

## Contribution to the characterization of biochars for the prediction of their carbon longevity

Calvelo Pereira, R<sup>a,b</sup>; Camps-Arbestain, M<sup>b,\*</sup>; Pardo Lorenzo, R<sup>a</sup>; Kaal, J<sup>c</sup>; Aitkenhead, W<sup>b</sup>; Macías, F<sup>a</sup>; Hedley, M<sup>b</sup>; Maciá-Agulló, JA<sup>d</sup>

<sup>a</sup>Dept. Edafología y Química Agrícola, Facultad de Biología, Universidad de Santiago de Compostela, 15782-Santiago, Spain; <sup>b</sup>Institute of Natural Resources, Private Bag 11222, Massey University, Palmerston North 4442, New Zealand; <sup>c</sup>Laboratorio de Arqueología del Paisaje, Universidad de Santiago de Compostela, Campus Sur, Monte da Condesa, 15782 Santiago de Compostela, Spain; <sup>d</sup>Instituto Nacional del Carbón (CSIC), P. O. Box 73, 33080-Oviedo, Spain  
 \*E-mail: M.Camps@massey.ac.nz

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### Introduction

The stability of biochar in soils determines how long biochar will contribute to (i) the mitigation of greenhouse gas emissions, and (ii) improved soil functions [1]. Knowledge of size of the labile fraction of biochars under the different biogeochemical soil conditions to which these are applied may be sufficient to determine the stable fraction of biochar needed for trading carbon offsets.

The objective of this study was to estimate the size of the labile component of different biochars produced from three plant residues (pine, poplar and willow) at two temperatures (400 and 550°C) through different methodologies.

Biochars were characterized by their elemental composition (C, H, O, N, S), TGA (volatiles, fixed C, ashes), pH-H<sub>2</sub>O, and BET. The fraction of total C in biochars oxidable with potassium dichromate (OC<sub>dichro</sub>) and potassium permanganate (OC<sub>per</sub>) was also determined. Platinum filament coil probe pyrolysis-GC/MS was performed on both feedstocks and biochars.

Biochars were mixed with two acid soils of contrasting chemical properties (Umbrisol,

Podzol), and inert sand at different doses (7.5 and 15 t ha<sup>-1</sup>) and incubated under biotic and abiotic conditions to assess their short-term degradability in the different substrates. Here, however, only the results from soil incubations are reported. Basal respiration of biochar-soil mixtures (10 g total) was measured with a Micro-Oxymax Respirometer (Columbus Instruments, Columbus, OH).

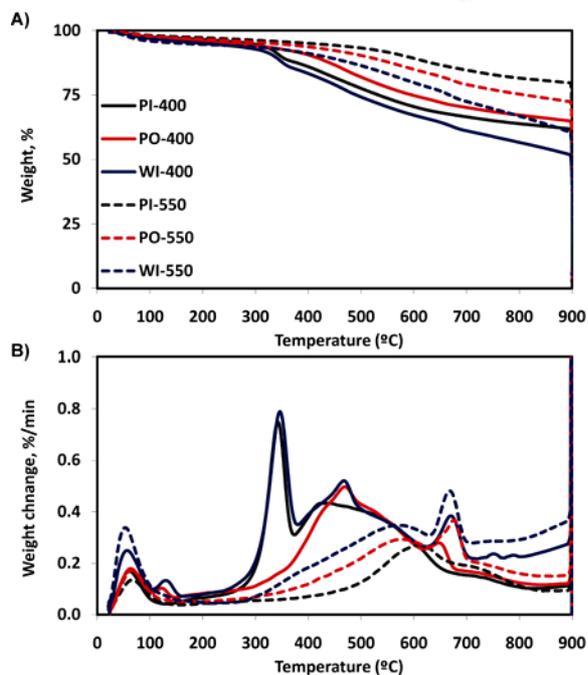
### Results and Discussion

All the biochars had a pH value above neutrality, except the biochar produced from pine at 400°C (Table 1). As expected, high temperature biochars (PI-550, PO-550, WI-550) had a smaller fraction of volatiles and a greater surface area (Table 1) than their corresponding low temperature biochars (PI-400, PO-400, WI-400). The fraction of volatiles was greatest for WI-400 and smallest from PI-550. For PI-400 and WI-400, the rate of temperature change showed a peak at 400°C (Fig. 1), which suggests that some volatiles produced during pyrolysis remained within the pores. On the other hand, analytical pyrolysis-GC/MS has confirmed that trapped aromatics (benzene and toluene) are present in PO-550 and WI-550 (TGA peaks around T 650°C; Fig. 1).

**Table 1.** Main physical and chemical properties of the biochars studied

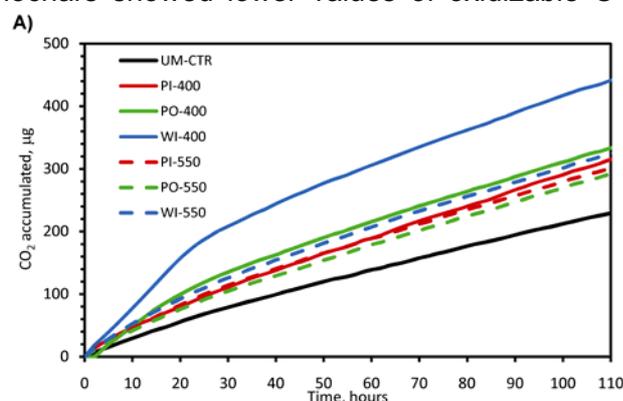
Sample	Feedstock				Biochar									
	C %	N %	pH	mass recovery %	C %	N %	H %	O %	Ash %	Atomic ratios		S <sub>BET</sub> m <sup>2</sup> g <sup>-1</sup>	OC <sub>dichro</sub> %*	OC <sub>per</sub> %*
PI-400	48.7	0.2	5.7	34.9	76.7	0.6	4.6	15.6	2.6	0.7	0.2	1	24.5	4.1
PO-400	47.9	0.5	7.2	29.7	75.5	1.0	4.2	15.2	4.0	0.7	0.2	3	29.4	3.9
WI-400	47.6	0.9	7.5	37.8	66.2	1.5	3.5	9.8	5.7	0.6	0.3	3	50.7	4.6
PI-550	48.7	0.2	5.2	28.4	84.7	0.6	3.5	8.1	3.1	0.5	0.1	368	11.6	0.9
PO-550	47.9	0.5	8.8	26.9	75.8	1.1	3.6	8.9	6.5	0.6	0.1	55	21.1	1.8
WI-550	47.6	0.9	8.6	28.8	79.1	1.7	3.5	10.6	5.2	0.5	0.1	149	21.9	0.5

\* expressed as fraction of total C in biochar



**Figure 1.** TGA spectra of the samples studied. A), weight, B) rate of change in weight.

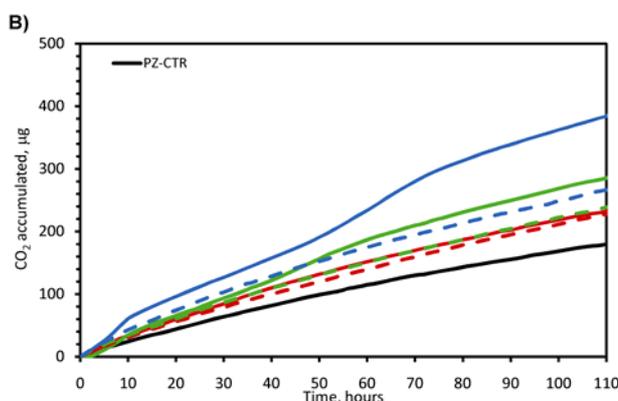
In relation to the oxidability of C with the different oxidant reagents used,  $OC_{per}$  values were <5% in all biochars, whereas  $OC_{dichro}$  values ranged between 11 and 50% (Table 1), although with both reagents, high temperature biochars showed lower values of oxidizable C



than the corresponding low temperature biochars.

Biochar-amended soils showed differences in basal respiration (Fig. 2). In general, as the temperature of pyrolysis increased, (i) the amount of  $CO_2$  evolved from substrates decreased, and (ii) the response of the different biochars to decomposition became more uniform and thus more predictable. However, unexpectedly, the biochar produced from pine wood at 400°C had a  $CO_2$  evolution pattern similar to the high-temperature biochars (Fig. 2). Several factors could have affected the pattern of the PI-400 biochar: (i) the acidic nature of the biochar, which resulted in a low liming ability, and (ii) the presence of compounds potentially toxic to soil microflora. In this sense, analytical pyrolysis-GC/MS found traces of retene-like compounds in this sample.

There was generally a good correlation between  $OC_{dichro}$  content and volatile C ( $r > 0.850$ ); the cumulative  $CO_2$  evolved from soil mixtures correlated well with both  $OC_{dichro}$  contents ( $r > 0.850$ ) and volatile C ( $r > 0.700$ ). However, these determinations could not predict the pattern observed for the PI-400 biochar.



**Figure 2.** Cumulative  $CO_2$  evolution from A) Umbrisol and B) Podzol mixtures with the different biochars; (dose:  $15 \text{ t ha}^{-1}$ ).

## Conclusions

The results obtained to date indicate that the nature of the feedstock and process conditions had a strong influence on the short-term lability of biochars. The labile fraction in biochar estimated using three tests (dichromate, permanganate, TGA analysis) correlated well between them. These tests also showed a good

relationship with the  $CO_2$  evolved from incubations. However, they were not able to predict the different pattern of the PI-400 biochar, which was probably caused by factors not related to C degradability.

<sup>1</sup> Lehmann, J. and S. Joseph, *Biochar for environmental management. Science and technology*. 2009, London: Earthscan. 416.