ESF – MOLTER Exchange visit Grant Final Report

Alice Budai exchange from Bioforsk (Ås, Norway) to the University of Zurich (Switzerland) between 01.11.2012 and 15.12.2012

Title

Biochar characterization in relation to its stability in soil

Purpose of the visit

The aim of my exchange visit to the University of Zurich was to work in collaboration with Dr. Samuel Abiven who is a collaborator in the biochar 3S project and who is also a co-supervisor of my PhD work. Through the resources available in his lab at the Department of Geography, I was able to analyze samples using a method that is well known in the soil science field. The resources included not only instrumentation but also expertise since significant improvements were recently made by a PhD student dedicated to the development of the method (Wiedemeier et al in prep, also Schneider et al 2010 and Schneider et al 2011). This method, named BPCA (benzene poly-carboxylic acid) method, allows comparative quantification of a molecular marker of pyrogenic carbon. Quantification of the amount and type of molecular markers present gives insight into the chemical structure of the material, namely the degree of condensation of the aromatic rings in the material. The information obtained, as part of the goals of the PhD and encompassing project, helps to characterize the biochar samples included in this study and it sheds light on the relationship between chemical composition of a material and its resistance to microbial breakdown in soil. Finally, performing BPCA analysis on this particular set of samples allows for comparison of the method with other characterization techniques.

Background

Anthropogenic activities have led to an increase in the amount of CO_2 in the earth's atmosphere over the last two centuries and currently only 50% of anthropogenic emissions are naturally sequestered by land and ocean. In order to mitigate global warming, technologies that reduce the amount of CO_2 entering the atmosphere are being explored. Sequestration of carbon in soil holds promise, particularly because agricultural soils, which are often depleted of their carbon content, are said to have the technical potential to sequester 1,2 to 3,1 Gt of C per year through altered management practices (Lal 2010). Increasing the carbon content of agricultural soil would not only aid in the mitigation of climate change, it is also a way to manage soil fertility.

Adding fresh biomass to soil will only slowly increase soil carbon stocks because much of the biomass is quickly converted to CO_2 during decomposition. Often the rate of loss of soil carbon is higher than the rate of increase in soil carbon from biomass inputs. A material obtained from pyrolyzing biomass named biochar has gained much attention because its turnover in soil is estimated on a millennial timescale

(Preston and Schmidt, 2006). However, estimation of turnover rates vary and an important question that remains to be answered is "how recalcitrant is biochar". One difficulty in answering this question stems from the large differences between biochars and that their stability result from the chosen feedstock and pyrolysis method used to produce them (Brewer et al. 2011). Therefore, biochars are not equal and a method for routine characterization of biochars will need to be identified before biochar addition to soil can be applied as a technology for carbon sequestration purposes. Biochar chemical structure is an appropriate candidate for the basis of such characterization, and BPCA (Schmidt et al., 2001) serves as one of two more thorough methods (nuclear magnetic resonance being the other one) for comparison of other more readily applied methods (such as near infrared spectrometry or thermogravimetry) in this project.

In addition to using different methods to characterize biochars based on their chemical structure (and surface, chemical, and thermal properties), their resistance to microbial breakdown is evaluated using soil incubation studies. The incubation experiment is monitored for one year and the results are expected to provide a base for estimating long-term stability. Finally, the importance of structure in inhibiting biomass decomposition is recently challenged (Schmidt et al 2011) and therefore studying the link between biochar chemical structure and its resistance to microbial breakdown in soil is expected to contribute greatly to current understanding of carbon stabilization in soil.

Description of the work carried out during the visit

Specifics of the work carried out include sample preparation (grinding) and sample analysis under supervision of Samuel Abiven and help from PhD student Daniel Wiedemeier who recently made improvements to the method. Extracting the molecular marker BPCA from biochar includes placing the samples into pressure chambers with acid which are then heated for 8 hours. After this digestion, a series of filtrations followed. The entire process took one week for six samples. Because the analyses were going smoothly, an additional 5 samples were selected for analysis by BPCA (a total of 20 biochar and feedstock samples were prepared). Analysis of the resulting BPCA mixture in liquid was performed using Ultra High Pressure Liquid Chromatography.

In addition to sample preparation and analysis, results were discussed with both Samuel Abiven and Daniel Wiedemeier. I was also able to participate in group meetings and attend department presentations. I presented my PhD project and work to the department on November 19th under the title "Searching for the Face of Stability in Biochar – an incubation and characterization study of biochars produced between 250 and 800^{o}C", as shown on the department website for 2012:

http://www.geo.uzh.ch/en/units/physical-geography-soilbio/events/soil-science-zvieri

Description of the main results obtained

The amount of carbon detected as BPCA marker (including B3CA, B4CA, B5CA and B6CA) is related to the amount of fixed carbon (also total carbon) contained in the biochar and feedstock samples. The relationship is linear and independent of feedstock (CC = corn cob, MS = miscanthus) (figure 1).

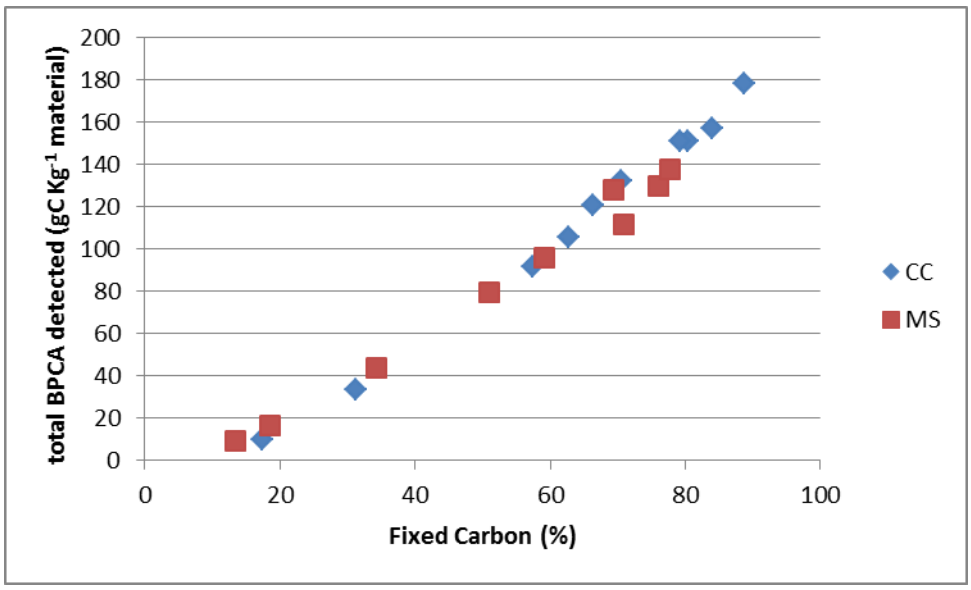

Figure 1: Relationship between percent fixed carbon estimated using proximate analysis and amount of carbon detected as BPCA per unit material (char and feedstock)

This initial result shows that the BPCA method gives clear results (samples were analyzed in triplicates, though only average values are shown here).

The amount of carbon detected as BPCA markers is related to temperature during pyrolysis, but this relationship is not linear (figure 2)

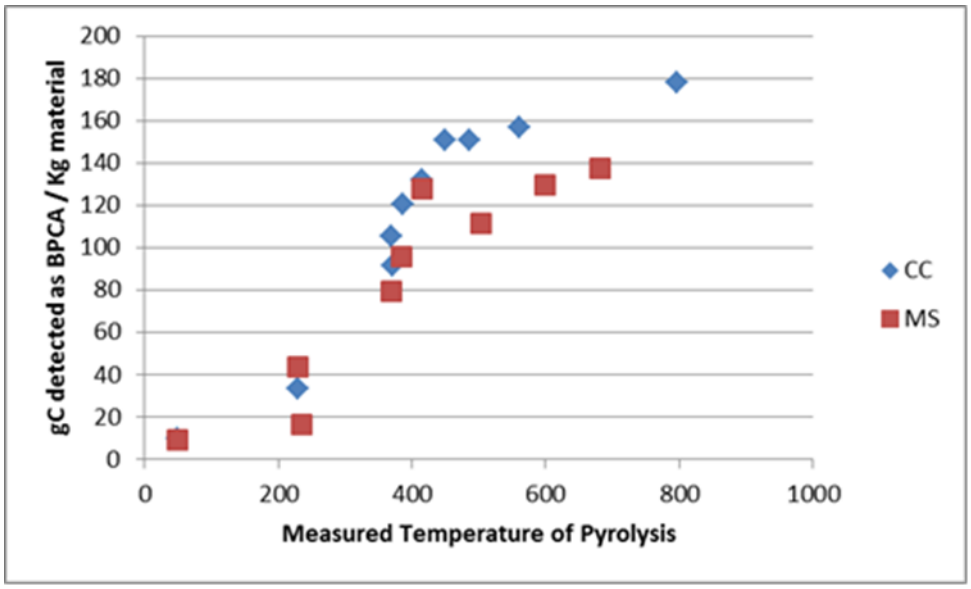

Figure 2: Relationship between average temperature experienced by the sample during pyrolysis and grams carbon detected as BPCA per unit material (char and feedstock)

The non-linear relationship between production parameters (temperature) and biochar properties (BPCAs detected) is an indication of the complexity of the pyrolysis process.

Results from the individual markers are as follows:

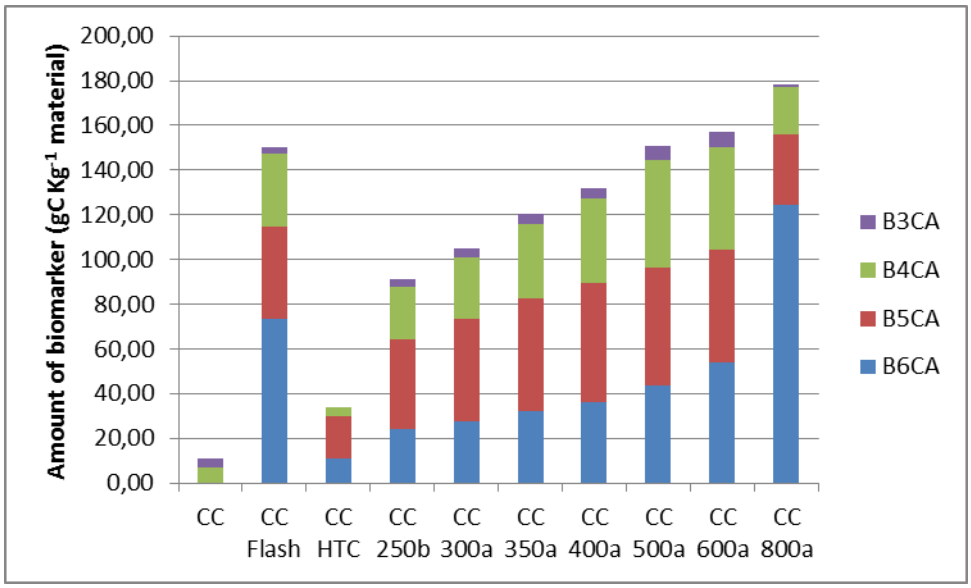

Figure 3: Proportions of the molecular markers B3CA, B4CA, B5CA, and B6CA detected in corn cob the biochars produced from corn cob.

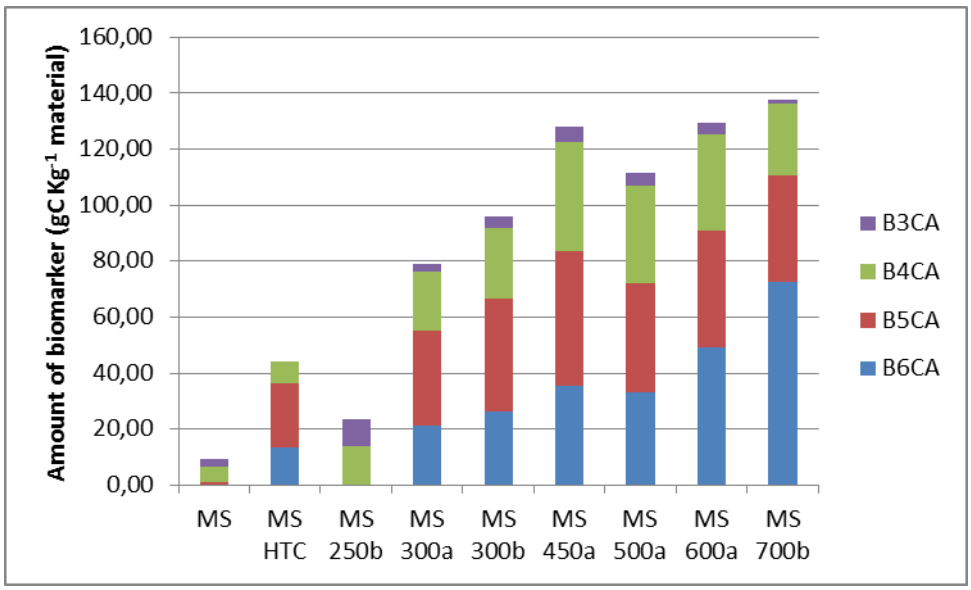

Figure 4: Proportions of the molecular markers B3CA, B4CA, B5CA, and B6CA detected in miscanthus the biochars produced from miscanthus.

Relationships between the individual markers and production conditions (temperature) as well as other properties analyzed in the samples using other methods will be explored further. These results, in light of stability estimations from an incubation experiment, are expected to give insight to the structure and the formation of carbon compounds resistant to microbial degradation in soil.

Future collaborations with host institution

Further analysis within the same project is planned for soil-biochar mixtures to compare the amount of BPCA remaining in the mixtures after incubation for 1 year as compared to before incubation. This work may be carried out in May. Small amounts of biochar were also left with Samuel Abiven for planned analysis using DRIFT (diffuse reflectance infrared fourier transform) Spectroscopy.

Project publications to result from the grant

Results from the BPCA method will be combined with results from other methods such as ^{13}C NMR (nuclear magnetic resonance) for publication in an international peer-reviewed journal. The article will be compiled later this year 2013.

References

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