

# Multi-methodological characterisation of Costa Rican biochars from small-scale retort and top-lit updraft stoves and inter-methodological comparison

Joeri Kaal<sup>a,b,\*</sup>, Roberto Calvelo<sup>c</sup>, Art Donnelly<sup>d</sup>, Anna McBeath<sup>e</sup>,  
Antonio Martínez Cortizas<sup>b</sup>, Hugh McLaughlin<sup>f</sup>

<sup>a</sup>*Institute for Heritage Science (Incipit), Spanish National Research Council (CSIC), Santiago de Compostela, Spain*

<sup>b</sup>*Departamento de Edafología e Química Agrícola, Fac. Biología, Universidade de Santiago de Compostela, Campus Sur, Santiago de Compostela, Spain*

<sup>c</sup>*New Zealand Biochar Research Centre, Soil and Earth Sciences Group, Institute of Agriculture and Environment, Massey University, Palmerston North, New Zealand*

<sup>d</sup>*SeaChar.Org, University Place, Seattle, USA*

<sup>e</sup>*College of Science, Technology and Engineering, James Cook University, Cairns, Australia*

<sup>f</sup>*NextChar, LLC, Amherst, MA, USA*

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## Abstract

We applied common (pH, elemental analysis, thermogravimetry) and less-common (infrared spectroscopy, GACS adsorption test, pyrolysis-GC-MS, hydrogen pyrolysis) analytical procedures to a set of biochars from Costa Rica (bamboo stalk, cacao chaff, sawmill scrap, coconut husk and orchard prunings feedstocks). The biochars were produced by high temperature combustion in a top-lit updraft stove (TLUD) and low temperature anaerobic charring in a retort (RET), the latter of which was heated by the gas that evolved from the TLUD. The RET biochars exhibit a smaller adsorption capacity, higher molecular diversity and larger proportion of thermolabile materials, because of the lower degree of thermochemical alteration (DTA) and therefore limited formation of the microporous polycondensed aromatic matrix typical of the TLUD biochars. Multivariate statistics showed that DTA, not feedstock composition, controls biochar organic chemistry. The TLUD biochars might be better candidates for soil amendment because of their adsorption capacities and will probably exert a more prolonged effect because of their chemical stability. The cross-comparison of the methods showed the complementarity of especially elemental analysis, GACS, thermogravimetry, hypy and pyrolysis-GC-MS.

**Keywords:** biochar, characterisation, Costa Rica, rural communities

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## 1 Introduction

Biochar is thermally modified biomass, such as charcoal obtained from urban, industrial, agricultural or forestry residues, destined for soil amendment. Applications using biochar are increasingly adopted to enhance soil productivity and promote carbon (C) sequestration

(e.g. Lehmann *et al.*, 2006; Fowles, 2007; Laird, 2008; Sohi *et al.*, 2008; Kookana *et al.*, 2011). In soil, biochar acts as a sponge-like material enhancing water and nutrient retention, reducing erodibility, providing a habitat for soil microorganisms while it also has a liming effect as a result of its ash content. These properties often culminate into improved soil productivity and reduced loss of topsoil in agricultural land (Carrión & Badal, 2004; Jeffery *et al.*, 2011; Lehmann *et al.*, 2011). The effects

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\* Corresponding author

Email: joeri@samage.net

of biochar are reportedly stronger in soils with low adsorption capacity and pH, and in poor tropical soils with fast organic matter turnover rates (Glaser *et al.*, 2002; Jien & Wang, 2013). However, these effects are diverse, depending not only on feedstock type and production conditions (e.g. temperature) (Bruun *et al.*, 2008; Peng *et al.*, 2011; Preston & Schmidt, 2006; Zimmerman, 2010; Zhao *et al.*, 2013), but also on the targeted crop and soil properties (Masiello, 2004; Haefele *et al.*, 2011), giving rise to the need for optimising biochar production conditions to the specific requirements of each soil type and land use (Abiven *et al.*, 2014). Obviously, a thorough analysis of the properties of such biochars is a prerequisite to evaluate their suitability for different soil amendment applications.

Among the non-industrial biochar manufacturing systems, often used in rural areas and small farms, is the “Jolly Roger Oven”, which consists of two adapted oil drums, the bottom drum of which is the top-lit updraft (TLUD) gasifier where intense burning converts the feedstock into charcoal (Kearns, 2012; McLaughlin & Clayton, 2012). The top drum, which is sealed, is heated by the exhaust rising from the TLUD and therefore acts like a retort (RET) oven in which the biomass is charred under oxygen-depleted conditions. In Costa Rica, several field studies, mostly in banana, coffee and cacao agroforestry contexts have demonstrated the potential of biochar to enhance soil properties and plant growth. For example, cacao biochar improved cacao seed production, especially when biochar was combined with a fertiliser such as poultry manure (Acosta Buitrago, 2013; Hojah da Silva, 2013). These studies have been performed with the focus on socio-economic benefits for indigenous communities, who sell the biochar produced in essentially smoke-free cook-stoves (Schultz, 2013). The directly appreciable utility of cleaner cook-stoves, for biochar production, is an essential ingredient of small-scale biochar applications in rural areas where migrating Ngöbe-Buglé indigenous populations (with very basic household equipment) account for a significant part of the harvesting labour of the aforementioned crops. Current applications in Costa Rica include the use of coffee prunings, again in TLUD cook-stoves, for biochar production (Scholz *et al.*, 2014). In addition, there is considerable interest in the potential alleviation of the damaging effects on cacao pods of the pathogens “mazorca negra” (*Phytophthora* sp.) and “molinia” (*Moniliophthora roreri*), by biochar application. The characterisation of the biochars applied had hitherto been limited to elemental composition and nutrient retention assays. Knowledge on the properties

of these biochars, which are currently under field trial experimentation, is needed to optimise their implementation strategy.

This study addresses the properties of the organic matter of TLUD and RET biochars obtained from several important feedstocks in Costa Rica: bamboo stalk, cacao chaff and sawmill scrap. In addition, we studied TLUD biochars of orchard prunings and coconut husk. This is not a typical characterisation study of small amounts of biochar produced in the laboratory, but of biochars that are being created in rural areas of Costa Rica and are currently used as a soil amendment. We analysed these biochars for ash content, elemental composition, pH-H<sub>2</sub>O, Fourier-transform infrared spectroscopy (FTIR), pyrolysis-gas chromatography-mass spectrometry (pyrolysis-GC-MS), hydrogen pyrolysis (hypy), thermogravimetry (TG) and gravimetric adsorption capacity scan (GACS). For the first time, hypy residues were analysed by pyrolysis-GC-MS to identify the nature of the residual volatiles. The assessment of general, molecular and adsorption properties is not only expected to shed light on the properties of these biochars and make cautious predictions on their likely effects on soil conditions, but also generate knowledge on biochar chemistry and on the complementarities of the methodologies applied.

## 2 Materials and methods

### 2.1 Feedstocks

Cacao chaff was obtained from fresh cacao pods at APPTA Fair Trade (Talamanca, Costa Rica). Bamboo stalk and coconut husk were obtained from their direct surroundings. The sawmill scrap was obtained from the nearby mill and the mixed orchard prunings were taken from the branches of isolated trees in a nearby banana field in the surroundings of the plant. The orchard prunings are composed mainly of, but not limited to, branches of *Inga edulis* (guabo) and *Erythrina* sp. (poró).

### 2.2 Biochar production

The Jolly Roger Oven setup is as described in detail by McLaughlin & Clayton (2012). For each biochar production, a 12” K-type probe was used to verify the temperature at various levels in the TLUD gasifier drum as the combustion front migrates through the barrel, which ranged between 500 and 800 °C over the course of one run with typical maximum heating temperature of 650 °C. The retort (RET) drum, set on top of the

TLUD, was sealed using local wet clay. The maximum temperature within a run was close to 450 °C (coinciding with the moment of maximum temperature in the TLUD). The coconut husk and orchard prunings biochars were produced in an Estufa Finca cookstove, which is a TLUD-system with a smaller volume than the TLUD from the Jolly Roger Oven. No RET biochars are available for these feedstocks. The Estufa Finca is used for cooking by rural communities and more than 4500 kg of the resultant biochar has already been sold and implemented into numerous agricultural fields. The temperature profile in the Estufa Finca is 550–650 °C. Biochars were homogenised and ball-milled to powder before analysis.

### 2.3 Biochar characterisation

#### 2.3.1 Chemical characterisation and thermal analysis

The elemental composition was determined in three different laboratories. Proportions of C, H, N, O and S were determined on a Vario MACRO cube CHNS elemental analyser (Elementar Analysensysteme GmbH, Hanau, Germany). In addition, C and N content were determined by dry combustion using a LECO analyser (model CHN-1000), and C content was measured on a Costech 4010 elemental analyser. Values for C content (three laboratories) were almost identical, with differences below 1 % and linear determination coefficients ( $r^2$ ) between 0.996 and 0.999 ( $P < 0.0001$ ). Nitrogen content showed larger differences ( $15 \pm 11$  %) because of the low N content of the biochars that were produced from materials other than cacao chaff, but were also strongly correlated ( $r^2 = 0.998$ ,  $P < 0.0001$ ). We only present data for the more complete elemental analysis using the Vario MACRO cube CHNS and those data are used for inter-methodological comparisons.

The pH in water was measured in 1:10 w:v in deionised water, after 60 minutes of equilibration in an orbital shaker.

Thermogravimetric TG and derivative (DTG) curves were obtained using an SDT Q600 instrument. The weight loss between 110 and 900 °C in a  $N_2$  atmosphere was considered as the biochar volatile matter content, whereas the loss of weight at 900 °C after the introduction of air current was considered as the stable, thermo-resistant fraction or fixed C ( $C_{\text{fixed}}$ ). The fraction of volatile matter with respect to the sum of volatile matter content and  $C_{\text{fixed}}$  is considered as the thermolabile fraction of biochar ( $C_{\text{thermo}}$ , ash-free, dry matter basis; expressed as %). Ash content is the fraction of the sample material remaining after combustion of

$C_{\text{fixed}}$  (Calvelo Pereira *et al.*, 2011). This method is also known as proximate analysis.

The inorganic C ( $C_{\text{inorg}}$ ) content of the biochars was estimated by measuring the weight loss associated with the endothermic peak at ca. 600–850 °C (Calvelo Pereira *et al.*, 2011; Wang *et al.*, 2014). Weight loss and/or peak area changes were assessed as  $CO_2$  mass loss but corrected to calculate  $C_{\text{inorg}}$ .

#### 2.3.2 Gravimetric Adsorption Capacity Scan (GACS)

The GACS adsorption test was applied using a custom-built modified TG analyser as described by McLaughlin (2010). Briefly, biochar is placed in 1.5 mL wire basket, suspended below an analytical balance in a heated  $N_2$ -purged chamber, with a thermocouple located above the sample inside the wire basket. The balance is tared at 100 °C, after which the chamber is heated to 300 °C at  $13.3$  °C  $min^{-1}$ . At that point, the purge gas is replaced by 1,1,1,2-tetra-fluoro-ethane (a refrigerant known as R134a) and the chamber allowed to cool to ambient temperature at  $4$  °C  $min^{-1}$ . The weight gain of the sample during cooling, caused by adsorption of R134a, is a measure of the adsorption capacity.

#### 2.3.3 Fourier-Transform Infrared spectroscopy (FTIR)

Attenuated total reflectance FTIR was performed using a Gladi-ATR (Pike Technologies) spectrometer, scanning in the  $4000$ – $400$   $cm^{-1}$  region. The weak signal implied that adequate baseline subtraction was not always feasible and that the FTIR spectra could not be reliably quantified.

#### 2.3.4 Pyrolysis-GC-MS

For pyrolysis-GC-MS, biochar samples were pyrolysed at 750 °C for 10 seconds, with a heating rate of  $10$  °C  $ms^{-1}$ . The relatively high analytical pyrolysis temperature proved the most suitable temperature for biochar analysis using pyrolysis-GC-MS (Kaal *et al.*, 2009). Briefly, 1–1.5 mg of sample was placed in fire-polished quartz tubes with quartz wool on both ends and pyrolysed using a resistive heating Pt-filament CDS Pyroprobe 5250. The pyrolysis products were transferred into a 6890N gas chromatograph (Agilent Technologies) by He flow ( $1$  mL  $min^{-1}$ ), separated on a HP-5MS polysiloxane-based column (temperature program 60–325 °C at  $20$  °C  $min^{-1}$ , 5 min dwell time) and identified using an Agilent 5975B mass spectrometer (70 eV electron ionization). The peaks in the pyrolysis chromatograms were identified on the basis of pyrolysis-GC-MS literature of biochar and the NIST '05 library. This resulted in a list of 108 pyrolysis products,

which was reduced to 101 compounds by combining unresolved isomers and eliminating potential contamination products (phthalates and styrenes). The 101 compounds were quantified using their primary ion fragments ( $m/z$ ). Relative proportions of each pyrolysis product are expressed as percentage of total quantified peak area (TQPA). TQPA is a rough measure of signal intensity and therefore sample pyrolysability (Kaal et al., 2009).

### 2.3.5 Hydrogen pyrolysis (hypy)

The proportion of stable polycyclic aromatic carbon (SPAC) of biochar, expressed as the percentage of total C ( $C_t$ ), was determined by hypy following (Meredith et al., 2012; Wurster et al., 2012; McBeath et al., 2015). Briefly, a Mo catalyst was added to ca. 100 mg of sample using an aqueous/methanol solution of ammonium dioxodithiomolybdate. Catalyst loaded samples were placed in the hypy reactor, which was pressurised with  $H_2$  to 150 bar with a purge gas flow of  $5 L min^{-1}$ . The reactor was heated initially at  $300^\circ C min^{-1}$  to  $250^\circ C$  and then at  $8^\circ C min^{-1}$  to  $550^\circ C$ , and then held at maximum temperature for 2 min. The  $C_t$  content of the sample residue after hypy was determined by elemental analysis using a Costech 4010. The error associated with the estimation of SPAC content is better than  $\pm 4\%$  of the measured value (McBeath et al., 2015). The hypy residues were analysed by pyrolysis-GC-MS (see above) to assess the presence and properties of volatile components.

### 2.4 Data evaluation

Differences between TLUD and RET biochars were tested using One-way ANOVA (SPSS 20), and con-

sidered significant when the probability of the null hypothesis (no difference between the groups) was below 0.05. Relationships between continuous variables were tested by Pearson linear determination coefficients ( $r^2$ ). A Principal Component Analysis (PCA) was performed in order to illustrate the relative similarities and differences between selected parameters, after standardisation (Z-scores) of the data.

## 3 Results

### 3.1 Elemental composition and pH

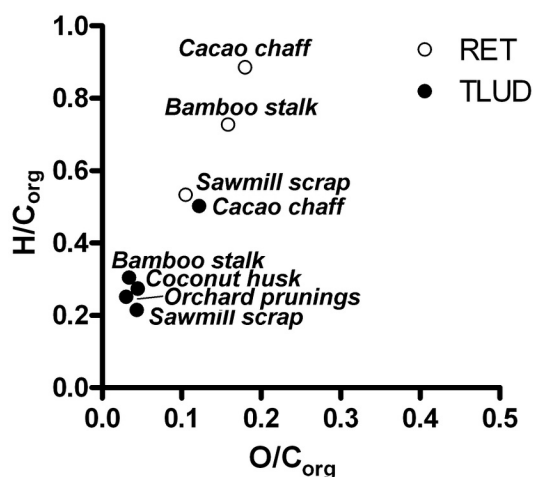
The  $C_t$  content of the biochars ranged between 550 and  $870 g kg^{-1}$  (Table 1). The cacao chaff biochars (RET and TLUD) have lowest  $C_t$  content, also if the  $C_t$  content is corrected for ash (not shown). The (atomic) ratios from elemental analysis are corrected for the minor contents of  $C_{inorg}$  as determined by thermogravimetry (see section 3.2). Cacao chaff biochars have the highest N content and lowest  $C_{org}/N$  ratio, reflecting the nature of this protein-rich feedstock. The N content and  $C_{org}/N$  ratios of the other biochars are  $< 10 g kg^{-1}$  and  $> 115$ , respectively (Table 1). The S content was below the detection limit except for the biochars from cacao chaff and bamboo stalk. The  $H/C_{org}$  ratio ranged from 0.21 to 0.88 and the  $O/C_{org}$  ratio from 0.03 to 0.18. They are higher for the RET biochars than for the TLUD biochars ( $P < 0.01$  and  $P < 0.05$ , respectively). The Van Krevelen plot (Fig. 1) shows that the cacao chaff TLUD biochar is closer to the range of the RET biochars.

The pH in water of the biochars ranged from 8.3 to 10.5 (Table 2). TLUD biochars seem to have slightly higher pH (9.9–10.5) than the RET biochars (8.3–10.0), but this difference is insignificant ( $P = 0.054$ ).

**Table 1:** Elemental composition of the biochars analysed (all values on dry matter basis)

Type	Feedstock	$C_t$ [g kg <sup>-1</sup> ]	$C_{org}$ [g kg <sup>-1</sup> ]	N [g kg <sup>-1</sup> ]	H [g kg <sup>-1</sup> ]	S [g kg <sup>-1</sup> ]	O [g kg <sup>-1</sup> ]	$C_{org}/N$ [-]*	$O/C_{org}$ [-]*	$H/C_{org}$ [-]*
Retort	Cacao chaff	552.5	549.9	48.9	40.8	2.3	132.6	13.1	0.181	0.884
	Sawmill scrap	741.3	734.7	6.2	32.7	<DL <sup>†</sup>	103.9	138.9	0.106	0.531
	Bamboo stalk	668.1	668.1	6.8	40.7	1.8	141.6	115.3	0.159	0.726
TLUD	Cacao chaff	571.6	570.0	24.2	24.0	3.6	93.4	27.4	0.123	0.501
	Sawmill scrap	836.6	833.8	8.2	14.9	<DL <sup>†</sup>	49.8	118.0	0.045	0.213
	Bamboo stalk	705.4	705.4	5.5	17.9	0.5	32.7	150.4	0.035	0.303
	Coconut husk	867.4	865.4	7.0	19.7	<DL <sup>†</sup>	52.9	143.8	0.046	0.272
	Orchard prunings	855.6	850.5	7.9	17.8	<DL <sup>†</sup>	35.6	125.3	0.031	0.250

\* Atomic ratio; <sup>†</sup> Below detection limit



**Fig. 1:** Van Krevelen plot of the biochars analysed (atomic ratios of  $O/C_{org}$  and  $H/C_{org}$ ).

### 3.2 Thermogravimetry

The ash content (on a dry weight basis) ranged from 50 to 285  $g\ kg^{-1}$  (Table 2). Highest ash contents were measured for the cacao chaff biochars (TLUD and RET). There are no significant differences between the ash contents of the TLUD and RET biochars. The RET biochars ( $35 \pm 10\%$ ) have a larger proportion of thermolabile C ( $C_{thermo}$ ) than the TLUD biochars ( $18 \pm 8\%$ ) ( $P < 0.05$ ). The proportion of  $C_{inorg}$ , which can be recognised from a peak in the differential mass loss curve around 650°C (Fig. 2), was up to 6.6  $g\ kg^{-1}$  with no apparent differences between feedstocks or production types. The differential mass loss curve obtained of the RET biochars (Fig. 2a) shows that the cacao biochar produced a broad (composed) peak between 200 and 500°C. The mass loss of the bamboo RET biochar is concentrated in a very broad band in the range 350–600°C, while the sawmill scrap RET biochar shows minor and gradually increasing weight loss in the same region. The differential mass loss curve of the TLUD biochars (Fig. 2b) shows few peaks, which is indicative of their thermal stability. In fact, the most prominent peak at ca. 650°C corresponds to  $C_{inorg}$ .

### 3.3 GACS adsorption capacity

The GACS test showed that the RET samples have much lower adsorption capacity for R134a (20–45  $g\ kg^{-1}$ ) than the TLUD equivalents (50–100  $g\ kg^{-1}$ ) ( $n=6$ ;  $P < 0.05$ ) (Table 2). The sawmill scrap TLUD biochar has the highest GACS value, showing an adsorption isotherm very similar to that of the CC#14 reference sample (McLaughlin, 2010), whereas the sawmill scrap RET biochar has the highest adsorption capacity of the RET biochars, which can be explained by the generally larger surface areas of biochars from

wood feedstock (Zhao *et al.*, 2013). From comparison with the GACS analyses of a reference set of pine- and oak-derived biochars produced at 350, 450 and 550°C, in general the RET biochars show adsorption behaviour similar to that of the 450°C chars, except for the Bamboo biochar which is more similar to pine-350°C, while the TLUD isotherms more closely resemble that of the 550°C biochars (McLaughlin, 2010).

Previous comparative tests of TLUD biochars using other measures of adsorption capacity showed that the GACS test is linearly related to e.g. the  $N_2$ -BET surface area (McLaughlin, 2010). The advantage of the GACS test using R134a over BET-surface analysis is that the latter requires more costly equipment and that R134a is larger and heavier than  $N_2$  or  $CO_2$ , more relevant to the adsorption of soil constituents such as nutrients and contaminants.

### 3.4 Fourier-Transform Infrared spectroscopy (FTIR)

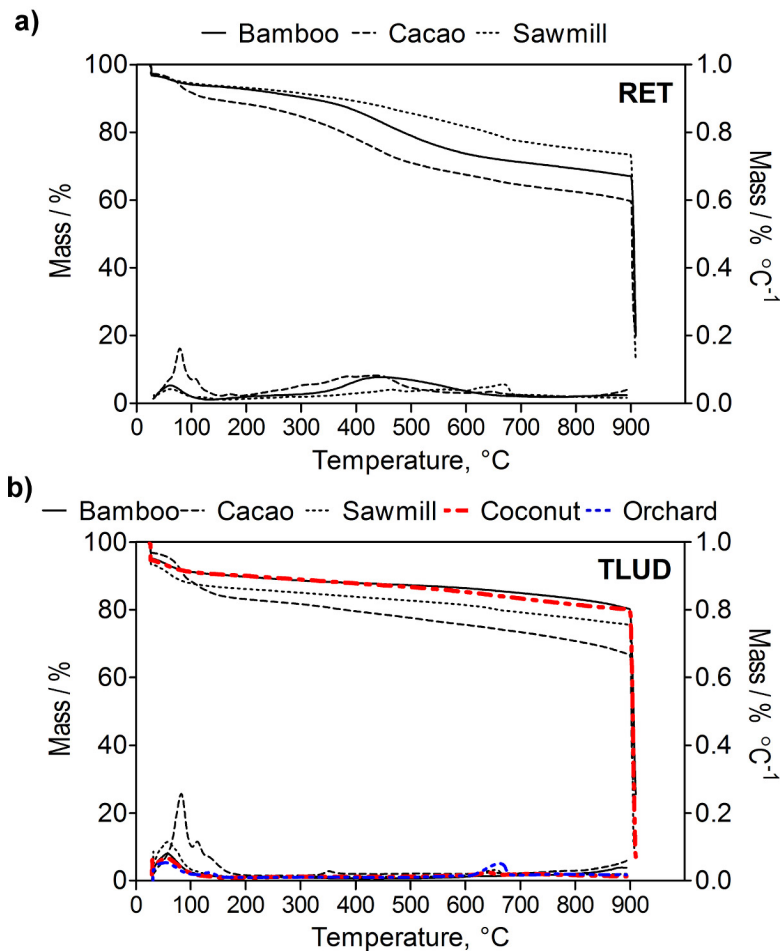
FTIR absorbance spectra are presented in Fig. 3. Several TLUD samples (sawmill scrap, bamboo stalk, coconut husk, orchard prunings) showed very weak absorbance, indicative of the virtual absence of any functional group other than hybridised C bonds in polynuclear aromatic clusters. The cacao chaff TLUD biochar showed slightly better signal, mainly of the O-H stretch ( $3400\ cm^{-1}$ ), C-O stretch ( $1030\ cm^{-1}$ ), phenolic O-H bend ( $1430\ cm^{-1}$ ) and aromatic ring stretch at ca.  $1610\ cm^{-1}$ , with minor aromatic bands at  $1720\ cm^{-1}$ . These groups can all be traced back to aromatic groups with partial substitution by hydroxyl groups, typical of high-temperature charcoal (Sharma *et al.*, 2004; Keilweit *et al.*, 2010; Rutherford *et al.*, 2012).

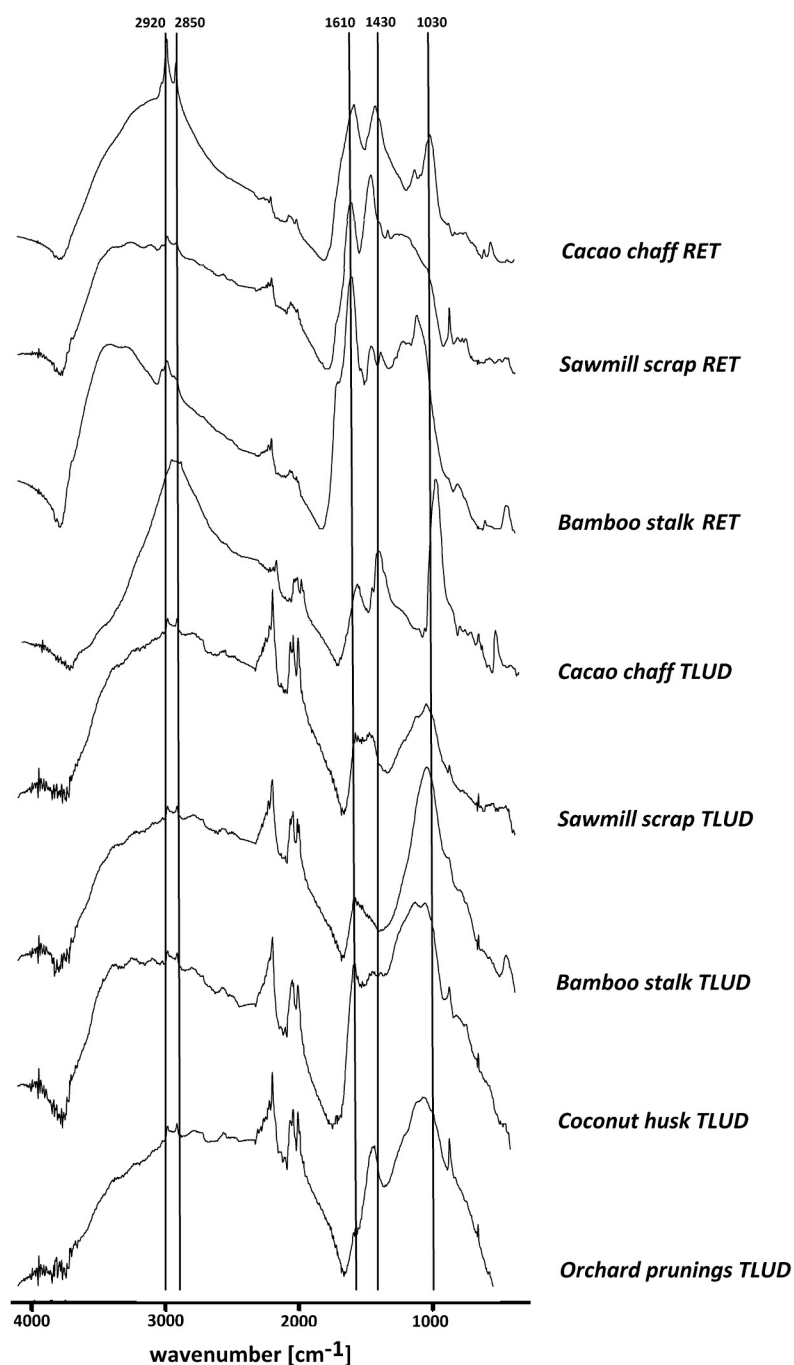
Qualitatively, the RET samples showed some more functional group diversity. Especially the cacao chaff sample exhibited significant peaks of symmetric and asymmetric methyl ( $CH_3$ ) and methylene ( $CH_2$ ) stretches at  $2920$  and  $2850\ cm^{-1}$ , traces of which can also be recognised in the bamboo RET sample. Furthermore, the band at  $1030\ cm^{-1}$  (aromatic C-O) is relatively narrow in the cacao RET and TLUD biochar and shifted towards  $1000\ cm^{-1}$ , which most likely corresponds to thermally altered protein (C-N stretch; Coates, 2000), and a slight broadening of the band at  $1650\ cm^{-1}$  might reflect overlap between aromatic C=C and C=N bands (cf. Apaydın-Varol & Eren Pütün, 2012). All RET biochars showed significant absorbance of the aforementioned O-H stretch, C-O stretch, phenolic O-H bend and the aromatic ring stretch. These results show that the biochars consist of a combination of aromatic and phenolic moieties, with traces of aliphatic groups in methyl and methylene groups.

**Table 2:** Proximate analysis, pH, adsorption capacity (GACS) and stable polycondensed aromatic carbon (SPAC, from hypy analysis) (all values on dry matter basis).

Type	Feedstock	ash [g kg <sup>-1</sup> ]	C <sub>inorg</sub> [g kg <sup>-1</sup> ]	C <sub>volatile</sub> [g kg <sup>-1</sup> ]	C <sub>fixed</sub> [g kg <sup>-1</sup> ]	C <sub>thermo</sub> * [-]	pH-H <sub>2</sub> O [-]	GACS [g kg <sup>-1</sup> ]
Retort	Cacao chaff	223	2.7	350	428	44.98	10.03	20.71
	Sawmill scrap	116	6.6	223	661	25.19	9.43	41.4
	Bamboo stalk	141	< DL <sup>†</sup>	304	555	35.35	8.33	26.85
TLUD	Cacao chaff	283	1.6	237	480	33.09	10.15	N/A
	Sawmill scrap	91	2.8	140	769	15.44	10.49	91.18
	Bamboo stalk	238	< DL <sup>†</sup>	120	642	15.77	10.13	56.22
	Coconut husk	53	1.9	121	826	12.8	10.33	70.62
	Orchard prunings	83	5.1	132	785	14.38	9.87	50.85

\* Thermolabile C (volatile matter / (volatile matter + Fixed C)\*100%); † Below detection limit

**Fig. 2:** Proximate of the biochars analysed: thermogravimetric (TG; mass change, %) and derivative (DTG; mass change with temperature, % °C<sup>-1</sup>) curves of retort (RET) (a) and TLUD (b) biochars.

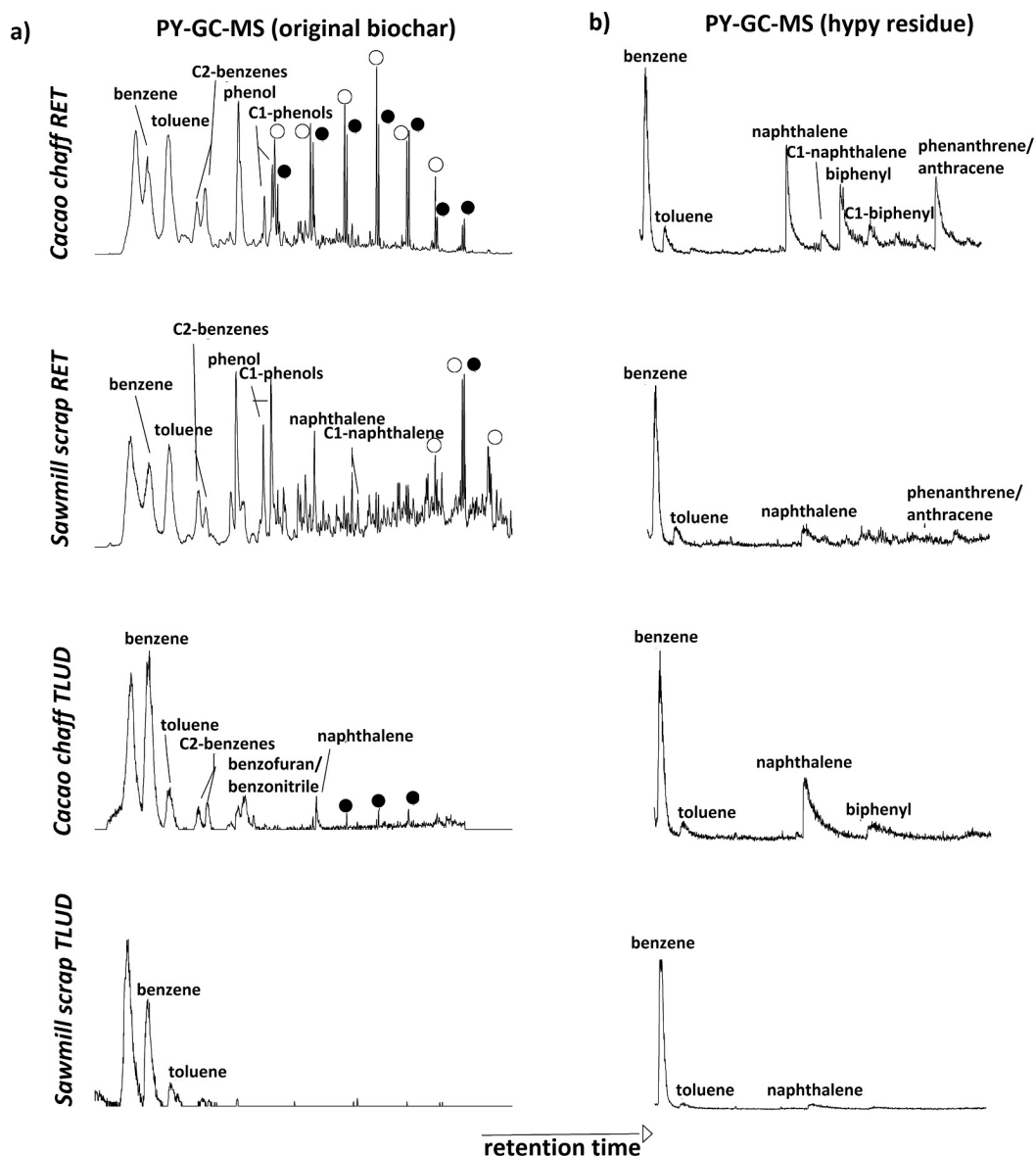


**Fig. 3.** FTIR spectroscopy spectra of the biochars analysed. Wavenumbers of selected bands are indicated (see text).

### 3.5 Pyrolysis-GC-MS

Example pyrolysis chromatograms are shown in Figure 4a. In all samples, aromatic hydrocarbons are the dominant pyrolysis products (Table 3). Monocyclic aromatic hydrocarbons (MAHs) with one to three alkyl C substitutions account for  $59 \pm 25\%$  of TQPA, and are more abundant in TLUD ( $67 \pm 29\%$ ) than in RET pyrolyzates ( $47 \pm 14\%$ ) ( $P < 0.05$ ). Polycyclic aromatic hydrocarbons (PAHs) account for  $9 \pm 5\%$ . The sum of MAHs, PAHs and benzonitriles, which represent the

more intensely charred fraction of Black C (Kaal *et al.*, 2009), account for  $70 \pm 21\%$ . The RET biochars show larger proportions of indenenes (indene and C<sub>1</sub>-indenenes) and benzofurans (C<sub>1</sub>- and C<sub>2</sub>-benzofurans), than the TLUD biochars ( $P < 0.05$ ). A homologous series of n-alkane/n-alkene pairs was detected in all samples except for the sawmill scrap TLUD biochar ( $11 \pm 9\%$ ). Other compounds that are based on methylene chain units, i.e. n-alkanoic acids and n-alkanoic acid methyl esters ( $3.5 \pm 7.0\%$ ), are particularly abundant in the TLUD biochar from bamboo stalk feedstock (20%).



**Fig. 4:** Total ion current chromatograms from pyrolysis-GC-MS of selected biochars. a) Original biochars. b) Hypy residues. Closed circles = n-alkanes, open circles = n-alkenes.

**Table 3:** Pyrolysis-GC-MS product groups from the biochars analysed and their relative proportions (%) of total quantified peak area (TQPA). TQPA and the benzene/toluene ratio are presented as well.

Type	Feedstock	MAH [%]	PAH [%]	ALK [%]	FA [%]	PHE* [%]	NC [%]	CARB [%]	LIG [%]	OTHER [%]	TQPA [-]	B/T [-]
Retort	Cacao chaff	38.6	4.3	25.6	0.6	12.9	14.5	0.8	0.3	2.4	2.5E+07	0.33
	Sawmill scrap	38.5	11.3	9.6	4.7	23.6	3.3	2.1	2.2	4.7	2.8E+06	0.54
	Bamboo stalk	63.0	9.9	2.1	2.1	9.9	3.7	2.9	4.0	2.3	3.9E+06	0.94
TLUD	Cacao chaff	81.2	5.7	4.8	0.0	0.0	4.0	0.0	0.0	4.4	2.5E+05	3.58
	Sawmill scrap	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.9E+04	3.10
	Bamboo stalk	22.4	17.9	15.9	20.3	10.8	2.7	2.6	3.3	4.1	5.6E+05	1.25
	Coconut husk	61.6	10.9	18.2	0.1	1.0	1.8	3.2	0.0	3.3	6.6E+05	2.48
	Orchard prunings	70.1	8.8	15.4	0.0	0.0	3.1	0.0	0.0	2.5	2.3E+05	1.51

MAH = monocyclic aromatic hydrocarbon, PAH = polycyclic aromatic hydrocarbon, ALK = n-alkanes and n-alkenes, FA = n-alkanoic acids and n-alkanoic acid methyl esters, PHE = phenols, NC = N containing compounds, CARB = carbohydrate products, LIG = lignin products, OTHER = other compounds



Pyrolysis products of lignin, which can be recognised from the methoxylic groups in guaiacols and syringols, account for  $1.2 \pm 1.7\%$ . The RET biochars have significantly larger relative proportions of guaiacols (guaiacol, 4-ethylguaiacol and C<sub>3</sub>-guaiacol). Among the RET biochars, this intact lignin is more abundant in the biochars from lignocellulosic feedstock (bamboo, 4.0%; sawmill scrap 2.2%) than in the cacao chaff (0.3%). In the TLUD biochars, lignin could only be detected in the bamboo biochar (3.3%). Considering that the methoxylic group of lignin is completely eliminated at 400–450°C even under anaerobic conditions (Kaal *et al.*, 2012a), the RET biochars were at least partially subjected to highest treatment temperatures (HTT) below that range. The presence of lignin in the bamboo stalk TLUD biochar suggests that some of the biomass was incompletely charred, as the HTT of that sample was well-above 600°C.

Phenols account for  $7.3 \pm 8.6\%$ , and are more abundant in the RET biochars ( $P < 0.05$ ). Nonetheless, the bamboo TLUD biochar also produced a significant proportion of phenols. Phenols can have multiple origins, including uncharred lignin and protein. Therefore, in the RET biochars, their precursor is unknown. Considering the presence of methoxyphenols in the bamboo TLUD biochar, the phenols probably originate from partially rearranged lignin as well (Kaal *et al.*, 2012b).

Nitrogen-containing compounds ( $4.1 \pm 4.4\%$ ) are more abundant in the cacao chaff biochars than in the other biochars, which reflects the abundance of protein in this feedstock. Benzonitrile is the unambiguous principal N-containing compound of strongly charred biomass (Kaal *et al.*, 2009). The C<sub>1</sub>-benzonitriles and indole, on the other hand, represent more weakly altered N-containing precursors, and they are enriched in the RET biochars. The same N-containing compounds were detected in the pyrolysates of chicken manure biochar (Schnitzer *et al.*, 2007).

Recognisable products of carbohydrates ( $1.5 \pm 1.4\%$ ) originate from charred polysaccharides such as cellulose and hemicellulose. Their low abundance is indicative of the thorough rearrangement of polysaccharides, which is generally known to be the most thermolabile of the main constituents of plant biomass. This also suggests that there are no uncarbonised cores in the biochars analysed (Skjemstad *et al.*, 1996). The RET biochars have significantly larger relative proportions of acetylfuran ( $P < 0.05$ ).

The benzene/toluene (B/T) ratio (Table 3) represents the degree of polycondensation of Black C samples, with high values corresponding to a higher abundance of

polycondensed aromatic clusters. The TLUD samples consist of more ( $P < 0.05$ ) polycondensed moieties represented by high B/T ratios ( $2.4 \pm 1.0$ ), even though the bamboo TLUD sample has a B/T ratio of 1.3, which is closer to the range of the RET biochar B/T ratios ( $0.6 \pm 0.3$ ). The naphthalene/methylnaphthalenes (N/C<sub>1</sub>N) ratio (Kaal *et al.*, 2009) cannot be applied as two TLUD biochars did not produce naphthalene (sawmill scrap) or methylnaphthalenes (cacao chaff).

The measure of signal intensity TQPA, varied considerably between  $5 \times 10^4$  and  $3 \times 10^7$  (Table 3). Retort biochars have significantly ( $P < 0.001$ ) higher TQPA ( $3 \times 10^6$ – $3 \times 10^7$ ) than TLUD biochars ( $5 \times 10^3$ – $7 \times 10^4$ ), which indicates that the fraction of non-pyrolisable polycondensed aromatic clusters is higher in the TLUD biochars. The theoretical relation between TQPA and the percentage of mass loss between 110°C and 750°C by thermogravimetry was confirmed by linear ( $r^2=0.58$ ,  $P < 0.01$ ) and exponential ( $r^2=0.70$ ,  $P < 0.05$ ) correlations.

### 3.6 Hypy and pyrolysis-GC-MS of hypy residues

The proportion of the organic C that remained after hypy treatment, i.e. stable polycyclic aromatic carbon (% SPAC), ranged between 16 and 50% for the RET biochars and 90–100% for the TLUD biochars (Table 4), being significantly higher in the latter ( $P < 0.001$ ). The proportion of SPAC of the sawmill scrap RET biochar is much larger (50%) than that of cacao chaff and bamboo stalk RET biochars (17–19%).

For the first time, hypy residues were analysed by pyrolysis-GC-MS to identify the nature of the residual volatiles (Fig. 4b), even though this might reflect only a minor portion of the C present after hypy. Benzene was more abundant ( $P < 0.05$ ) among the pyrolysis products of the hypy residues of TLUD biochars (11–43% RET, 43–87% TLUD), whereas C<sub>2</sub>-benzenes were more abundant in the RET biochars ( $P < 0.05$ ) (Table 4). The PAHs identified were naphthalene, methylnaphthalene, biphenyl, methylbiphenyl, phenanthrene/anthracene, fluorene, dihydroanthracene, phenyl-naphthalene and pyrene. Traces of benzonitrile could be identified in the bamboo (1.7%) and cacao (2.6%) RET biochars only. Alkylbenzenes and alkylnaphthalenes were very scarce. No other compounds were detected. These results show that the hypy efficiently removed all labile components (carbohydrates, phenols and aliphatic structures) from the biochars. In comparison with the pyrolysate compositions before hypy treatment, after hypy the proportions of benzene and PAHs, in particular that of 3 and 4 ring PAHs, increased considerably. The

B/T ratio also increased 2–18-fold. Clearly, the more condensed nature of the TLUD biochars can still be recognised after hyppy treatment.

## 4 Discussion

### 4.1 Inter-method comparison

Figure 5a shows the Factor 1–Factor 2 plot of the loadings of the selection of parameters from the different methodologies: elemental analysis ( $C_{org}$ ,  $C_{org}/N$ ,  $H/C_{org}$ ,  $O/C_{org}$ ), pH-H<sub>2</sub>O, GACS adsorption capacity, thermogravimetry (ash content,  $C_{thermo}$ ), pyrolysis-GC-MS ( $\Sigma$ (MAHs, PAHs, benzonitrile),  $\Sigma$ (lignin, carbohydrates, phenols), TQPA, B/T ratio) and hyppy (% SPAC, B/T post-hyppy). Principal component 1 (PC1) explains 57% of total variance. High positive loadings (> 0.71, i.e. > 50% of variance explained) are observed for  $H/C_{org}$ ,  $O/C_{org}$ ,  $C_{thermo}$ ,  $\Sigma$ (lignin, carbohydrates, phenols) and TQPA. This set of parameters reflects the abundance of labile components of the biochars. Strong negative loadings are observed for  $C_{org}$ , GACS adsorption capacity, B/T (pre- and post-hyppy),  $\Sigma$ (MAHs, PAHs, benzonitrile) and % SPAC. These parameters reflect the degree of aromatisation, aromatic polycondensation and surface area. Clearly, PC1 is indicative of the degree of thermochemical alteration (DTA), with negative values corresponding to more strongly altered biomass. With increasing DTA, there is a progressive conversion into a microporous network of polyaromatic clusters, independent of the feedstock used. The rationale for the link between this process and the outcome of the methodologies applied is as follows: (1) with increasing DTA, there is a progressive elimination of func-

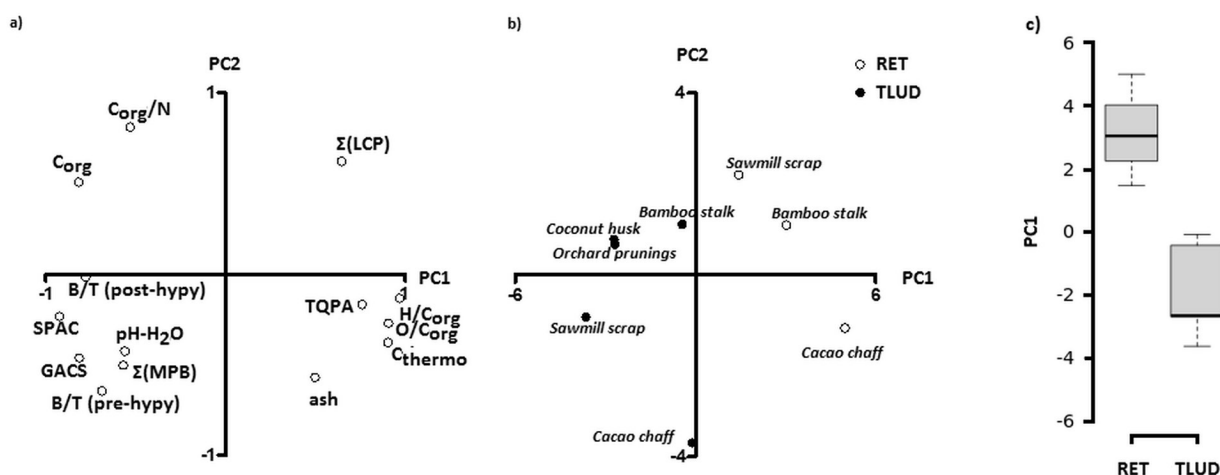
tional groups and accumulation of the C-dominated aromatic clusters, which explains the positive loadings of  $H/C_{org}/N$  and  $O/C_{org}$  and negative loading of  $C_{org}$  and, qualitatively, the elimination of non-aromatic bands in the FTIR spectra. (2) Obviously, with increasing DTA, the thermal stability measured by thermogravimetry increases, hence the positive loading of  $C_{thermo}$ . (3) The polyaromatic clusters that accumulate with increasing DTA are well-known to be responsible for the surface area of biochars, which explains the negative loading of the GACS adsorption capacity. Furthermore, more complete burnout of volatiles with increasing DTA will have contributed to the enhanced adsorption capacity. (4) With increasing DTA, the susceptibility of the biochar to analytical pyrolysis decreases, and therefore TQPA has a positive loading. The B/T ratio, on the other hand, is inverse to the abundance of alkyl-cross bridges between aromatic groups, which are progressively eliminated with increasing DTA, hence B/T has a negative loading on PC1. Considering the large differences in DTA between the biochars, it is not surprising that most variables are related to DTA, which also turned out to control most biochar properties in other characterisation studies (Zhao *et al.*, 2013, and references therein). Moreover, the degree of aromatic polycondensation, reflected by DTA, was the controlling factor in biochar stability after soil amendment (Kuz'yakov *et al.*, 2014) and laboratory ageing experiments (Mašek *et al.*, 2013).

The main source of variation in DTA is the difference between the RET and TLUD biochars: the RET samples have positive scores on PC1 (1.5–5.0), while the TLUD biochars have negative scores (-0.1– -3.6) (Fig. 5b). The RET-derived biochars more closely resemble the nature of the feedstock than the TLUD-derived biochars, be-

**Table 4:** Proportion of hydrogen pyrolysis (hyppy)-resistant stable polycyclic aromatic carbon (SPAC) and the composition of the pyrolysates obtained PY-GC-MS of the hyppy residue.

Type	Feedstock	SPAC [% C <sub>t</sub> ]	MAH [%]	PAH [%]	BN [%]	B/T [-]
Retort	Cacao chaff	19.2	43.0	54.4	2.6	5.6
	Sawmill scrap	49.9	54.4	45.6	0.0	5.3
	Bamboo stalk	16.8	20.7	77.6	1.7	1.7
TLUD	Cacao chaff	97.6	53.1	46.9	0.0	6.7
	Sawmill scrap	103.2	86.1	13.9	0.0	22.1
	Bamboo stalk	89.6	69.2	30.8	0.0	5.7
	Coconut husk	91.8	72.7	27.2	0.1	13.2
	Orchard prunings	102.2	91.0	9.0	0.0	27.3

MAH= monocyclic aromatic hydrocarbon, PAH = polycyclic aromatic hydrocarbon, BN = benzonitrile, B/T = benzene/toluene ratio.



**Fig. 5:** Principal component analysis of selected parameters. a) PC1 and PC2 loadings (B/T = benzene toluene ratio; before and after hyppy);  $\Sigma(MPB)$  = sum monocyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons and benzonitrile;  $\Sigma(LCP)$  = sum lignin, carbohydrates and phenols; GACS = adsorption capacity; SPAC = stable polycyclic aromatic carbon;  $C_{thermo}$  = thermolabile C. b) PC1 and PC2 scores of the retort and TLUD biochars. c) Boxplot of the PC1 scores of the retort and TLUD biochars.

cause the TLUD stove conditions induce a higher DTA to the feedstock. As such, using thermogravimetry, the RET biochars have larger proportions of  $C_{thermo}$  and, using FTIR, the RET biochars show more extensive O-containing functional groups (mostly -OH and -OCH<sub>3</sub>), which is corroborated by the presence of phenols from moderately charred lignin and methoxyphenols from non- and weakly-charred lignin in lignocellulose-derived biochars, and evidence of intact peptide material in the cacao chaff-derived RET biochar. On the other hand, the TLUD biochars are composed primarily of clusters of polycondensed aromatic structures, which explain their higher SPAC content, GACS adsorption capacity, B/T ratio and low  $C_{thermo}$  and TQPA values. Apart from the difference in PC1 scores between RET and TLUD biochars, it is worth mentioning that the sawmill scrap RET biochar seems to have been subjected to higher DTA than the other RET biochars, as evidenced by the intermediate PC1 scores,  $H/C_{org}$  and % SPAC levels.

PC2 (22% of total variance) has a large positive loading for  $C_{org}/N$  and moderate positive loadings for  $C_{org}$  and  $\Sigma$ (lignin, carbohydrates, phenols), whereas negative loadings correspond to ash content, GACS adsorption capacity and the B/T ratio. The cacao-derived biochars have the highest negative scores on PC2. In combination with the strong loadings of  $C_{org}/N$ , this suggests that PC2 reflects the influence of feedstock type, in particular its N content.

There are several observations that cannot be fully explained from DTA and the contrast between TLUD and

RET biochars. Firstly, the pyrolysis-GC-MS pyrolysate of the bamboo TLUD biochar is a clear outlier as it contains traces of lignin and n-alkanoic acids, which are thermolabile above 400–450°C (Kaal *et al.*, 2012a,b), yet this sample is predominantly composed of polycondensed aromatic structures, evidenced by the high GACS adsorption capacity and SPAC content. Hence, this biochar must contain a fraction of biomass that was incompletely charred, possibly isolated in a corner of the TLUD barrel or within larger fragments of bamboo feedstock. This minor proportion of weakly and non-charred biomass will cause strongly biased results by pyrolysis-GC-MS because of the different thermal stabilities (and therefore pyrolysabilities) of the two components. It is probably reflected in the corresponding DTG curve at 250°C (Fig. 2b).

Secondly, the N content of the biochars is very low, with the exception of the cacao chaff biochars, which can be explained by their high protein content. As expected, the sum of N-containing pyrolysis products by pyrolysis-GC-MS is correlated to N content ( $P < 0.001$ ) and inverse to the C/N ratio ( $P < 0.05$ ), but also inverse to  $C_{thermo}$  ( $P < 0.05$ ), which might suggest that N functionalities in general and/or the cacao chaff biochars have a higher proportion of thermolabile material. The relatively thermolabile nature of even strongly carbonised N moieties (evidenced by benzonitrile) is in agreement with Sigua *et al.* (2014) who found that biochars from N-rich feedstocks (manures) were mineralised faster than lignocellulose-derived biochars.

The methodologies applied allowed for a detailed assessment of the organic matter present in the biochars analysed. All evidence combined, the  $H/C_{org}$  and SPAC seem to be the most reliable parameters to determine DTA of biochar, which is related directly to biochar stability. The pyrolysis-GC-MS results were in agreement with these parameters, but overestimate the abundance of labile biochar components for biochars with apparently heterogeneous HTT, which calls for cautious interpretation. Nonetheless, pyrolysis-GC-MS is the method that gives the most detailed information on the molecular properties of the biochars. Thermogravimetry allowed for correcting the elemental analysis data for  $C_{inorg}$ , which is essential to calculate the  $H/C_{org}$ . In addition, it provides an indication of the abundance of labile structures. FTIR data could not be quantified and in this case FTIR appeared less useful for biochar characterisation. The GACS adsorption test provides a useful and cost-efficient estimation of effective surface area.

#### 4.2 Detailed biochar characterisation

**RET biochars.** The cacao chaff biochar has a high N content some of which corresponds to intact proteins, which suggests that it may have beneficial short-term impacts on soil productivity (Jeffery *et al.*, 2011). Because of its high ash content it could be suitable for local application in cacao plantations, which require ash-rich biochars (Chepote *et al.*, 2007; Hojah da Silva, 2013). However, this biochar has very low DTA and adsorption capacity, which implies that it will probably be degraded to a significant extent after implementation into soil and that it is probably of limited use for water and nutrient retention as well. The sawmill scrap biochar has the highest C and SPAC contents, the lowest proportion of  $C_{thermo}$  and strongest GACS adsorption capacity, which implies that it is probably the most stable biochar after soil amendment and has a strong water and nutrient retention. The large proportion of  $C_{thermo}$ , small SPAC and low DTA suggest that the bamboo stalk biochar consists mainly of labile components which limits its potential as a long-term soil enhancement. This biochar has the lowest adsorption capacity, the lowest pH-H<sub>2</sub>O and high  $C_{org}/N$  ratio, suggesting that this biochar is not efficient in liming or improvement of the adsorption complex neither.

**TLUD biochars.** The biochar from cacao chaff has a very large SPAC content (98%) and a pyrolysis-GC-MS fingerprint typical of biochars with high DTA (dominated by MAHs and PAHS). By contrast, the relatively large proportion of  $C_{thermo}$  (33%) suggests that a significant fraction of this biochar might be susceptible to degradation, which implies that there remains uncertainty

on its stability of this biochar. The N-rich nature of the feedstock is reflected by the low  $C_{org}/N$  and abundance of benzonitrile. The TLUD biochars from sawmill scrap, coconut husk and mixed orchard prunings have high GACS adsorption capacity and consist almost completely of polyaromatic domains, with very little thermolabile material ( $C_{thermo}$  12–15%, SPAC 92–103%). These biochars may be expected to be resistant to degradation and increase a soil's adsorption capacity on the long-term. Finally, the high SPAC,  $C_{org}$ , B/T and adsorption capacity, in combination with the small proportion of  $C_{thermo}$  (16%), suggests that the bamboo biochar has high stability and adsorption capacity. However, this biochar also contains incompletely charred organic matter (aliphatic material and traces of lignin and carbohydrates). It has the highest  $C_{org}/N$  ratio of the biochars analysed (150) and, following Haefele *et al.* (2011), such biochars should be preferably applied to poor and sandy soils. This would also apply to the other biochars, except for the cacao RET and TLUD biochars.

## 5 Conclusions

The methods applied here, and particularly the combination of GACS, thermogravimetry, elemental analysis, hpy and pyrolysis-GC-MS, are complementary as their cross-comparison allowed for a better understanding of the results from each of them individually. The retort biochars were subjected to a lower degree of thermochemical alteration (DTA) than the TLUD biochars. From the statistical assessment of all data by PCA, the properties that reflect DTA become more pronounced in the order: Cacao RET < Bamboo RET < Sawmill scrap RET < Cacao TLUD < Bamboo TLUD < Coconut TLUD < Orchard prunings TLUD < Sawmill scrap TLUD. In general, the TLUD biochars have greater stability and adsorption capacity, suggesting that their potential as a C sink and long-term sponge for water and nutrients exceed that of the RET biochars. On the other hand, and in addition to a limited retention capacity, the RET biochars contain labile material that might act as a nutrient source. In addition, the RET biochars have appeared excellent cooking fuels.

### Acknowledgements

We thank Carmen Pérez Llaguno (Department of Soil Science, University of Santiago de Compostela) and Aida González Pazos (IR-Raman facility of the RI-AIDT, University of Santiago de Compostela) for analytical services. We thank Walter Rodríguez for the facilities offered at the APPTA fair trade plant (Tala-

manca, Costa Rica), Gabriela Soto, Tamara Benjamin (CATIE) and Kate Selting (Seachar) for their generous support, and two anonymous reviewers for their valuable comments.

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