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- 1 Influence of pyrolysis temperature and production unit on formation of
- 2 selected PAHs, oxy-PAHs, N-PACs, PCDDs, and PCDFs in biochar A
- 3 screening study
- 4 Eva Weidemann¹, Wolfram Buss², Mar Edo¹, Ondřej Mašek², Stina Jansson^{1*}
- 5 ¹Department of Chemistry, Umeå University, Umeå, Sweden
- 6 ² UK Biochar Research Centre, School of GeoSciences, University of Edinburgh, Edinburgh, UK
- 7 *Corresponding author:
- 8 Stina Jansson
- 9 Department of Chemistry
- 10 Umeå University
- 11 SE-901 87 Umeå, Sweden
- 12 Phone: +46 90 7867622
- 13 E-mail: stina.jansson@umu.se

14 Abstract

15 The influence of reactor type and operating conditions of the pyrolysis unit on the final concentration of toxic contaminants in biochar remains unclear. Therefore, we determined the concentrations of polycyclic 16 17 aromatic hydrocarbons (PAHs), oxygenated polycyclic aromatic hydrocarbons (oxy-PAHs), nitrogen-18 containing polycyclic aromatic compounds (N-PACs), polychlorinated dibenzo-p-dioxins (PCDDs), and 19 dibenzofurans (PCDFs) in biochars produced from three different feedstocks (softwood, wheat straw, and 20 anaerobic digestate). Different-scaled pyrolysis units (one batch and two continuous units) at two different 21 temperatures (550 °C and 700 °C) were considered. The results revealed that the type of biomass had a 22 significant influence on the PAH, oxy-PAH, and N-PAC content of the biochars. The configuration and type of the pyrolysis unit influenced only the wheat straw pyrolyzed at 550 °C. PCDDs and PCDFs occurred at very 23 low levels in the biochars. In terms of PAH, PCDD, and PCDF content, the biochars assessed in this study 24 25 represent a low risk to the environment, regardless of the temperature and type and size of the pyrolysis 26 unit. 27 28 29 30 31

32 Keywords

33 Polychlorinated dibenzo-*p*-dioxin; polychlorinated dibenzofuran; polycyclic aromatic hydrocarbons;

- 34 oxygenated polycyclic aromatic hydrocarbons; nitrogen-containing polycyclic aromatic compounds.
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41 Introduction

During pyrolysis, materials undergo thermochemical decomposition at temperatures above 300 °C in an oxygen-limited environment. The yield and chemical composition of the resulting pyrolysis products vary with the characteristics of the feedstock and the process variables, e.g., heating rate and residence time of the process (Mohan et al. 2006; Zhao et al. 2013). To date, the liquid and gas fraction has been the most analyzed pyrolysis product. However, biochar from lignocellulosic biomass has gained significant attention due to its properties and potential use in environmental and agricultural applications (e.g. as soil amendment and replacement for or supplement to activated carbon (Lehman and Joseph 2009)).

49 Thermal decomposition of biomass yields a complex mixture of condensable hydrocarbons, i.e. tar, which 50 consists of single- to five-ring aromatics, phenolic compounds, and complex polycyclic aromatic 51 hydrocarbons (PAHs) (Wolfesberger et al. 2009). The tar-like products are highly branched at moderate 52 temperatures (~500 °C) (Pakdel and Roy 1991), but (in general) highly condensed and less oxygenated at 53 high temperatures (>700 °C) (Elliott 1986; Baker and Elliott 1986). Oxygenated-PAHs (oxy-PAHs) and 54 nitrogen-containing heterocyclic polycyclic aromatic compounds (N-PACs), which typically occur as PAH co-55 pollutants in soils and groundwater (Lundstedt et al. 2003; Arp et al. 2014), display similar toxicity to PAHs 56 (Andersson et al. 2015). Therefore, oxy-PAHs should be considered for inclusion in biochar regulations. Oxy-57 PAHs may form through either biological, chemical or photo-oxidation (Andersson et al. 2015) or catalytic transformation of PAHs (Nielsen 1999), whereas N-PACs form via pyrolysis of lignocellulose materials and 58 59 sewage (Britt et al. 2002). N-PACs have been reported from the pyrolysis of sewage sludge (Fullana et al. 60 2003) During thermochemical processes, PAHs (Weber et al. 2001) and oxy-PAHs (Hajizadeh et al. 2011) may also act as precursors for the formation of chlorinated aromatics, such as polychlorinated dibenzo-p-61 62 dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs).

Biochar intended for soil application must fulfill certain property- and composition-related requirements,
to prevent harm to the ecosystem (Buss and Mašek 2014). Therefore, several guidelines with suggested
threshold values for contaminants (including PAHs, PCDDs or PCDFs) in biochar have been established, and
the importance of contaminant analysis has been emphasized (British Biochar Foundation 2014;
International Biochar Initiative 2015; European Biochar Foundation 2016).

Biochars with low concentration of contaminants may be achieved by selecting suitable feedstocks and
controlling the operating conditions in the pyrolysis unit. Therefore, knowledge of the variation in different
process variables associated with different pyrolysis units is essential for producing high-quality biochar.
However, a relationship between the pyrolysis temperature and the concentration of PAH in biochar

remains elusive (Freddo et al. 2012; Hale et al. 2012; Kloss et al. 2012; Devi et al. 2015).Buss et al. (2016-a) have attributed this to a simultaneous increase in PAH formation and evaporation from the biochar with increasing temperature. The influence of the scale, reactor type, and configuration of the pyrolysis unit on the PAH concentration of the biochar remains unclear. In addition, the concentration of chlorinated organics in biochar has rarely been assessed (Hale et al. 2012; Wiedner et al. 2013), and to the best of our knowledge the concentrations of oxy-PAH and N-PAC in biochars have yet to be reported.

In this study, we evaluate organic contaminants (PCDD, PCDF, PAH, oxy-PAH, and N-PAC) found in biochars from different biomass materials treated in different types of pyrolysis units. Three different feedstocks (softwood pellets, wheat straw pellets, and anaerobic digestate) were pyrolyzed at two different temperatures (550 °C and 700 °C), using three pyrolysis setups (one batch and two continuous units) of different scales.

83

84 Materials and methods

85 Feedstocks

The biochars were produced from three different types of biomass: commercial softwood (pine and spruce)
pellets (Premium Puffin, Puffin Pellets); commercial wheat straw pellets (Agripellets Ltd.), and anaerobically
digested sewage sludge (AD) from water-treatment works. The characterization of these feedstocks,
proximate and ultimate analysis, are shown in Table 1.

90

91 Pyrolysis experiments

92 The pyrolysis experiments were conducted in three different pyrolysis reactors (one batch reactor and two 93 continuous reactors) located at the UK Biochar Research Centre (UKBRC), University of Edinburgh. Key 94 characteristics of the units are presented in Table 2 and further details can be found in the referenced 95 articles.

An overview of the performed pyrolysis experiments and the collected samples is provided in Table 3. In the two continuous reactors (Stage II (Buss et al. 2016-b) and III (Buss and Mašek 2014)), mean residence times of 20 min were applied for all materials. The residence time was estimated by establishing first the temperature profile of the biomass/char bed along the rotary kiln reactor (Stage III, Table 2) as well as the residence time distribution of particles in the reactor. Based on this information, the corresponding heating rate experienced by particles in the reactor and their residence time at the peak temperature were calculated. Therefore, while the mean residence time of particles in continuous reactor was 20 minutes, the

residence time at peak temperature was only between 5–10 minutes, depending on the material used. Thus, obtained parameters were then used as settings in the batch reactor to reproduce the conditions in the continuous pyrolysis unit as closely as possible. In the Stage I reactor (Crombie et al., 2013), the retention time at the highest treatment temperature was adapted to reflect the retention times in the heated areas of the furnace of the continuous reactors. Therefore, softwood was exposed for 10 min (each) to temperatures of 550 °C and 700 °C, whereas wheat straw was exposed for 5 min and 6 min, respectively.

109

110 Sample extraction and cleanup

We determined the fraction of 16 EPA priority PAHs (US EPA, 2015), eleven oxy-PAHs (Arp et al. 2014;
Andersson et al. 2015), four N-PACs (Arp et al. 2014), PCDDs, and PCDFs (homolog sums and WHO₂₀₀₅-TEQ)
(Van den Berg et al. 2006)) occurring in biochars and liquid samples. The target PAHs, oxy-PAHs, and N-PACs
are listed in Table 4.

115 The chars were extracted, at 150 °C, via pressurized liquid extraction (Dionex 350, Thermo Fisher Scientific, 116 Waltham, USA) using toluene of analytical grade quality (Fluka, ≥99.7%), following the procedure outlined 117 by Gao et al. (2015). The liquid fraction was extracted via liquid/liquid extraction using n-hexane. For PCDD 118 and PCDF analysis, the extracts were all cleaned-up using a multi-layer silica column followed by 119 fractionation with an AX-21 carbon/celite column (see Liljelind et al. (2003) for further details of the 120 method). For analysis of PAHs, oxy-PAHs, and N-PACs in the char samples, clean-up was conducted using 121 open columns containing 5 g KOH-silica, eluted with dichloromethane. The clean extracts were 122 concentrated to ~1 mL of toluene. The liquid samples were cleaned via the same procedure, using n-hexane 123 (rather than dichloromethane) as the eluent. Further details of the method for PAH, oxy- PAH, and N-PAC 124 analysis are provided elsewhere (Arp et al. 2014). All samples were single samples.

125

126 Instrumental analysis

The analyses were all performed on a GC-HRMS – Hewlett-Packard 5890 gas chromatograph (Agilent Technology, Santa Clara, USA) coupled to an Autospec Ultima Mass Spectrometer (Waters Corporation, Milford, USA), using a DB5 column (60 m: length, 0.32 mm: internal diameter, 25 μm: film thickness) (Agilent Technology, Santa Clara, USA). The main purpose of using HRMS was to make it possible to separate oxy-PAHs from PAHs, and the method used was previously described by Arp et al. (2014). The mass spectrometer was operated in electron impact ionization/selected ion-monitoring mode and analytes were quantified using the isotope dilution technique. PAHs, oxy-PAHs, and N-PACs were identified by comparing retention times to quantification congeners in the reference standard, while PCDD and PCDF werecompared with published GC-MS chromatograms (Ryan et al. 1991; Bacher et al. 1992).

136

137 QA/QC

All laboratory work was performed using validated methods, and laboratory blanks were extracted with the samples and treated as samples (i.e., single samples) throughout the clean-up process. The reported concentrations (signal-to-noise ratio: 10) were all higher than the limit of quantification (LOQ). For all reported concentrations, blank concentrations were below five times sample concentrations. Due to this cutoff, Acenaphthylene was removed from the reported results due to analytical uncertainties.

143

144 Results and discussion

145 PAHs in the biochars

The total PAH concentrations measured in the biochars varied considerably, from 0.82 to 19.6 $\mu g \cdot g_{biochar}^{-1}$, 146 147 and seemed to be largely influenced by the feedstock type. This is particularly striking for concentrations in 148 the three biochars produced at 550 °C (Fig. 1). For the same pyrolysis unit, the PAH concentrations of the 149 wheat straw-derived biochars were (in some cases) almost seven times higher than those obtained from 150 the softwood feedstock. The PAHs in biochars from all three feedstocks consisted mainly of two- and three-151 ring species, regardless of the pyrolysis temperature and unit scale. Furthermore, multi-ringed species, i.e., 152 four- to six-ringed PAHs, occurred more abundantly in the wheat straw-derived biochar than in the other feedstocks. However, consistent with a previous study (Keiluweit et al. 2012), wheat straw-derived biochars 153 154 produced at 700°C contained higher concentrations of PAHs than those produced at 550°C. The unit size 155 had a substantial impact on PAH formation only for wheat straw pyrolyzed at 550 °C, where PAH formation 156 was positively correlated with the unit size.

The International Biochar Initiative (IBI) guidelines have established threshold values, 6 and 300 μ g·g_{biochar}⁻¹, lower and upper limit respectively, for the total PAH concentration of biochar (see Fig. 1) (International Biochar Initiative, 2015). The PAH concentrations of the softwood-derived biochars were all less than the lower limit (6 μ g·g_{biochar}⁻¹), regardless of the pyrolysis temperature and the type and size of the unit . All biochars produced in this study meet the IBI PAH standards, and are thereby considered safe for use as soil amendments; softwood yielded the biochar with the lowest potential risk for PAH-related effects.

163

164 Oxygenated-PAHs and N-PACs in the biochars

165 Oxy-PAHs and N-PACs occurred at detectable levels in all biochars, but the corresponding concentrations 166 were lower than those of the PAHs (Fig. 2). The total oxy-PAH and N-PAC concentrations ranged from 34 to 3100 ng·g_{biochar}⁻¹ and 0.4 to 477 ng·g_{biochar}⁻¹, respectively. The oxy-PAHs and N-PACs consisted mainly of 167 168 three-ringed species, and slightly higher concentrations of the multi-ringed oxy-PAH species were 169 generated during wheat-straw pyrolysis than during softwood pyrolysis. As in the case of PAHs, compared 170 with the pyrolysis reactor size the feedstock exerted a larger influence on oxy-PAH formation. Furthermore, 171 the reactor size had a substantial impact only on the oxy-PAH concentration in the biochar generated from 172 wheat straw pyrolyzed at 550 °C. The highest concentration of oxy-PAH, which was more than 18 times 173 higher and almost 6 times higher than those of softwood and wheat straw, respectively, was generated 174 during Stage 1 pyrolysis (at 550 °C) of anaerobic digestate. In this case, the elevated oxy-PAH concentrations are attributed to the composition of the digestate feedstock, which differs from those of the other two 175 176 feedstocks.

177 The highest concentration (477 ng·g_{biochar}⁻¹) of N-PACs occurred in wheat straw (rather than the anaerobic digestate) pyrolyzed at 550 °C (Stage II), despite the anaerobic digestate having higher total N content than the wheat straw (Table 1). This possibly indicates that not total content, but actual N speciation (organic/inorganic) dictates the formation magnitude of the N-PAC species. Discussion on the toxicity of oxy-PAHs and N-PACs is ongoing, and therefore threshold values for these compounds in biochar are lacking (Andersson et al. 2015).

183

184 Distribution of PAH, oxy-PAH, and N-PAC between biochar and the liquid fraction in Stage I (SI)

The liquid fraction, which was only collected from Stage I (batch reactor, Table 2), constituted 44-49% of 185 186 the total product yield of the pyrolysis process (Table 3). The distribution of PAH, oxy-PAH, and N-PAC 187 between the biochar and liquid fraction showed that these products occurred mainly in the liquid fraction. 188 In figure Fig. 3 the concentrations of PAH and oxy-PAH is shown. For example, the PAH concentration of the 189 liquid fraction ranged from 28.6 to 351 $\mu g \cdot g^{-1}$ while the concentrations of biochar were 1.7 to 5.6 $\mu g \cdot g^{-1}$ 190 making the concentration in the liquid 5–140 times larger than in the char. The distribution of the PAH and 191 oxy-PAH in the liquid fraction tended to be lighter species, with less rings, compared to the char. All six-192 ringed PAHs the liquid samples were below LOQ, N-PAC concentrations in the liquid fraction were compared 193 to the PAH and oxy-PAH concentrations too low to be included in the Fig 3, but except for wheat straw 194 pyrolyzed at 550 °C, 80 % or more of the total N-PAC were found in the liquid fraction. For the wheat straw 195 sample equal amounts were found in both liquid and char. Fagernäs et al. (2012) found that 62%, 37%, and only 0.6% of the PAHs occurred in the tars, gases, and the char, respectively. We did not measure the PAH
concentration of the gases, but found that a considerably higher amount of PAHs occurred in the pyrolysis
liquids than in the solids/char (PAH content of the solids: 0.3–9.3%). This demonstrates that PAH separation
from char, via evaporation, is very effective. However, to prevent PAH deposition onto the biochar, contact
between pyrolysis vapors (liquids and gases) and char in the very cold sections of the pyrolysis unit must be
avoided.

Regardless of the operating conditions during the softwood and wheat straw runs, the PAH, oxy-PAH, and N-PAC content of the biochars decreased with increasing pyrolysis temperature, whereas the PAH content of the liquid fraction increased. These results suggest that although pyrolysis at 700 °C yields more PAHs (than pyrolysis at 550 °C), this process can generate biochars with lower levels of these potentially toxic compounds, as most PAHs evaporate from the char.

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208 Polychlorinated dibenzo -p-dioxins and furans

209 Consistent with a previous study (Wiedner et al. 2013), the results from this screening study showed that extractable polychlorinated aromatics species occur at almost negligible levels in the biochar matrix. Some 210 211 PCDDs and PCDFs in the biochar, although detectable, were non-quantifiable (LOQ_{PCDF}: 0.2 pg·g_{biochar}⁻¹, LOQ_{PCDD}: 0.3 pg·g_{biochar}⁻¹). Monochlorinated dibenzofuran (MoCDF) was the only homolog that occurred with 212 concentrations exceeding blank concentrations by some margin (defined as blank concentration times five), 213 214 and this occurred in only seven of the thirteen biochars. Formation of MoCDF occurred more easily (and 215 was therefore favored) at lower pyrolysis temperature and at larger pyrolysis unit (Stage II and Stage III) 216 (data not shown), than at high pyrolysis temperatures and smaller scale. However, quantification of mono-217 to trichlorinated dioxins and furans in the liquid fraction was prevented by considerable matrix interference. 218 Similarly, highly chlorinated congeners (hepta- and octachlorinated dioxins and furans) in the liquid fraction 219 obtained from softwood and anaerobic digestate at 550 °C were non-quantifiable (LOQ 4 pg·g_{biochar}⁻¹).

As the potential concentration of toxic PCDD and PCDF congeners in the biochars could not be calculated, approximate values were obtained by assigning to each congener a concentration equal to the LOQ values. Using this criterion, maximum concentrations of 0.6–0.9 pg_{TEQ} . $g_{biobiochar}$ -1, which are slightly higher than TEQ concentrations reported for biochars generated from slowly pyrolyzed biomass (Hale et al. 2012), are expected for the toxic components of the biochars. The estimated worst-case TEQ concentrations are lower than the PCDD and PCDF threshold (17 pg_{TEQ} . $g_{biochar}$ -1) established by IBI for biochars that will be used as soil amendment (International Biochar Initiative, 2015). As in the case of PAHs, regardless of the temperature, configuration or size of the pyrolysis unit, the biochars are expected to have low environmental impactwhen used for soil-improvement purposes.

Using LOQ concentrations yielded an estimated worst-case TEQ concentration of ~1 pg_{TEQ} · $g_{biochar}$ -1 for the liquid fraction.

231 Conclusions

The influence of temperature and type/size of the pyrolysis unit on the concentration of four groups of toxic contaminants was evaluated in biochars from three different biomass feedstocks representing three major types of biomass, namely: forestry and agricultural residues, and organic waste. The results revealed that the type of biomass has a significant influence on the concentration of PAH, oxy-PAH, and N-PAC; the configuration and type/size of the pyrolysis unit have a significant effect only on wheat straw pyrolyzed at 550 °C.

238 This study represents the first-ever investigation where the content of oxy-PAH and N-PAC contaminants in 239 biochars is determined. The results showed that in all cases this content is considerably lower than the PAH 240 concentration. Regardless of the pyrolysis temperature, the PAH, oxy-PAH, and N-PAC concentrations were 241 much higher in the liquid fraction compared to the char fractions. The PDCCs and PCDFs occurred at 242 negligible levels in the studied biochars. Moreover, in terms of PAH, PCDD, and PCDF content, and 243 regardless of the temperature and pyrolysis unit, the biochars are expected to have low negative 244 environmental impact related to these contaminants when used for soil amendment. This demonstrates 245 that biochar with extremely low content of organic pollutants can be produced from a range of materials 246 and by using various technologies, which is an important milestone on the way to widespread biochar 247 deployment and commercialization.

248

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254

255 References

Andersson JT, Achten C (2015) Time to say goodbye to the 16 EPA PAHs? Toward an up-to-date use of
 PACs for environmental purposes. Polycyc Aromat Comp 35

259 Arp HPH, Lundstedt S, Josefsson S, Cornelissen G, Enell A, Allard A-S, Kleja DB (2014) Native Oxy-PAHs, N-260 PACs, and PAHs in historically contaminated soils from Sweden, Belgium, and France: their soil-porewater 261 partitioning behavior, bioaccumulation in Enchytraeus crypticus, and bioavailability. Environ Sci Technol 262 48:11187-11195 263 264 Bacher R, Swerev M, Ballschmiter K (1992) Profile and pattern of monochloro- through 265 octachlorodibenzodioxins and -dibenzofurans in chimney deposits from wood burning. Environ Sci Technol 266 26:1649-1655 267 268 Baker EG, Elliott DC (1986) Catalytic hydrotreating of biomass-derived oils, Pacific Northwest Lab., 269 Richland, WA (USA) 270 271 British Biochar Foundation (2014) Biochar quality mandate Version 1.0 272 273 Britt PF, Buchanan AC, Owens Jr CV, Skeen JT (2002) Formation of nitrogen containing polycyclic aromatic 274 compounds from the CO-pyrolysis of carbohydrates and amino acids, in: ACS Division of Fuel Chemistry, 275 Preprints, pp. 400-403 276 277 Buss W, Graham MC, MacKinnon G, Mašek O (2016-a) Strategies for producing biochars with minimum 278 PAH contamination. J Anal Appl Pyrol 119:24–30 279 280 Buss W, Graham MC, Shepherd JG, Mašek O (2016-b) Suitability of marginal biomass-derived biochars for 281 soil amendment. Sci Total Environ 547:314-322 282 283 Buss W, Mašek O (2014) Mobile organic compounds in biochar - a potential source of contamination -284 phytotoxic effects on cress seed (Lepidium sativum) germination. J Environ Manage 137:111–119 285 286 Crombie K, Mašek O, Sohi SP, Brownsort P, Cross A (2013) The effect of pyrolysisconditions on biochar 287 stability as determined by three methods. GCB Bioenergy 5:122–131 288 289 Devi P, Saroha AK (2015) Effect of pyrolysis temperature on polycyclic aromatic hydrocarbons toxicity and 290 sorption behaviour of biochars prepared by pyrolysis of paper mill effluent treatment plant sludge. 291 Bioresource Technol 192:312-320 292 293 Elliott DC (1986) Analysis and comparison of biomass pyrolysis/gasification condensates: final report, in: 294 Pacific Northwest Lab., Richland, WA (USA), Medium: ED; Size: Pages: 100 295 296 European Biochar Foundation (2016) European biochar certificate - guidelines for a sustainable production 297 of biochar, in: http://www.europeanbiochar.org/en/download 298 299 Fagernäs L, Kuoppala E, Simell P (2012) Polycyclic aromatic hydrocarbons in birch wood slow pyrolysis 300 products. Energ Fuel 26:6960-6970 301 Freddo A, Cai C, Reid BJ (2012) Environmental contextualisation of potential toxic elements and polycyclic 302 aromatic hydrocarbons in biochar. Environ Pollut 171:18-24 303 304 Fullana A, Conesa JA, Font R, Martín-Gullón I (2003) Pyrolysis of sewage sludge: nitrogenated compounds 305 and pretreatment effects. Journal of Analytical and Applied Pyrolysis, 68, 561-575.

Gao Q, Haglund P, Pommer L, Jansson S (2015) Evaluation of solvent for pressurized liquid extraction of PCDD, PCDF, PCN, PCBz, PCPh and PAH in torrefied woody biomass. Fuel 154:52–58. Hajizadeh Y, Onwudili JA, Williams PT (2011) PCDD/F formation from oxy-PAH precursors in waste incinerator flyash. Chemosphere 85:1672–1681 Hale SE, Lehmann J, Rutherford D, Zimmerman AR, Bachmann RT, Shitumbanuma V, O'Toole A, Sundqvist KL, Arp HPH, Cornelissen G (2012) Quantifying the total and bioavailable polycyclic aromatic hydrocarbons and dioxins in biochars. Environ Sci Technol 46:2830–2838 International Biochar Initiative (2015) Standardized product definition and product testing guidelines for biochar that is used in soil Version 2.1 Keiluweit M, Kleber M, Sparrow MA, Simoneit BRT, Prahl FG (2012) Solvent-extractable polycyclic aromatic hydrocarbons in biochar: influence of pyrolysis temperature and feedstock. Environ Sci Technol 46:9333-Kloss S, Zehetner F, Dellantonio A, Hamid R, Ottner F, Liedtke V, Schwanninger M, Gerzabek MH, Soja G (2012) Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties. J Environ Qual 41:990–1000 Lehmann JJ, Joseph S (2009) Biochar for environmental management: science and technology Liljelind P, Söderström G, Hedman B, Karlsson S, Lundin L, Marklund S (2003) Method for multiresidue determination of halogenated aromatics and PAHs in combustion-related samples. Environ Sci Technol 37:3680-3686 Lundstedt S, Haglund P, Öberg L (2003) Degradation and formation of polycyclic aromatic compounds during bioslurry treatment of an aged gasworks soil. Environ Toxicol Chem 22:1413–1420 Mohan D, Pittman CU, Steele PJ (2006) Pyrolysis of wood/biomass for bio-oil: a critical review. Energ Fuel 20:848-889 Nielsen T, Feilberg A, Binderup ML (1999) The variation of street air levels of PAH and other mutagenic PAC in relation to regulations of traffic emissions and the impact of atmospheric processes. Environ Sci Pollut Res 6:133–137 Pakdel H, Roy C (1991) Hydrocarbon content of liquid products and tar from pyrolysis and gasification of wood. Energ Fuel 5:427–436 Ryan JJ, Conacher HBS, Panopio LG, Lau BPY, Hardy JA, Masuda Y (1991) Gas chromatographic separations of all 136 tetra- to octapolychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans on nine different stationary phases. J Chromatogr A 541:131–183 US EPA (2015) Code of federal regulations, Appendix A to 40 CFR, Part 423, Priority pollutants, in: U.S. EPA

Van den Berg M, Birnbaum LS, Denison M, De Vito M, Farland W, Feeley M, Fiedler H, Hakansson H,
 Hanberg A, Haws L, Rose M, Safe S, Schrenk D, Tohyama C, Tritscher A, Tuomisto J, Tysklind M, Walker N,
 Peterson RE (2006) The 2005 World Health Organization reevaluation of human and mammalian toxic
 equivalency factors for dioxins and dioxin-like compounds. Toxicol Sci 93:223–241

- 357
- Weber R, Lino F, Imagawa T, Takeuchi M, Sakurai T, Sadakata M (2001) Formation of PCDF, PCDD, PCB, and PCN in de novo synthesis from PAH: mechanistic aspects and correlation to fluidized bed incinerators.
- 360 Chemosphere 44:1429–1438
- 361

Wiedner K, Rumpel C, Steiner C, Pozzi A, Maas R, Glaser B (2013) Chemical evaluation of chars produced
 by thermochemical conversion (gasification, pyrolysis and hydrothermal carbonization) of agro-industrial
 biomass on a commercial scale. Biomass Bioenerg 59:264–278

365

Wolfesberger U, Aigner I, Hofbauer H (2009) Tar content and composition in producer gas of fluidized bed
 gasification of wood-influence of temperature and pressure. Environ Prog Sustain Energy 28:372–379
 368

- 369 Zhao L, Cao X, Mašek O, Zimmerman A (2013) Heterogeneity of biochar properties as a function of
- 370 feedstock sources and production temperatures. J Hazard Mater 256–257:1–9
- 371

FIGURE CAPTIONS

Fig.1 Total concentration and distribution of different-sized PAHs (numbers of rings) in each biochar. SI-SIII: size of the pyrolysis equipment (Stage I, Stage II, and Stage III, respectively) and AD: anaerobic digestate. Red dashed line represents the range of lower-limit threshold values (set by IBI (International Biochar Initiative, 2015)) for PAHs in biochar used in soil.

Fig. 2 Concentrations (plotted on different scales) of oxy-PAH (columns) and N-PAC (bullets) in biochar from the different pyrolysis units. SI-SIII: size of the pyrolysis equipment (Stage I, Stage II, and Stage III, respectively) and AD: anaerobic digestate

Fig. 3 Distribution of PAH, O-PAH, and N-PAC in char, and PAH and O-PAH in the liquid fraction. N-PAC in the liquid fraction is not shown since the corresponding concentrations were below the limit of quantification (LOQ)









Table 1 Proximate and ultimate analysis for the studied feedstocks

	Unit	Softwood	Wheat Straw	Anaerobic Digestate
Moisture	wt ¹ .% (a.r) ²	6.71 ± 0.03 (5)	7.22 ± 0.22 (5)	5.72 ± 0.27 (6)
Volatiles	wt.% (d.b.) ³	83.6 ± 0.4 (5)	76.3 ± 0.5 (5)	64.6 ± 0.4 (6)
Fixed Carbon	wt.% (d.b.)	14.4 ± 0.4 (5)	16.6 ± 1.1 (5)	7.7 ± 0.3 (6)
Ash	wt.% (d.b.)	1.1 ± 0.1 (5)	7.0 ± 0.3 (5)	27.8 ± 0.5 (6)
С	wt.% (d.b.)	49.9 (2)	45.2 (2)	38.0 (2)
Н	wt.% (d.b.)	6.6 (2)	5.4 (2)	0.60 (2)
Ν	wt.% (d.b.)	< 0.10 (2)	0.58 (2)	4.29 (2)

¹wt: weight; ²a.r.: as received; ³d.b.: dry basis; (n): number of replicates

Idule Z Characteristics of the pyrolysis reactors used in this stu	Table 2	Characteristics	of the p	pyrolysis	reactors	used in	this stud	v
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Name	Operation mode	Temperature	Type of heating	Capacity	Carrier gas flow	Ref.
Stage I	batch	max ~ 1200 °C	infra-red furnace	30 - 50 g∙run ⁻¹	0.3 L·min ⁻¹	Crombie et al., 2013
Stage II	continuous - auger	max ~ 850 °C	electric split-tube furnace	500 g·h⁻¹	1 L∙min ⁻¹	Buss et al., 2016-b
Stage III	continuous - rotary kiln	max ~ 850 °C	set of electric heaters	30 - 50 kg·h⁻¹	10 L∙min ⁻¹	Buss et al., 2014

			Sta	ge l		Sta	ge II	Stag	ge III
Feedstock		550 °C	Yield (%) 550 °C	700 °C	Yield (%) 700 °C	550 °C	700 °C	550 °C	700 °C
	Biochar	Х	21 ± 1.1 (4)	Х	19 ± 0.5 (4)	Х	Х	Х	Х
Softwood	Liquid	Х	46 ± 1.1	Х	45 ± 0.9				
	Gas		33 ± 2.1		36 ± 0.8				
	Biochar	Х	25 ± 0.5 (3)	Х	23 ± 0.8 (3)	Х	Х	Х	Х
Wheat Straw	Liquid	Х	44 ± 0.3	Х	44 ± 0.8				
	Gas		31 ± 0.7		33 ± 0.8				
	Biochar	Х	25 ± 1.5 (7)						
Anaerobic Digestate	Liquid	Х	49 ± 1.3						
	Gas		26 ± 1.2						

 Table 3 Overview of pyrolysis experiments. X denotes the samples that were analyzed for contaminants. In addition, the product yields for the Stage I unit are shown with the number of replicates in parentheses

PAH	ΠAr	Oxy-PAH	ПАr	N-PAC	NAr
Naphthalene	2	1-Indanone	2	Quinoline	2
Acenaphthylene		1-Acenaphthenone		Benzo[h]quinoline	
Acenaphthene		9-Fluorenone	2	Acridine	3
Fluorene	3	Anthracene-9,10-dione	5	Carbazole	
Phenanthrene		2- Methylanthracene- 9,10- dione			
Anthracene		Cyclopentaphenanthrenone			
Fluoranthene		Benzo[a]fluorenone			
Pyrene	Λ	Benz[de]anthracen-7-one	4		
Benzo[a]anthracene	4	Benz[a]anthracene-7,12-dione			
Chrysene		Naphthacene-5,12-dione			
Benzo[b]fluoranthene		Benzo[cd]pyren-6-one	5		
Benzo[k]fluoranthene	5				
Benzo[a]pyrene	J				
Dibenz[ah]anthracene					
Indeno[cd]pyrene	6				
Benzo[ghi]perylene	0				

Table 4 List of analyzed PAH, oxy-PAH, and N-PAC and the number of aromatic rings (n_{Ar}) in each structure

 $n_{\mbox{\scriptsize Ar}}$: number of aromatic rings in each structure