Morphological investigation and physical characterization of ancient fragments of pyrogenic carbon

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Abstract. In the latest years, the attention toward the use of pyrogenic carbon as a climate mitigation strategy has increasingly grown. Biochar (BC) contains substantial amount (60-90%) of pyrogenic carbon, which is a recalcitrant material and it is hardly decomposed by biotic and abiotic oxidation. The carbon mitigation potential of biochar is associated to the fact that carbon is not easily released back into the atmosphere, even after very long incubation time in the soil. Several studies have been addressing the understanding of the fate of pyrogenic carbon in the soil in a quantitative way, but only a few actually considered materials that were produced in the past and they were not fully able to estimate the fraction of carbon that was oxidized on centennial time scales. In this paper, an old deposits of biochar in soils of the Eastern Alps (Trentino, Val di Pejo) was dated at 1859 by means of a dendroanthracological approach. Carbon decomposition in those soils was then investigated to calculate the fraction of carbon that was lost over 155 years. Part of this study is focused on the morphological and physical characterization of several fragments of biochar, using a scanning electron microscope (SEM). Such study enabled the identification of specific morphological features of tracheids in the old biochar, which were tentatively associated to a differential oxidation of the structures that were created during carbonization from lignin and cellulose.

1. Introduction

In the last decades, the growing concern for global climate changes multiplied the efforts of the scientific community to understand the impact of those changes on flora, fauna and the humans and to identify potential adaptation and mitigation strategies. The cause of the global mean temperature rise and of the related augmented climate variability is attributed to the increasing anthropogenic Green House Gases (GHGs) presence in atmosphere. As reported by the Intergovernmental Panel on Climate Change in 2007 [1], the main effects of continued GHG emissions are: rising sea levels; damage to many global ecosystems; increase of droughts and heavy precipitation events; rising acid levels in the oceans. Biochar based strategies, which consider the application of large amounts of charred material to agricultural soils have been identified among those methods able to mitigate climate changes and in a recent study Woolf et al. (2010) [2] quantified the theoretical carbon sequestration potential of biochar following its incorporation into agricultural soils as large as 1.8 Gt C per year.

Currently, a wide range of disciplines are involved in understanding the potential feedbacks of these strategies to improve biochar characterization, and to understand its properties as soil amendment in laboratory and field experiments [3, 4]. Biochar is produced by the thermo-chemical conversion of biomass under the conditions of low temperature (500°C ÷ 600°C) and little amount of oxygen (pyrolysis process). Different kinds of feedstocks can be used to produce biochar (agricultural residues, biomass crops and agroforestry products) in an ideal ecological-agro-climate cycle increasing soil fertility, sequestering organic carbon and producing energy via the pyrolysis exothermic reaction [5, 6]. Little information exists about the recalcitrance of biochar, and most of investigations were made on relatively young biochars (no more than 3 years old). Starting from the recent identification of a biochar kiln platform in Trentino, Val di Pejo (Eastern Alps in north of Italy) dated 1859 it was possible to extract ancient biochar and soil samples, and to perform an exhaustive characterization of the recalcitrance of an ancient and exactly dated biochar.

Our study aims at the physical and morphological characterization of biochar. In particular, we have compared the old biochar with the modern one, studying their density and morphological structure trying to understand if the biochar is really recalcitrant in soil on a long time scale.

2. Materials and methods

Samples of old biochar were taken in Val Pejo (Trentino, Eastern Alps, North Italy). They have been dated 1859 and their feedstock was coniferous larch wood. Using the same feedstock, a modern biochar was produced through a thermo-chemical process, which resembles the one that formed the old biochar: approximately 600°C in oxygen free atmosphere [7]. Before any investigation, both old and modern biochar underwent a thermal treatment for 48h at the temperature of about 80°C. The dry samples were cut in order to have a homogenous shape and each sample was weighed. The density data were collected analyzing 30 samples for each kind of biochar. This carbon based material has a high porosity, as analyzed by a penetrometer instrument under low pressure at about 10^{+4} Pa.

Morphology investigations were performed by scanning electron microscope (SEM) technique. We used XL 20 FEI SEM, with CRYO-GATAN ALTO 2100 technology. The measurements were performed on the samples dried under vacuum, following the common procedure. To study the inflation of the pores of old and modern biochar, the modern biochar was oxidized to simulate aging. We produced two samples using a H_2O_2 thermal bath at temperature of 30°C for 72h and at 75°C for 120h. The banding deformation of the pores was verified by SEM analysis. Several images were collected for each sample, in order to have accurate information concerning different areas on the internal surface of the biochar.

3. Results and discussion

SEM analysis revealed that biochar samples were the result of thermo-chemical transformation of larch wood. This conclusion is supported by a microstructure of paired lenticels[1] that is universally considered a typical discriminant for the identification of the wood of this conifer species [8]. In figure 1, we show the SEM image of a cross-section of old biochar, where the lenticels appear in pairs.

After drying, old and modern biochar were weighed and density data were collected by analyzing 30 samples for each old and modern biochar. This carbon based material is characterized as highly porous, as analyzed by penetrometer instrument under low pressure at about 10^{+4} Pa. We collected data of both the volume of carbon and the empty pore space volume. The averaged density of the old biochar $\langle \rho_{old-BC} \rangle$ is about twice the density of the

[1] A porous tissue consisting of cells with large intercellular spaces in the periderm of the secondarily thickened organs.

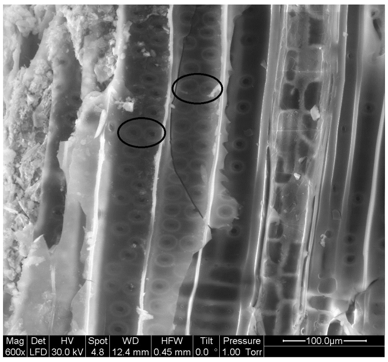


Figure 1. SEM image of transverse section of old biochar. The lenticels inside the pores appear coupled, as highlighted in the black circles.

modern biochar $\langle \rho_{mod-BC} \rangle$:

$$\langle \rho_{old-BC} \rangle = 0.42 \pm 0.08 \text{ gr/cm}^3,$$
$$\langle \rho_{mod-BC} \rangle = 0.24 \pm 0.03 \text{ gr/cm}^3.$$

We have considered the ratio (RT) between the pores thickness and the internal radius. We calculated that the average ratio for old biochar is almost twice that of the modern biochar:

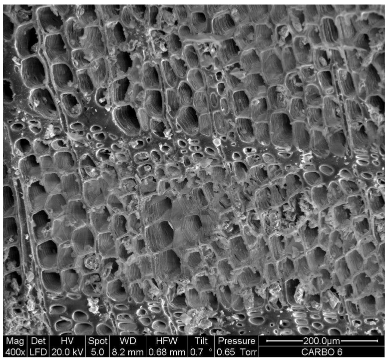
$$RT_{old-BC} = 0.36 \pm 0.01,$$
$$RT_{mod-BC} = 0.21 \pm 0.01.$$

These results seem very peculiar because both biochars come from the same feedstock and the modern biochar has been produced trying to replicate as closely as possible the chemical process and the thermo-chemical conditions undergone by the old biochar. To study the different density between old and modern biochar a SEM investigation was performed. In figure 2, SEM images for both biochars are shown. The different porosities we measured could signify, in fact, that in old biochar the pores have thicker walls than the pores in modern biochar. These results have been achieved analyzing the SEM images in 4 different areas of each biochar sample. On these images, that were collected for 30 old and modern biochar samples, a statistical analysis has been performed. The pores appear thicker in old biochar and this is coherent to the observation of an increased density.

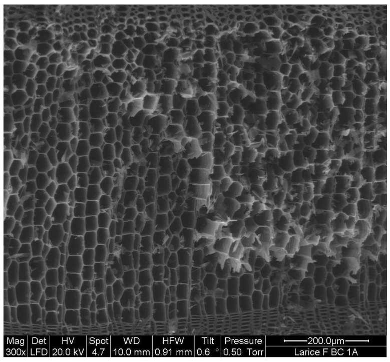
Biochar is composed of carbon aromatic rings, and Kinoshita et al. found that aromatic molecules, when oxidized, are modified due to bending of the plane structure [9]. Indeed, the oxidation of aromatic rings often translates into increased molar mass (m.m.), as for benzene (C_6H_6 m.m. = 78.11 gr/mol) oxidized to 1,2-dihydroxybenzene ($C_6H_6(OH)_2$, m.m. = 110,1 gr/mol). Is the observed inflation effect associated to oxidation of the old biochar in soil over long time scales?

In order to verify our hypothesis concerning the oxidation mechanism in old biochar, an oxidation process in modern biochar has been done. Before performing the chemical oxidation process, SEM investigation was repeated on modern larch biochar; afterwards, modern larch biochar samples were treated by H_2O_2 bath at room temperature for 72h and were then analyzed by SEM, as shown in figure 3 a) and b).

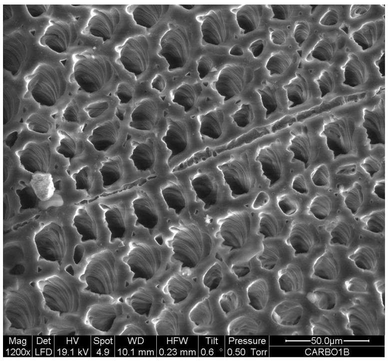
Comparing the results of the modern biochar with and without oxidation, we observe no significant difference. We presumed that the oxidation process, in terms of residence time and temperature, was not sufficiently strong in order to obtain the effects observed in the old biochar pores. To stress the oxidation process, we increased the temperature to 75°C and the residence



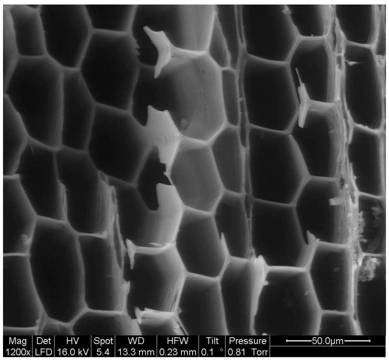
a) Old biochar comes from larch coniferous tree.



b) Modern biochar comes from larch coniferous tree



c) Old biochar comes from larch coniferous tree, on a finer scale.



d) Modern biochar comes from larch coniferous tree, on a finer scale.

Figure 2. Comparison between old (left) and modern (right) biochar by SEM technique. The pores in old biochar appear thicker than in modern biochar.

time in the thermal bath to 120 h. In figure 3 c) and d), the results relative to the SEM images are reported. Also in this case, we did not observe any significant difference in the modern biochar treated by H_2O_2.

Further investigations are forthcoming to understand the density variation between old and modern biochar and the recalcitrance of pyrogenic carbon for a long period in soil.

4. Conclusions

As a result of this analysis we can conclude that biochar stored in soil over long time scales changes its morphology. The study of the density highlights that old biochar density is almost the double of the modern biochar one. This result is confirmed by SEM analysis, where we have observed a thickening of pores inside the old biochar. Our first hypothesis assumed that the probable cause was an oxidation effect, but this is not confirmed by our experiments. Therefore, the inflation of pores is under investigation by X-ray diffraction. For instance, another hypothesis could be the presence of inorganic salts absorbed from the soil.

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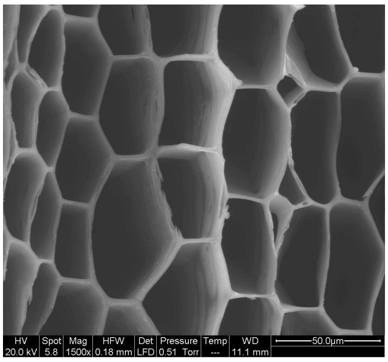
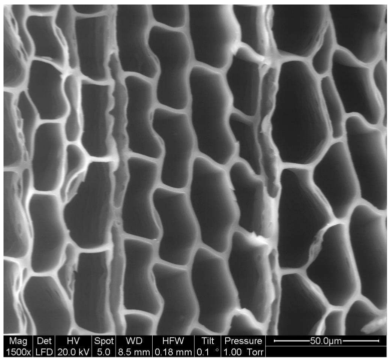
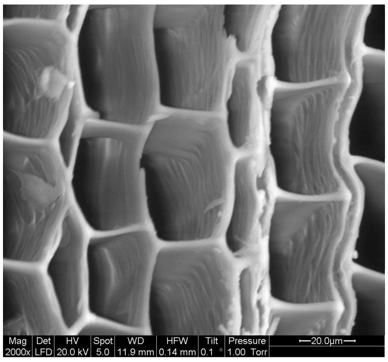


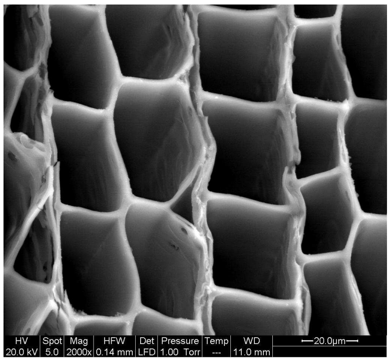
a) Modern biochar without H_2O_2 treatment.



b) Modern biochar with H_2O_2 treatment for 72 h.



c) Modern biochar without H_2O_2 treatment, on a finer scale.



d) Modern biochar with H_2O_2 treatment for 120 h, on a finer scale.

Figure 3. a) and b) images show the modern biochar, without and with H_2O_2 treatment (35% - 130 Vol.) at 30°C for 72 h, respectively; c) and d) images show the modern biochar without and with thermal bath of H_2O_2 at about 75°C for 120 h, respectively.

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