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Aufbau eines Standardmess-verfahrens zum Nachweis des Sequestrierungspotenzials von Biokohlen durch $^{13}CO_2$-Emission

Set-up of a new method to determine the sequestration potential of biochar products by means of $^{13}CO_2$ emission

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Introduction

Biochar is considered an amendment to improve soil quality, and recently to increase the carbon sequestration potential (SP) of soils. In due time, biochar may be subjected to product certification similar to other soil amendments. This requires an efficient method to test the degradation (v.v. the SP) of various biochar products under standard conditions. As of yet, the life time has not been determined that shall specify and merit certification of a biochar product.

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Hence, it seems appropriate to have a method at hand, which allows a continuous monitoring of the process of biochar degradation.

We present a method to determine biochar degradation - as per expectation a rather slow process compared to general soil respiration - by means of respired $^{13}CO_2$ emission (Vargas et al., 2011) from high labeled biochar products. The method is based on an automated system, in which a wavelength-scanned cavity ring down spectroscope (WS-CRDS) is coupled to a series of open-dynamic chambers (ODC) via a set of valves controlled by a microprocessor. Berryman et al. (2011) have described the general use of CRDS in $^{13}CO_2$ soil respiration research. However, their set up is based on a sample manifold to analyze single batch samples. In our set up the $^{13}CO_2$ emission from individual incubations of biochar in soil can be measured in minutes, consecutive in a large number of ODCs. This allows (1) replicates to comply with standards of statistic, (2) repeated measurements of the same sample over months, and (3) the results of continuous $^{13}CO_2$ emission be turned into an equation characterizing the biochar degradation.

Set up of the new method

The WS-CRDS is the key component facilitating the fast detection of $^{13}CO_2$ from the headspace of ODC containing the biochar/soil samples. Midwood and Millard (2011) have recently shown the general applicability of WS-CRDS for ODC set up. The WS-CRDS technique uses a high frequency of distinct tunable laser beams, which recirculate many times through a sample within a measurement cell to interact with a sufficient number of ^{13}C in CO_2. Interaction of the laser light with ^{13}C results in a decline of laser intensity and as

a result in ring down time at the detector, which in comparison to an evacuated cell is proportional to the amount of ^{13}C in CO_2 (http://www.picarro.com/isotope_analyzers/co2_ambient; Wahl et al. 2006)). Intercomparison with the current standard instrument, i.e., an isotope ratio mass spectrometer (at the Helmholtz Zentrum München) showed a high accuracy of $^{13}CO_2$ quantification (3-point calibration: 2, 11, and 22 ppm, R^2 = 0.99) of the WS-CRDS (model G1101-I, Picarro, Sunnyvale, CA, USA), similar to results presented by others (Wahl et al. 2006; Berryman et al. 2011).

A continuous flushing with an external pump maintains steady state conditions of the headspace in 24 ODCs (1-L laboratory glass bottles) and the connecting tubing to 24 valves. A microprocessor plus four additional valves provide flushing of 23 ODCs, while one ODC is connected through to the WS-CRDS.

Terra-preta-similar biochar (Tp) and biochar (BC) application (12 ODC each) were mixed with 200 g and 300 g of soil, respectively. Applications of Tp and BC contained 1% wt/wt in luvisol and amounts equal to 50% relative to carbon contents in LUFA soil, respectively.

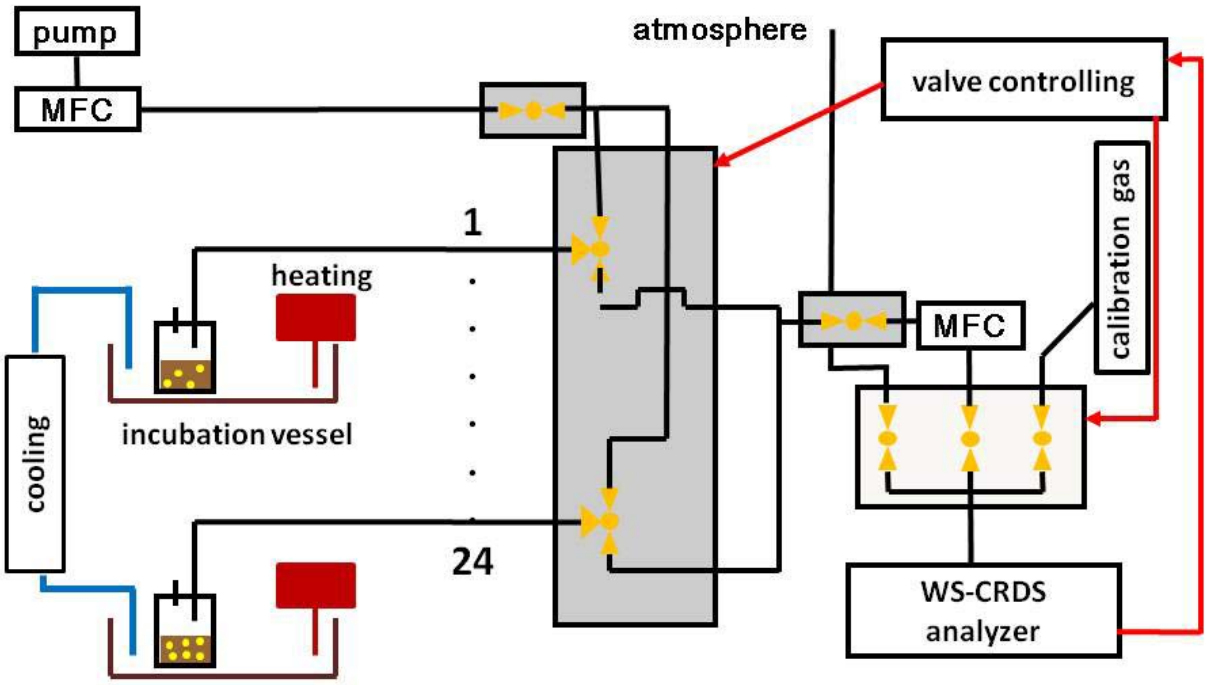

Fig. 1: Diagram of the automated system to measure $^{13}CO_2$ emission from biochar application in soil. From left to right: The incubation of 24 ODC (incubation vessel) in temperature adjusted water bath. ODCs flushed via a mass flow controller (MFC) and an external pump. The (grey) valve islands connect the ODCs to the flushing or the WS-CRDS. Further connections allow calibration and check by standard gas and ambient air, respectively.

Each sample is measured against a reference containing LUFA standard soil only, thus allowing for the correction of background ^{13}C from both the soil and the ambient air passing the ODC. Soil moisture is kept constant at 40% of water holding capacity. Biochar educts are either derived from C4 plant species or from plant material grown under $^{13}CO_2$-enriched conditions.

First experiments

(1) Degradation of Terra-preta-similar biochar (Tp).

Four types of Terra-preta-similar biochar were prepared. They contained similar amounts of biochar from *Miscanthus spp.* (C4), but various amounts of fermented plant material including either silage of corn (C4) or woody chips of *Miscanthus spp*. (Tab. 1.). Over the course of four weeks, the $^{13}CO_2$ efflux from the two preparations containing corn silage were several times higher than those from the samples containing woody chips of *Miscanthus spp. (Fig. 2).*

Tab.1. Composition of Terra-preta-similar applications.

Vol%	Silage corn	Biogas digestate	Biochar (Misc.)	wood chips (Misc.)
◇**	65	20	15	0
×	45	40	15	0
Δ	0	20	15	65
○	0	40	15	45

**Symbols referring to Fig. 2.

Basically, the experiment demonstrated the segregation between carbon sources that are easy degradable (corn silage) and those that either require a longer exposure to or a special population of micro-organisms.

2) Degradation of biochar carbon

Biochar from (a) pyrolysis, (b) hydro-thermal cabonization (HTC), and (c) the educt *Miscanthus spp.* were incubated with one of four LUFA standard soils
(LUFA 2.1, 2.2., 2.3, and 2.4).

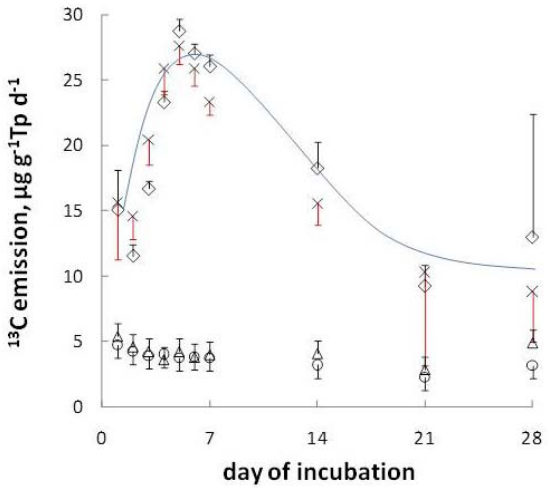

Fig. 2: Degradation of Terra-preta-similar products. Data represent mean + or - 1SD of four samples. Symbols referring to the different composition of applications according Tab. 1.

Essentially, the experiment showed continuous $^{13}CO_2$ efflux from the application containing *Miscanthus spp.* educt but also from the HTC biochar over the course of five weeks. In contrast, the results with pyrolysis biochar showed almost no release of $^{13}CO_2$ but rather a tendency to CO_2 deposition. Deposition of CO_2 was also observed with crunched Calsitherm, i.e., insulation boards mainly consisting of Ca-silicate (data not shown). The CO_2-absorbing properties of this mineral compound are known (Bye and Chigbo, 1977).

With respect to carbon sequestration, the results suggest that biochar from pyrolysis has potential to function at least as a midterm carbon storage, whereas the HTC biochar applied in the experiment did not provide evidence for meeting the requirements of a reasonable storage product.

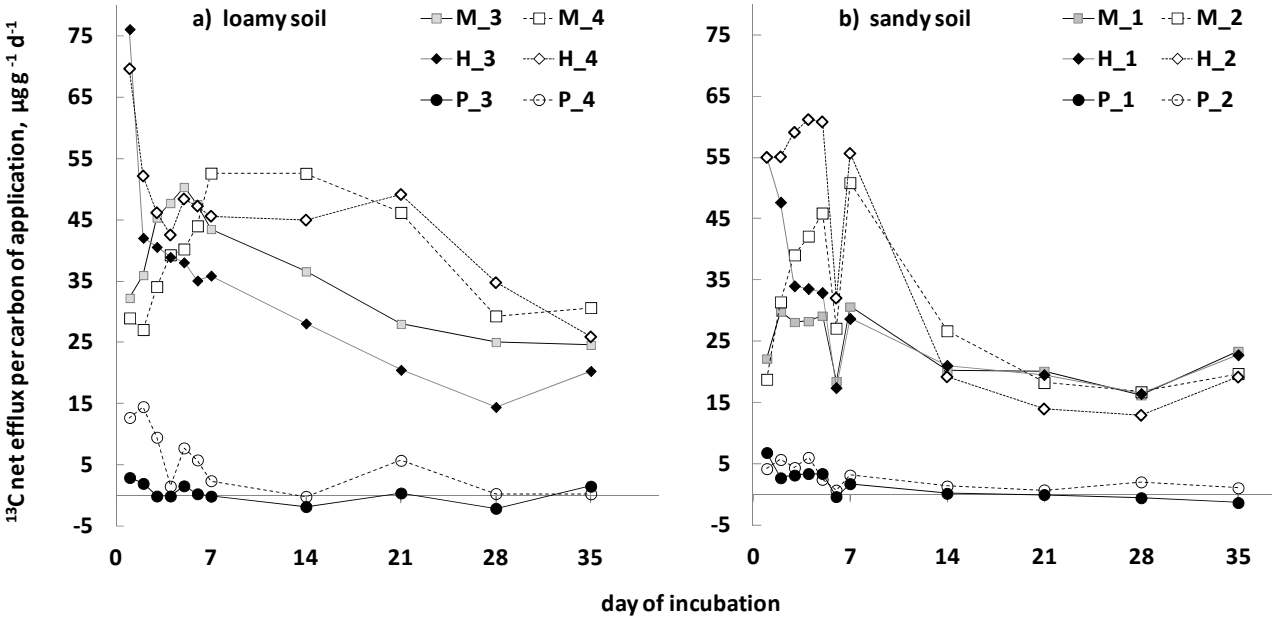

Fig. 3: Degradation of biochar products in four LUFA soils: a) in loamy soils: 3=LUFA3, 4=LUFA4; b) in sandy soils: 3=LUFA1, 4=LUFA2. H=HTC biochar, P=pyrolysis biochar, M=Miscanthus educt.

Conclusions

We developed a method to screen the degradation of biochar including a large number of samples under standardized conditions. The method can facilitate to determine the half-life of diverse biochar products in soil provided a labeling of educts is possible, e.g., through use of biomass from C4 plants or of plants grown in ^{13}C-enriched atmosphere. The measurement set up can be adapted to sample from multiple soil-borne enclosures to examine biodegradation in-situ.

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