrolysable residue – humin) [18]. The main part of the SOM refers to the labile SOM (providing the cycle of soil carbon for one or more years) and the humic acids (disintegration time which may be from several tens to hundreds of years).

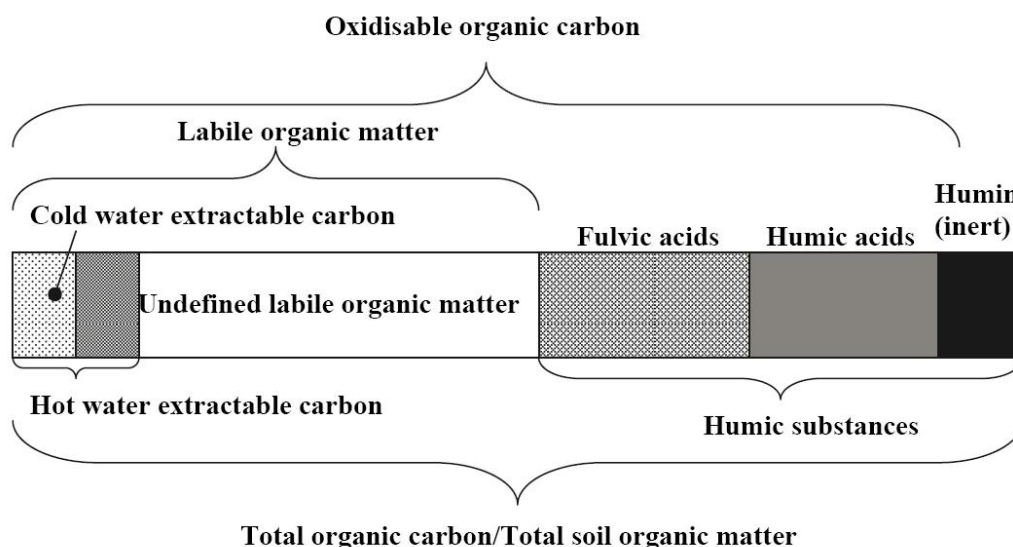


Figure 3: Fractionation of soil organic matter by classical methods (Strosser, 2010)

In this article becomes necessary to define with concepts the oxidation (decomposition) stable SOM and the inert SOM. Under an inert (black) carbon usually understood the charred plant residues (charcoal) and shoot-graphite which can accumulate in the upper soil horizons and the stability of which is estimated at hundreds or even thousands of years [8]. To assess the black carbon content in soils used different techniques which are represented as variants of hard thermal, chemical oxidation and hydrolysis [19, 20] reflecting the different parts of the substances continuum attributable to a pool of inert SOM. In the paper P.Rovira and V.Ramon [21] for assess the coal content as part of the inert (black) OM carried out the treatment of soil with concentrated HNO_3 at $t = 105^\circ\text{C}$, followed by determination of the residual carbon by dry combustion. But even such a hard approach according to (by) authors gives only an approximate characteristic the coal content in the soil. In that view same authors in the upper humus horizons of Mediterranean forest soils the charcoal content does not exceed 5% and shoot-graphite 2% of the total organic carbon content.

Under the stable SOM to oxidation usually understand a part of the SOM which is not oxidized when treatment concentrated solutions of oxidizers H_2O_2 , $\text{Na}_2\text{S}_2\text{O}_8$, NaOCl et al. [22-26]. Considered that treatment with H_2O_2 and similar reagents can be regarded as an imitation of the biochemical degradation of OM, which to a large extent is the oxidation process [27]. The resistance to oxidation due to different reasons. There are works that related (explain) the stability of this OM pool with its chemistry [28] and interaction with soil mineral surfaces and sesquioxides [24, 28-30]. There is also the view, that the significant part of sustainable OM may be intercalated in the inter-packet space of clay minerals [31, 32].

According to E.E. Schulte, B. Hoskins [33] the methods of wet combustion as distinct from dry combustion do not involve the carbon of the coal and graphite. In fact, the method of Wilkie-Blake includes the oxidation only active part of OM: 60-80% of the total carbon in various soils [12] the average completeness of combustion is taken as 75% [34]. Only a very small part of the difference between the total organic carbon content determined by dry combustion and carbon determined by Walkley-Black method in soils can be attributed to the inert pyrogenic (or black) carbon. Correspondingly (accordingly) the fraction 4 was determined by the Chan method a combination of the coal and soot will include a significant part of OM the unavailable to dichromate oxidation in mineral soil horizons.

In other words the SOM resistant to wet ashing (combustion) is not always characterized by chemical inertness. How this conclusion can be rightly considered for biochar subjected deep pyrolysis process, in which there are no mineral surfaces providing the stabilization of OM - apparently remains open. However, with a high degree of confidence we can assume that the fraction 4 was estimated by Chan will present the inert biochar material and the carbon which can persist in the soil for a long time without substantial transformation. The remaining components of the pool of biochar OM should be considered as part of the OM which can improve the availability of soils by active OM, but can not provide the sequestration of atmosphere carbon for a long period.

CONCLUSION

The Chan method developed to evaluate the oxidizability SOM can be modified and adapted to assess the oxidizability of biochar OM. The separation of biochar OM pool into 4 fractions: more oxidizable (fraction 1 and 2) and passive pool (fraction 3 and 4) may be informative since it allows to estimate the amount of active and inert OM introduced into the soil with biochar obtained from various vegetable origin in various pyrolysis conditions. The use of Chan method may be particularly promising for determining the biochar place in the total pool of SOM and prediction of their behavior in the soil.

The content of organic carbon extracted from biochar with hot water and mixture $\text{Na}_4\text{P}_2\text{O}_7\text{-NaOH}$ strongly correlated with the content of OM fractions determined by the Chan method. Therefore these methods can be used to quickly examination the properties of biochar different origin.

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