Biochar for carbon sequestration in soils: Effect of feedstock and pyrolysis conditions on physical and chemical biochar characteristics

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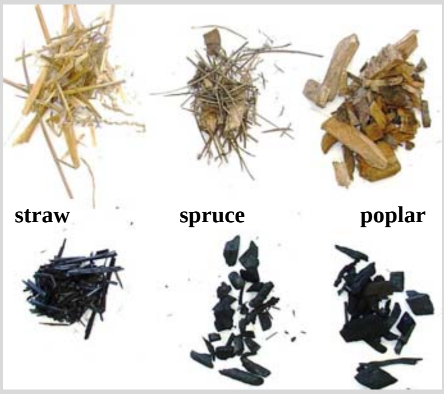
take-home message **the biochars showed:**
- **moderate potential as soil amendment (mostly at higher pyrolysis temperatures)**
- **high potential for C sequestration due to high aromaticity and stability**
- **high heterogeneity and variable degree of toxicity (PAHs and heavy metals)**

INTRODUCTION

Pyrolysis is the thermal decomposition of organic material under anoxic conditions resulting in the solid residue called biochar. Due to the concentration of stable, carbon-enriched organic compounds, biochar may contribute to climate change mitigation by carbon sequestration in the soil. In addition, biochar application has the potential for soil amendment by increasing soil pH and offering additional adsorption sites and, thus, an increased nutrient and water holding capacity. Concomitantly, biochars may be conducive to ecotoxicological risks in terms of the formation of polycyclic aromatic hydrocarbons (PAHs) during pyrolysis as well as heavy metals.
The extent of biochar contribution to the above mentioned advantages varies depending on feedstock and highest treatment temperature (HTT); hence, before applying biochar to soil, an extensive study on biochar properties may prove to be useful in order to meet the respective purpose of biochar application to soil that may slightly vary according to the state of the treated soil.

MATERIALS & METHODS

Straw (*Triticum aestivum*), spruce (*Picea abies*) and poplar (*Populus tremula*) were slowly pyrolysed at three temperatures (400°C, 460°C and 525°C).



Elemental composition was measured by dry combustion. Surface area was determined according to Brunauer- Emmett-Teller N_2 adsorption on a Flow Sorb II 2300 (Micromeritics; DIN 66131). Cation exchange capacity (CEC) was calculated as the sum of Na, K, Mg, Ca, Al, Fe and Mn extracted with $BaCl_2$. PAH (EPA 16) content was determined in accordance with US EPA method 610 (acetonitrile extraction; high-performance liquid chromatography with fluorescence and UV detectors). Differential Scanning Calorimetry (DSC) was performed by heating up feedstocks and biochars to 600°C at 5°C min^{-1} (Netzsch STA 409 PC). Fourier-transform infrared spectroscopy (FTIR) was performed on a Tensor 27 SN 1683 (Bruker Austria; resolution 4cm^{-1}; 64 scans) after preparing pellets (5 mg sample; 195 mg KBr). Water-extractable trace elements were measured by ICP-MS (Elan 9000; Perkin-Elmer). Statistical analyses were performed using SPSS 15.0 for Windows (ANOVA; Tukey's post-hoc test).

RESULTS

Biochars showed high pH (6.9-9.2) and high electrical conductivity (EC; 0.42-4.92 mS cm^{-1}). Ash content was highest for straw-derived biochars, increasing with pyrolysis temperature (up to 12.7 wt.%).

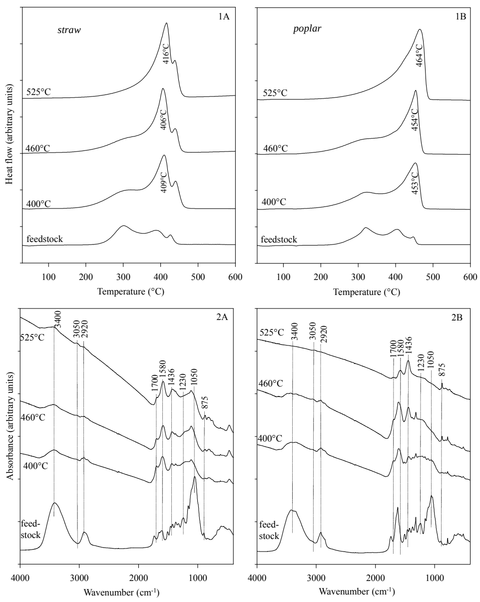


Figure 1 *Differential Scanning Calorimetry (1) and Fourier-transform infrared spectroscopy (FTIR; 2) and of straw (A) and poplar (B) derived biochars that were pyrolysed at 400°C, 460°C and 525°C. One increment of the y-axis corresponds to 10 Wg^{-1} for DSC and 0.2 absorbance units for FTIR.*

Table 1 *Basic parameters of biochars pyrolysed at 400°C, 460°C and 525°C. SA: BET-N_2 surface area; CEC: cation exchange capacity; PAH: polycyclic aromatic hydrocarbons. Values were determined in triplicate.*

	pyrolysis temperature	elemental H/C	SA (m^2g^{-1})	CEC ($mmol_ckg^{-1}$)	PAHs (mg kg^{-1})
straw	400°C	0.73 ± 0.07	4.8 ± 0.5	161.6 ± 15.6	5.2 ± 2.9
	460°C	0.5 ± 0.09	2.8 ± 1.8	117.0 ± 21.2	10.7 ± 5.6
	525°C	0.44 ± 0.03	14.2 ± 4.0	97.7 ± 19.4	33.7 ± 22.1
spruce	400°C	1.03 ± 0.03	1.8 ± 0.1	73.5 ± 2.9	30.7 ± 9.0
	460°C	0.49 ± 0.01	14.2 ± 2.2	54.7 ± 6.0	5.8 ± 2.0
	525°C	0.46 ± 0.11	40.4 ± 16.0	52.2 ± 1.4	1.8 ± 0.6
poplar	400°C	0.77 ± 0.01	3.0 ± 0.6	144.0 ± 5.6	4.3 ± 1.8
	460°C	0.59 ± 0.01	8.2 ± 0.1	128.3 ± 17.7	17.9 ± 3.6
	525°C	0.40 ± 0.01	55.7 ± 19.5	107.6 ± 7.6	2.0 ± 0.75

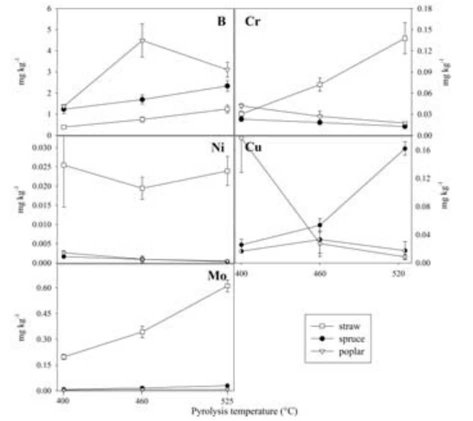


Figure 2 *Water extractable trace elements of straw, spruce and poplar-derived biochars. Error bars indicate standard deviation.*

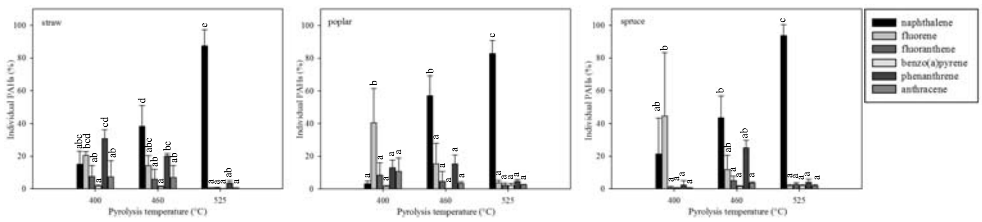


Figure 3 *Individual PAHs in % of total extracted PAHs in straw, poplar and spruce-derived biochars (means and standard deviation). Statistically significant differences were determined separately for each biochar type. Different letters indicate significant differences ($p < 0.05$; n=3; ANOVA, Tukey's test).*

SUMMARY & CONCLUSIONS

- Surface area of wood-derived biochars significantly increased with increasing pyrolysis temperature ($p < 0.05$) due to the formation of micropores, whereas the loss of functional groups led to a decrease of CEC.
- Total PAH (EPA 16) showed no consistent trends; PAH content of biochars partly exceeded the limit value of 6 mg kg^{-1} of the Austrian Compost regulation and the suggested limit value of EPA. Pyrolysis temperature had a significant influence on the composition of PAHs with naphthalene being the dominant PAH in biochars produced at 525°C, which indicates a change in degree of toxicity of the biochars.
- Water-extractable B, Cr, Ni and Mo content were dependent on feedstock. Except for Cr, trace metal concentrations were lower than in other agricultural amendments (Lau and Wong, 2001; Ciba et al., 2003; Toor et al., 2007)
- H/C ratios decreased with increasing pyrolysis temperature for all biochars indicating an increase in aromaticity. DSC results proved an increase in (thermal) stability and aromaticity with poplar being comparatively more recalcitrant than straw-derived biochars. Rising aromaticity is also shown in the FTIR spectra with increasing bands at 3070-3000, 1610-1580, 1436 and 875 cm^{-1} (the two latter may also indicate carbonate).
- FTIR showed the loss of labile O-H and aliphatic compounds (3500-3200 and 2980-2820 cm^{-1}) as well as the formation of carboxylic groups (1700 cm^{-1}); the latter decreases with increasing pyrolysis temperature.

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