



Molecular characterization of the thermally labile fraction of biochar by hydropyrolysis and pyrolysis-GC/MS



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ABSTRACT

Agroenvironmental benefits and limitations of biochar in soil applications require a full understanding of the stability and fate of the various carbon fractions. Analytical hydropyrolysis (HyPy) enables the determination of the stable black carbon (BC_{HyPy}) and thermally labile (semi-labile; non-BC_{HyPy}) fractions in biochar and soil samples. The non-BC_{HyPy} fraction can be analysed at a molecular level by gas chromatography-mass spectrometry (GC-MS). In the present study, HyPy was applied to the characterisation of biochars produced from pine wood, beech wood and corn digestate with the same pyrolysis unit at low (340–400 °C) and high (600 °C) temperatures. Results were compared with those from Py-GC-MS. HyPy provided consistent information concerning the thermal stability of biochar samples, with BC_{HyPy} levels related with the relative abundance of the charred fraction estimated by Py-GC-MS and the hydrogen/carbon (H/C) ratios. The non-BC_{HyPy} fractions were featured by the presence of polycyclic aromatic hydrocarbons (PAHs) from two to seven rings, including alkylated derivatives up to C₄. Partially hydrogenated PAHs were also detected. The yields of non-BC_{HyPy} were higher for those biochars produced at lower temperatures and always more abundant than the levels of solvent-extractable PAHs. The methylated/parent PAH ratios from HyPy and Py-GC-MS exhibited lower values for the most charred biochar. The observed differences in the abundance of the stable fraction and the molecular chemistry of the semi-labile fraction can be usefully utilised to drive the process conditions to the desired properties of the resulting biochars and to predict the impact of biochar amendment to soil organic pools. The concentrations of priority PAHs in the semi-labile fraction was evaluated in the mg g⁻¹ level suggesting that it could be an important fraction of the polyaromatic carbon pool in soil.

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1. Introduction

Biochar is the carbonaceous solid formed by the pyrolysis of biomass which attracts research interest due to its potential value for long-term carbon sequestration. The addition of biochar to soil has been proposed as a strategy that not only sequesters carbon in soils but also mitigates different environmental issues. Research has demonstrated that biochar has considerable potential as a sustainable tool for carbon sequestration, soil amelioration, greenhouse gas emissions reduction and fertilizer runoff reduction, as well as waste management [1].

A key requirement for the use of biochar as tool for agroenvironmental management is that the carbon in the biochar is stable, meaning that a substantial fraction of the carbon sequestered is not re-mineralized on at least centennial timescales [2,3]. However, a variable component of the carbon in many biochars is degradable on annual to decadal timescales and hence, only a proportion of total carbon in biochar provides long-term carbon sequestration [4–6]. In fact, an increasing number of studies suggest that biochars in the environment are subject to biological, physical and chemical action, and that their chemical constitutions progressively change [7,8]. Moreover, the labile fraction, which evolves in the short-term during its storage in soil, can influence the soil microbial community structure [9], and therefore affect the functioning of the soil [10]. Biochar application on land may impact the carbon cycle in the ocean due to the mobility of the water soluble labile fraction

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[11,12]. The knowledge of recalcitrance of carbon in biochar and the potential contamination from labile components are crucial issues for evaluating the agro environmental impact of biochar.

A number of approaches have been proposed to assess stability and the carbon sequestering potential of different biochars, including solid state nuclear magnetic resonance spectroscopy (solid state ^{13}C NMR) [13,14], thermal analysis (thermogravimetry, TG) [15,16], molecular markers by means of pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) [17,18], benzene polycarboxylic acid method [19], O:C or H:C molar ratios [20,21], chemical oxidation [14,22], accelerated ageing technique [23], and hydropyrolysis (HyPy) [24–26].

Among these techniques, the HyPy is interesting for the very high conversions of labile organic matter and accurate quantification of black carbon (BC) in different environmental matrices, including biochar [27] and biochar amended soil [8]. Moreover, HyPy integrated with GC-MS also allows for the molecular characterisation of the biochar semi-labile fraction defined as non- BC_{HyPy} . Additional benefits from HyPy include minimal product rearrangements and absence of generation of secondary char [28] as is often encountered in other chemical or thermal oxidative methods. In HyPy, the sample mixed with a sulphided molybdenum catalyst is pyrolyzed in the presence of hydrogen at high pressure to promote the reductive removal of thermally labile organic matter leaving a refractory and highly aromatic carbonaceous residue. This carbonaceous residue that remains after HyPy comprehends polyaromatic units greater than 7 fused rings [29,30] and can be quantified by elemental analysis. Therefore, HyPy method removes all labile organic matter (non- BC_{HyPy}), so isolating a highly stable portion of the biochar composed of highly condensed aromatic clusters and defined as BC_{HyPy} [25] or as stable polycyclic aromatic carbon (SPAC) [27,31]. The non- BC_{HyPy} fraction of chars that is evolved by thermal reductive cleavage has been shown to contain PAHs comprising ≤ 7 rings. Thus this fraction that is composed of ≤ 7 rings is supposed to be less permanent compared to larger PAH structures that constitute the BC_{HyPy} macromolecular network and has been defined as “semi-labile” [8]. This semi-labile fraction, due to its susceptibility to biological and chemical oxidation [27], is likely to be stable on timescales of years to decades. The labile fraction, which evolves on timescales of months to years, is also very important because can influence the soil microbial community structure [9,32]. HyPy was recently applied to investigate the impact of biochar amendment in an agricultural soil on the BC_{HyPy} and non- BC_{HyPy} fractions and their fate over time [8]. Biochar addition increased remarkably the BC_{HyPy} fraction, while the level of non- BC_{HyPy} PAHs was less influenced due to the large reservoir of these PAHs in original soil. However, more studies are needed to understand the role of this fraction in soil amended with biochar.

The aim of the present study is to quantify the BC_{HyPy} and characterise non- BC_{HyPy} fractions in biochar samples produced from different feedstock and process conditions with the same pyrolysis unit. Results were also compared with Py-GC-MS data to evaluate if these two analytical pyrolysis techniques provide a set of coherent complementary information on biochar stability and the molecular characteristics of thermally labile fraction. In particular, the attention was focused to the distribution of PAHs produced by HyPy and Py-GC-MS as molecular proxies.

2. Experimental

2.1. Samples

Three different types of biomass were used as feedstock materials: pine wood chips – with an average size of 3 cm \times 2 cm \times 0.5 cm – from Robeta Holz OHG (Milmersdorf, Germany); beech wood

spheres – with a diameter of 25 mm, provided by Meyer and Weigand GmbH (Nordlingen, Germany); corn digestate derived from maize silage provided by ATB Potsdam (Potsdam, Germany).

Biochar samples were produced by pyrolysis of the raw material using a stainless steel fixed-bed reactor of 102.5 cm height and 22 cm of internal diameter. The inert atmosphere was provided by a N_2 flow entering the reactor (20 L min^{-1} and 50 L min^{-1}) from the bottom through a stainless steel grate to get a uniformly distributed flow. The raw material (in the range of kilograms) was uniformly placed inside the reactor in a stainless steel container of 21 cm of diameter and 56 cm height, standing directly on the previously mentioned grate. The reactor was externally heated with a wire heater with a maximum power of 3000 W placed on the external reactor wall. Both flanges in the reactor were also heated and insulated to reduce heat losses. The N_2 flow was preheated before entering the reactor as well. The temperature operation of this preheater was 600 °C.

Pyrolysis were performed at three different temperatures, 340 °C, 400 °C and 600 °C. The biochar samples obtained were labeled as PW400, PW600, BW340, BW600, CD400 and CD600 (where PW, BW, CD stand for pine wood, beech wood and corn digestate, respectively; 340, 400 and 600 indicated the pyrolysis temperatures in degrees centigrade) (Table 1).

2.2. Biochar bulk characterization

Biochar samples were thoroughly homogenized and oven-dried at 40 °C for 72 h, and stored at -20 °C prior to analysis. Elemental composition (CHNS) was determined by combustion using a Thermo Scientific FLASH 2000 Series CHNS/O Elemental Analyzer (Thermo Fisher Scientific, Waltham, U.S.A.). The biochar samples were acid tested for the presence of carbonates. The carbonate content of each biochar was determined on duplicate samples by comparing total organic carbon measured after hydrochloric acid (HCl) treatment and total carbon. In particular, about 3–4 mg of biochar sample were reacted with 40 μL of 1.5 M HCl and then heated at 60 °C for 1 h; this procedure was repeated for 4–5 times, till the samples stop reacting with HCl. Only corn digestate biochars (CD600 5.1% and CD400 4.2%) were found to contain carbonates. The measured carbonate content values were used to correct the respective total carbon (TC) to total organic carbon (TOC) of biochar.

Ash was determined as the residual mass left after exposure at 600 °C for 5 h. The oxygen content was calculated from the mass balance: Oxygen (%) = 100 – Ash content (%) – C (%) – H (%) – N (%). Moisture contents were determined (ASTM D-3173) at 105 °C.

2.3. Extractable polycyclic aromatic hydrocarbons (PAHs)

Analyses of extractable PAHs in biochars were conducted in triplicate as described in Fabbri et al. [33], but using 16 PAHs deuterated of each of the 16 US EPA PAHs instead of 3 PAHs deuterated. The measured PAHs included naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(ah)anthracene, benzo(ghi)perylene, and indeno(1,2,3-cd)pyrene.

Briefly, about 0.5 g of biochar was spiked with 0.1 mL of a 5 mg L^{-1} solution of deuterated 16 EPA PAHs (prepared from Dr. Ehrenstorfer PAH-Mix 9 deuterated, 10 $\text{ng } \mu\text{L}^{-1}$) and soxhlet extracted with acetone/cyclohexane (1:1, v/v) for 36 h. The solution was filtered, added with 1 mL of *n*-nonane (keeper to prevent the extraction solution being reduced to dryness with loss of analytes), carefully evaporated by rotatory vacuum evaporation at 40 °C and cleaned up by solid phase extraction onto a silica gel cartridge before analysis with a Agilent HP 6850 GC coupled to a Agilent HP 5975 quadrupole mass spectrometer (Agilent Technologies, Inc.,

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