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Citation for published version:

Buss, W, Jansson, S & Mašek, O 2019, 'Unexplored potential of novel biochar-ash composites for use as organo-mineral fertilizers', *Journal of Cleaner Production*, vol. 208, pp. 960-967.
<https://doi.org/10.1016/j.jclepro.2018.10.189>

Digital Object Identifier (DOI):

[10.1016/j.jclepro.2018.10.189](https://doi.org/10.1016/j.jclepro.2018.10.189)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Journal of Cleaner Production

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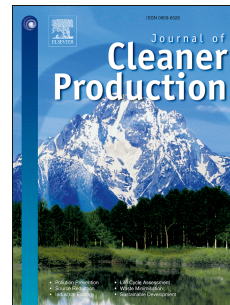
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Accepted Manuscript

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PII: S0959-6526(18)33205-0

DOI: [10.1016/j.jclepro.2018.10.189](https://doi.org/10.1016/j.jclepro.2018.10.189)

Reference: JCLP 14591

To appear in: *Journal of Cleaner Production*

Received Date: 18 May 2018

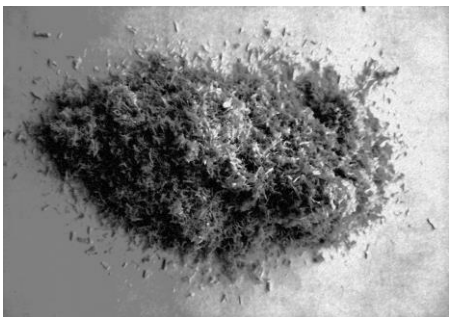
Revised Date: 10 October 2018

Accepted Date: 16 October 2018

Please cite this article as: Buss W, Jansson S, Mašek Ondř, Unexplored potential of novel biochar-ash composites for use as organo-mineral fertilizers, *Journal of Cleaner Production* (2018), doi: <https://doi.org/10.1016/j.jclepro.2018.10.189>.

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Bioenergy



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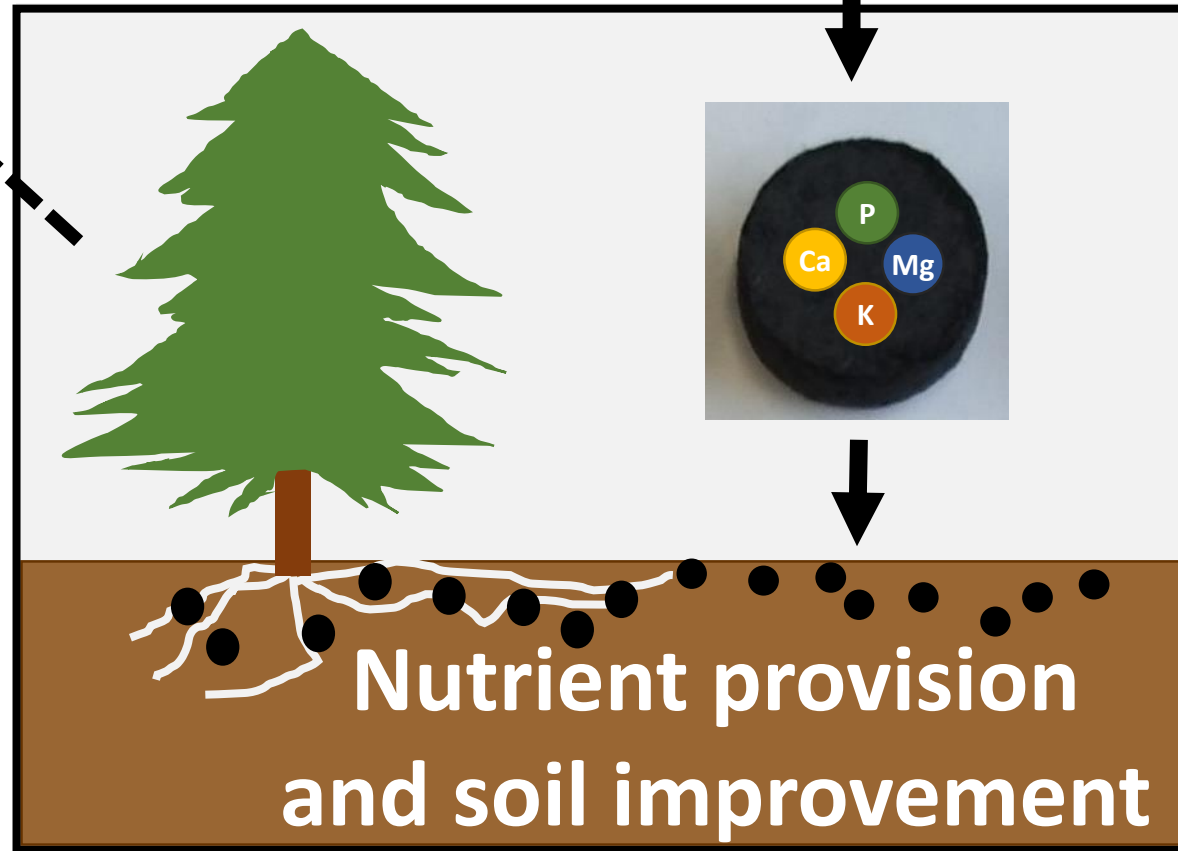
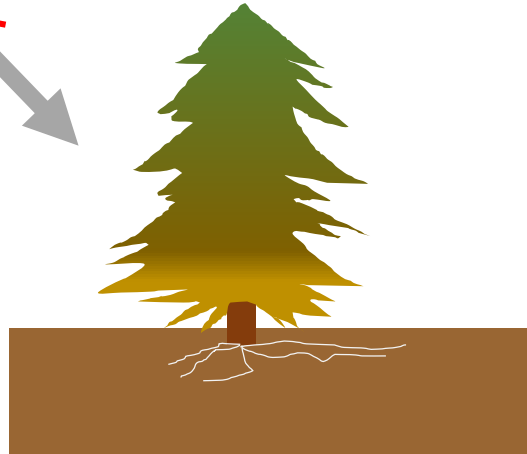
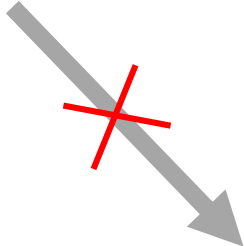
Pyrolysis

Wood ash

Spruce wood



Landfill



Nutrient provision
and soil improvement

Unexplored potential of novel biochar-ash composites for use as organo-mineral fertilizers

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Abstract

Application of wood ash on forest and agricultural soils can provide nutrients and increase soil pH, however, it changes the soil chemistry rapidly and temporarily, often resulting in reduced plant growth and potassium leaching. Biochar from woody materials are nutrient poor and need nutrient enhancement prior to soil application. In this study, spruce residues were mixed with spruce/pine ash in different ratios (0-50%) to produce biochar-ash composites at 450°C. The biochar yield (ash-free basis) increased by 80-90% with the addition of 50% ash due to catalytic biochar formation. Consequently, nearly half the amount of wood is needed to produce the same amount of (ash-free) biochar. Mineral release was moderated in the composites compared to pure ash, demonstrated by a lower electric conductivity and % available K content (a factor of 2.5-4.4 lower than in wood ash). Furthermore, the % available chromium content, which is a key potentially toxic element in wood ash, decreased by a factor of 50-160. Soil application of biochar-ash composites decreases the risk of Cr toxicity, salinity stress and leaching of K in soil substantially compared to ash application. Biochar-ash composites are a novel product with vast unexplored potential for use in forestry and agriculture.

26 **Keywords**

27 pyrolysis; potentially toxic element; potassium; heavy metal; forestry; agriculture

28 **Abbreviations**

29 PTE, potentially toxic element; DSC, differential scanning calorimetry; TGA,
30 thermogravimetric analysis; ICP-OES, inductively coupled plasma – optical emission
31 spectrometry

32 **Total Word Count: 8140**

33 **1 Introduction**

34 Bioenergy is already the biggest contributor to renewable energy generation in the EU, of
35 which solid biomass combustion makes up the main share (European Commission, 2017).
36 Furthermore, in the Fifth IPCC assessment report, bioenergy generation with carbon dioxide
37 carbon capture and storage (BECCS) is mentioned as a key technology for mitigation of
38 climate change and hence is likely to expand in the near- and mid-term future (IPCC, 2014).
39 Although biomass combustion produces renewable energy, in contrast to e.g. wind or solar
40 power, it also creates ash as a by-product; wood combustion generates around 1% waste ash
41 which is mostly landfilled (Demeyer et al., 2001; Pitman, 2006). Therefore, in light of
42 sustainable resource use and to reduce disposal costs, investigating possible re-use options for
43 wood ash is a very important strategy to increase the sustainability of bioenergy generation.
44 Due to the high alkalinity of wood ash (pH 8.9-13.5) it can be applied to soil as liming agent
45 to increase the pH (Demeyer et al., 2001; Khanna et al., 1994; Sano et al., 2013). Therefore, it
46 is well suited for reducing the Al and Mn toxicity in acidic forest soils and to increase
47 availability of nutrients already present in soil (Kahl et al., 1996; Nkana et al., 1998).
48 Additionally, in itself it is a good source of nutrients and in particular, it can supply high
49 amounts of available potassium (K) (Demeyer et al., 2001; Pitman, 2006).
50 The effects of wood ash on soil pH and nutrient status of the soil, however, are only short-
51 lived due to the high solubility of K and Na oxides, hydroxides and carbonates which leach
52 quickly (Ulery et al., 1993). Furthermore, the high K availability, general salinity (high
53 electric conductivity (EC)) and high pH, change the soil chemistry rapidly which can result in
54 toxicity in plants and soil organisms and shifts in soil microbial composition (Augusto et al.,
55 2008; Bang-Andreasen et al., 2017; Demeyer et al., 2001; Etiegni et al., 1991b; Jagodzinski
56 et al., 2018; Qin et al., 2017; Staples and Van Rees, 2001). Therefore, means to create an ash-

57 containing material which supplies nutrients in a more controlled way makes the use of ash in
58 forestry and agriculture much more attractive and therefore, reduces the amount of ash being
59 landfilled and closes the nutrient loops.

60 Charcoal applied to soil can improve nutrient retention by increasing the cation exchange
61 capacity (CEC) and thus reduce nutrient leaching (Ippolito et al., 2015). The use of charcoal
62 for environmental applications, such as the use in soil, has been extensively studied in the
63 past 10 years and charcoal used for this purpose is generally referred to as biochar (Lehmann
64 and Joseph, 2015). In addition to increases in soil CEC, biochar can have a high water
65 holding capacity, increase soil microbial abundance and have further beneficial effects (Li et
66 al., 2017; Masiello et al., 2015; Thies et al., 2015).

67 Charred biomass is already present in boreal forest soils in high quantities from forest fires
68 and can comprise up to 40% of the total soil carbon (DeLuca and Aplet, 2008). Therefore, the
69 addition of biochar to soils is not an unnatural intervention and analyses of biochar produced
70 from uncontaminated feedstocks have shown minimal organic contamination (Buss et al.,
71 2016a, 2015; Weidemann et al., 2017). Yet, biochar from woody materials have low nutrient
72 contents (Buss et al., 2016b; Xu et al., 2017) and need nutrient enhancement prior to soil
73 application.

74 Mixing of wood ash and wood-derived biochar, e.g. made from forest residues, could be a
75 very valuable proposition; the carbon providing general soil improving effects and the ash
76 providing nutrients. Besides direct nutrient provision (Chia et al., 2014), mineral-enriched
77 biochar can improve the plant nutrient use efficiency (Blackwell et al., 2015; Lin et al.,
78 2013). Furthermore, enriched biochars can increase the carbon sequestration potential (lime,
79 clay, ash and manure-enrichment) (Mohammadi et al., 2016), the redox potential (Fe-
80 enrichment) (Pace et al., 2018) and the porosity of biochar (Fe-clay-enrichment) (Rawal et

81 al., 2016). There are two possible ways to produce mineral-enriched biochar; one option is to
82 mix the minerals and biochar after pyrolysis (Blackwell et al., 2015; Chia et al., 2014; Lin et
83 al., 2013); the other option is to mix the minerals with the biomass feedstock before pyrolysis
84 (as e.g. done in Pace et al., 2018 and Rawal et al., 2016).

85 As wood ash contains high concentrations of K, Na, Ca and Mg (Pitman, 2006), which are
86 known to catalyse biochar formation and increase biochar yield (Eom et al., 2012; Fuentes et
87 al., 2008; Nowakowski et al., 2007), mixing of biomass feedstocks and wood ash prior to
88 pyrolysis could bring additional benefits. However, to our knowledge so far no study has
89 investigated the effects of wood ash-amendment prior to pyrolysis. There is a need to study
90 the effects of wood ash on biochar formation and on the properties of the resulting biochar.

91 The research question that was addressed in this study was whether biochar-ash composites
92 have superior properties over pure biochar or pure ash application for forestry and
93 agriculture. In this study, spruce forestry residues amended with extra 0%, 5%, 10%, 20%
94 and 50% spruce/pine ash were pyrolysed at 450°C and characterised for agronomically
95 relevant parameters (total/available nutrient and potentially toxic elemental content, pH, EC).
96 Additionally, the influence of wood ash on pyrolysis was investigated via thermogravimetric
97 analysis (TGA) and differential scanning calorimetry (DSC).

98 **2 Materials and Methods**

99 **2.1 Feedstock preparation**

100 A protocol for developing ash-enriched wood pellets was specifically developed for this
101 study. The aim was to blend wood ash and spruce wood residues (*Picea abies*) to create a
102 composite material with high degree of contact between the organic and mineral components
103 (to maximize potential catalytic reactions) that could be pyrolysed in a continuous pyrolysis
104 unit. Pelletizing ensured that the mixture remained homogenous and density separation of the
105 two materials was avoided. Furthermore, pelletizing enables easy storage and handling of the
106 final biochar-ash composites.

107 The ash originated from a district heating plant in Bureå south of Skellefteå in Sweden, and is
108 owned by Skellefteå Kraft AB. It is a 2MW moving inclined grate (HOTAB) with a
109 Danstoker boiler (steam temperature 140°C, 4.2 bar). A blend of pelletized spruce and pine
110 sawdust was used in the biomass boiler with a mean moisture content of 6.7%, ash content of
111 0.3%, a bulk density of $\sim 680 \text{ kg L}^{-1}$ and a heating value of $\sim 20.3 \text{ MJ kg}^{-1}$ dry matter. After
112 combustion, the ash is ejected via a screw to a container in which fly ash and bottom ash
113 were mixed, and where samples were collected.

114 To fully incorporate the ash into the wood and subsequently into the biochar, the spruce wood
115 was ground to a particle size of $< 2 \text{ mm}$ using a blender (Philips HR 2810/A) and the wood
116 ash was sieved to $< 0.5 \text{ mm}$. Different ash-to-spruce ratios were prepared: 0%, 5%, 10%,
117 20% and 50% on dry-basis. A customised stainless-steel die with a 1-inch diameter was used
118 to produce pellets with 3 g dry weight. The respective amounts of spruce and wood ash were
119 mixed in polypropylene bags; 2 mL of water was added for better mixing, to avoid density
120 separation and to decrease dust formation. Two pellets were produced at a time in the die,
121 separated by a stainless-steel spacer. The die was closed with a vice to ensure that the same

122 amount of pressure was applied to all pellets of the same treatment. Due to the higher density
123 of wood ash compared to spruce, increasing wood ash concentrations increased the density of
124 the pellets. Hence, to ensure similar pressures, additional spacers were added with increasing
125 wood ash concentration. The extra height of the spacers and the resulting densities of the
126 pellets are shown in SI Table 1.

127 Afterwards, the die was placed in an oven for stable pellet formation through binding of the
128 materials. Different residence times and oven temperatures were tested to obtain stable
129 pellets, and 160°C for 1.5 h was selected and used for production of 12-16 pellets with 3 g for
130 each of the five treatments.

131 For biochar yield comparison untreated spruce cylinders with a diameter and height of 15 mm
132 were prepared as well.

133 **2.2 Biochar production**

134 **2.2.1 Continuous auger reactor**

135 Feedstock amounts of 36-45 g were pyrolysed in the Stage II, auger reactor, pyrolysis unit of
136 the UK Biochar Research Centre. Details about the unit can be found elsewhere (Buss et al.,
137 2016b). A highest treatment temperature (HTT) of 450°C was chosen to minimize the
138 availability of minerals present in the ash (Buss et al., 2016a). A mean residence time in the
139 heated zone of 450°C of 20 min was used (corresponds to around 10 min at HTT) and a
140 nitrogen carrier gas flow rate of 1.5 L min⁻¹. The biochar yield on dry basis and biochar yield
141 based on dry, ash-free basis (daf) (g daf biochar / g daf feedstock) were calculated (ash
142 contents measured in TGA, see 2.3.1).

143 **2.2.2 Thermogravimetric analysis (TGA) - pyrolysis**

144 Micro-pyrolysis was performed with a Mettler-Toledo TGA/DSC1 to replicate the conditions
145 in the continuous unit (450°C HTT, 10 min RT at HTT, 90°C min⁻¹ heating rate) for accurate

146 biochar yield determination. The pellets were cut into smaller pieces and ~40 mg was
147 pyrolysed in 150 μ L crucibles. The analysis was performed in triplicates. Differential
148 scanning calorimetry (DSC) curves were automatically derived by the TGA. Mean \pm standard
149 deviation of biochar yield on dry basis and biochar yield based on dry, ash-free basis (daf) (g
150 daf biochar / g daf feedstock) were calculated.

151 **2.3 Biochar characterisation**

152 The biochar from the auger reactor (Stage II) was ground up using a mortar and pestle as
153 preparation for the following analysis. To ensure representative sampling, most of the
154 produced biochar was ground-up, mixed thoroughly and sub-samples were taken. The
155 analyses were performed in triplicates if not stated otherwise.

156 **2.3.1 Proximate analysis**

157 A Mettler-Toledo TGA/DSC1 was used to perform proximate analysis (Buss and Mašek,
158 2014) which distinguished between moisture, volatile matter (VM), fixed carbon (FC) and
159 ash content. It used a temperature of 110°C for moisture determination (in nitrogen), 900°C
160 in a nitrogen atmosphere to determine the volatile matter loss and introduced air at 900°C to
161 oxidize the stable carbon (fixed carbon) and the ash fraction remained.

162 **2.3.2 pH and electric conductivity (EC)**

163 EC and pH were determined as recommended by the International Biochar Initiative (IBI)
164 through biochar extraction with distilled water (Rajkovich et al., 2012). A solid-to-liquid ratio
165 of 1:20 was used and the samples were shaken at 150 rpm on an orbital shaker for 1.5 h.

166 The samples were analysed with a Hach HQ40d portable meter using a Hach conductivity
167 probe CDC 401 and the gel-filled pH-electrode Hach 51935-00.

168 **2.3.3 Extractions and digestions**

169 To determine the total content of potentially toxic elements (PTEs) and nutrients, modified
170 dry ashing was used to digest the biochars (and feedstocks) which was optimised for use on
171 biochar previously (Enders and Lehmann, 2012). The method combines dry ashing at 500°C
172 (also used for ash content determination, Table 1) with wet digestion using HNO₃ and H₂O₂.
173 The original method was modified in two aspects as previously explained (Buss et al., 2016b)
174 to increase the limit of detection.

175 The availability of elements in biochar was determined through extraction with 0.01 M CaCl₂
176 which has shown to correlate well with plant uptake for P and K (and B, Mn, Mo and Na) in a
177 study on biochar where typical soil extractants were compared (Shepherd et al., 2017). 1.5 g
178 of biochar was extracted with 15 mL of 0.01 M CaCl₂ in 50 mL polypropylene centrifuge
179 tubes. Subsequently, the tubes were shaken on an orbital shaker for 2 h at 150 rpm and were
180 filtered with Whatman No. 1 filter paper. Three blanks with only 0.01 M CaCl₂ were included
181 in the procedure.

182 The digests/extracts were analysed via Inductively Coupled Plasma – Optical Emission
183 Spectrometry (ICP-OES) as described below. In addition, the % available of the total
184 elemental content and the propagated error using the mean (AV) and standard deviation (SD)
185 of the total (n = 3) and the CaCl₂-extractable concentrations (n = 3) were calculated.

186 **2.3.4 Elemental analysis**

187 The samples were filtered with Whatman No. 1 filters and analysed via ICP-OES (Varian
188 Vista Pro). Calibration from 0.01 ppm to 25 ppm were used and if outside the detection
189 range, the samples were diluted. The 1 ppm standard was added as quality control after every
190 15 samples. More details on the ICP analysis data processing can be found elsewhere (Buss et
191 al., 2016b).

192 2.4 Data processing and statistics

193 A regression line was fitted to the data from EC measurements (dependent parameter) and
194 either the ash addition prior to pyrolysis or the actual ash content in the biochar (independent
195 parameter) using Sigma plot (Version 13.0, Systat Software Inc.).

196 **3 Results and Discussion**

197 **3.1 Biochar production**

198 The biochar yield (dry basis) of ash-amended and pelletized spruce wood increased with the
199 percentage of spruce/pine ash addition from 25.6% (no ash addition) to 65.8% (50% ash
200 addition) (Table 1). This is expected due to the addition of minerals in the form of wood ash
201 which mostly remain in the pyrolysis solids and hence increase the char yield. However, the
202 biochar yield based on the amount of dry, ash-free (daf) biochar and feedstock also increased
203 with wood ash addition. The maximum daf biochar yield was observed at the highest wood
204 ash addition (50%) with a relative increase in biochar yield of 78.1% compared to pyrolysis
205 of pure spruce pellets (Table 1, Figure 1). To our knowledge we report for the first time that
206 external wood ash addition can increase the daf biochar yield.

207 The daf biochar yield of the treatment amended with 20% wood ash was lower than expected
208 (27.9% daf) compared with the biochar yields from the other treatments pyrolysed in the
209 auger reactor (Table 1, Figure 1). The pellets of the 20% (and 50%) treatment were brittle
210 after pyrolysis and although all twelve pellets could be recovered from the continuous
211 pyrolysis unit, most likely small pieces broke off which affected the biochar yield. Therefore,
212 for accurate yield determination, to confirm the results and to investigate the underlying
213 mechanism the samples were also pyrolysed in a TGA in triplicates.

214 In the TGA, the daf biochar yields were slightly lower than in the auger reactor (Table 1),
215 probably due to reduced secondary biochar formation resulting from reduced particle size and
216 a lower residence time of vapours trapped within the particles (Antal and Grønli, 2003). But
217 generally, the yields were in a similar range confirming the yield increases caused by wood
218 ash addition as observed in the auger reactor (Figure 1). In the TGA 50% ash addition
219 resulted in a daf biochar yield increase of $89.8\% \pm 17.4$ (Figure 1, SI Table 2).

220 The DSC curves derived from pyrolysis at 450°C in the TGA clearly show a reduction of the
221 endothermic peak with wood ash addition (Figure 2) as also described when biomass was
222 impregnated with individual minerals, such as potassium acetate (Fuentes et al., 2008). The
223 10% ash treatment resulted in the highest exothermic peak which decreased with higher ash
224 addition and 50% ash-amended spruce showed the lowest energy flow per mg of material. It
225 is also apparent that the exothermic peak shifts to a lower temperature with a higher addition
226 of wood ash. The catalytic effects of individual minerals during pyrolysis are well established
227 in the literature (Eom et al., 2012; Fuentes et al., 2008; Nowakowski et al., 2007) but here we
228 were able to demonstrate that wood ash can have the same effect. This is based on catalytic
229 processes which lower the activation energy needed for reactions to take place.

230 To our knowledge, we documented for the first-time biochar yield increases as a result of the
231 amendment of woody biomass with wood ash. A key step was the pelletizing which ensured a
232 homogenous distribution of the externally added ash in the pellets and allowed efficient
233 reactions between the mineral and organic phase. Consequently, catalysis effects between
234 wood ash and biomass (spruce) took place which boosted the biochar yield. As a result, wood
235 ash addition improved the conversion efficiency of spruce to biochar significantly; 80-90%
236 less spruce was needed to yield the same amount of (ash-free) biochar, and thus brings major
237 economic and environmental advantages.

238 **3.2 Key biochar properties related to soil amendment use**

239 **3.2.1 Electric conductivity (EC) and pH**

240 Spruce/pine ash addition elevated the EC of our biochars substantially (Table 1). In soil, the
241 EC increases linearly with the dose of wood ash application (Bang-Andreasen et al., 2017). In
242 contrast, Figure 3 shows an exponential increase of EC with ash content in the five biochars
243 and the wood ash sample. Pure wood ash had an EC of $13250 \pm 380 \mu\text{S cm}^{-1}$, 4.8 times and
244 11.2 higher than the EC in the biochar sample amended with 50% and 20% ash, respectively,
245 highlighting biochar's immense sorption capacity. While pure ash releases most of its
246 minerals immediately, biochar can buffer this release and hence reduce the EC of the biochar-
247 ash composites drastically. This is an important finding for the application of biochar-ash
248 composites.

249 Increasing contents of wood ash in biochar also increased the pH of the composite. Pure
250 wood ash was highly alkaline with a pH of 12.75 (Table 1), comparable to the pH of ashes
251 reported elsewhere (Someshwar, 1996). The pH of the biochar amended with 50% wood ash
252 prior to pyrolysis was 0.7 pH units lower. A direct comparison of the pH values as done for
253 the EC in Figure 3 is not possible because the pH scale is a logarithmic scale, but these
254 results clearly show that biochar can buffer the EC and pH effects of wood ash.

255 Increasing soil pH is important for forest soils as they are predominantly acidic. However,
256 due to the rapid changes in soil pH and soil EC imposed by wood ash (Ulery et al., 1993;
257 Williams et al., 1996), over application, which results in phytotoxicity (Etiegni et al., 1991b;
258 Jagodzinski et al., 2018; Staples and Van Rees, 2001) and shifts in microbial composition
259 (Bang-Andreasen et al., 2017) happens readily. Therefore, the ability of biochar to buffer the
260 release of minerals from ash, and associated soil pH and EC effects, is invaluable in creating
261 a safe and more effective biochar-ash product that can still increase the pH but in a more

262 controlled way and over a longer period of time. In follow-up studies the liming performance
263 of biochar-ash composites should be directly compared with pure wood ash and lime.

264 **3.2.2 Nutrients**

265 The wood ash sample contained around 25% Ca, 4% K, 5% Mg, 3% Mn and 1.4% P (Table
266 2) which is similar to wood ash reported elsewhere (Etiegni et al., 1991a). Due to the
267 comparatively low temperature treatment (450°C), nutrients did not evaporate during
268 pyrolysis and the total nutrient concentrations in the ash-amended biochars were proportional
269 to their wood ash additions.

270 Magnesium (Mg) and manganese (Mn) were largely unavailable (Table 2, SI Table 3), as
271 previously reported for various combustion wood ashes in Sano et al. (Sano et al., 2013). The
272 calcium (Ca) availability was not measured in our study as the extraction was performed with
273 CaCl₂. Other studies reported low Ca availability in combustion ashes (Nieminen et al.,
274 2005).

275 The availability of phosphorus (P) was very low in both, wood ash and biochar, below the
276 limit of detection in most cases (0.26 mg kg⁻¹) (Table 2). Phosphorus in wood ash and biochar
277 is bound predominantly in unavailable forms, e.g. in calcium phosphates (Liang et al., 2017;
278 Sano et al., 2013; Steenari et al., 1999; Uchimiya and Hiradate, 2014). However, in Erich and
279 Ohno, the plant stimulating effect of wood ash could be attributed to increases in plant P
280 supply (Erich and Ohno, 1992). In addition, elevating the soil pH of acidic soils can increase
281 the availability of P already present in soil; the ideal soil pH for maximum P availability is
282 6.0-6.5 (Blume et al., 2016) and therefore addition of alkaline biochar (such as the biochar-
283 ash composite) can have an indirect positive effect on plant P supply. Overall, the potential
284 supply of P in biochar-ash composites to plants needs more investigation.

285 Potassium (K), was highly available in wood ash, $59.8 \pm 4.3\%$ of the total content was
286 available which is similar to Khanna et al. (Khanna et al., 1994) where 68% of K was water-
287 extractable and Sano et al. (Sano et al., 2013) where 78.5-103.8% of K was water-extractable.
288 Incorporation of wood ash into spruce wood and subsequent pelletizing and pyrolysis at
289 450°C reduced the percentage of available K to $\sim 14\%$ in the 5%, 10% and 20% ash-amended
290 treatments which is a reduction by a factor of 4.1-4.4 (Figure 4, SI Table 3). The K
291 availability increased in the 50% ash amendment to 24% which is still less than half of the
292 availability in the pure ash treatment. The biochar surfaces capable of retaining nutrients were
293 most likely saturated and hence the K availability increased in the 50% ash-amended biochars
294 compared to the 20% amended ones.

295 Many studies concluded that no long-term K fertilization effects can be expected when pure
296 wood ash is applied to soils (Kahl et al., 1996; Sano et al., 2013; Ulery et al., 1993; Williams
297 et al., 1996) and even phytotoxic effects are possible due to the high K availability (Etiegni et
298 al., 1991b). With the use of wood ash in biochar, instead of instant leaching of K, we can
299 expect a more moderate supply of K initially and medium to long-term effects. This is a
300 significant and novel finding that makes the use of biochar-ash much more attractive for
301 fertilization than the use of pure wood ash.

302 **3.2.3 Potentially toxic elements (PTEs)**

303 Pure wood ash exceeded several threshold values for total PTEs for biochar and other soil
304 amendments, while the unpyrolysed spruce wood did not exceed any of the threshold values
305 (Table 3, SI Table 4). Cadmium (Cd) and chromium (Cr) are of particular concern as, e.g. the
306 premium biochar threshold limit values for application of biochar to soil (EBC, 2012) were
307 exceeded 4-fold and 7-fold by the ash, respectively. The concentrations of Cu, Ni and Zn in
308 wood ash were just above limit values as well. Such PTE values are not atypical. Compared
309 to average PTE concentrations in 26 wood ashes: As 23.2 mg kg^{-1} , Cd 5.0 mg kg^{-1} , Cr 39.0

310 mg kg^{-1} , Cu 75.3 mg kg^{-1} , Mo 14.0 mg kg^{-1} , Ni 23.5 mg kg^{-1} and Zn 443 mg kg^{-1}
311 (Someshwar, 1996), in our study only the Cr content in wood ash was slightly higher, but still
312 well within range reported in other studies ($16\text{-}810 \text{ mg kg}^{-1}$) (Pohlandt-Schwandt, 1999). The
313 origin of Cr can be both, contamination of the feedstock, but also the furnace steel (Buss et
314 al., 2016b; Sano et al., 2013). As expected, the 50% ash-amended biochar exceeded the Cd
315 and Cr threshold values and some of the threshold values for Cu and Ni (Table 3). The 20%
316 ash treatment was just above the total Cd concentration and was still 3-fold higher than the
317 limit for Cr in premium biochar (EBC, 2012).

318 In the German Federal Soil Protection Ordinance, five threshold values for available PTEs,
319 based on a salt extraction ($1 \text{ M NH}_4\text{NO}_3$) similar to the one applied in our study (0.01 M
320 CaCl_2) have been reported for protection of plant growth and crop quality. None of the
321 threshold values were exceeded by our wood ash and biochars (Table 3) (apart from Zn by
322 pure spruce wood). This clearly demonstrates the ability of ash and biochars to sorb PTEs
323 strongly and efficiently.

324 In the German Ordinance, no threshold value exists for Cr and the percentage available (0.01
325 M CaCl_2 -extractable) of the total elemental content in wood ash was high for Cr with 8%
326 (Figure 4, SI Table 5). Cr is released readily from wood ash (Demeyer et al., 2001) and
327 therefore, high Cr availability is a frequent problem in combustion ash, in particular Cr (VI)
328 which is the oxidation state that demonstrates higher stability and availability in alkaline
329 environments such as wood ash provides (Kabata-Pendias, 2011; Pohlandt-Schwandt, 1999;
330 Sano et al., 2013). While Cr (III) is essential for animals and humans, Cr (VI) is toxic to
331 plants, animals and humans (Kabata-Pendias, 2011; Pohlandt-Schwandt, 1999). Therefore, Cr
332 possess a high risk to soils when wood ash is used in agriculture or even when landfilled
333 (Pohlandt-Schwandt, 1999).

334 The incorporation of wood ash into spruce and conversion into biochar reduced the
335 availability of Cr drastically from $8.00 \pm 0.25\%$ (pure ash) to $0.05 \pm 0.00\%$ (20% ash biochar)
336 - $0.15 \pm 0.01\%$ (5% ash biochar) which is a reduction by a factor of 54-160 (Figure 4, SI
337 Table 5). Substantially reduced Cr availability in different types of biomass after pyrolysis
338 was also observed in other studies (Buss et al., 2016a; Farrell et al., 2013). However, here we
339 showed that even externally added Cr in the form of wood ash which is not already
340 incorporated into the plant structure is efficiently immobilised. This mitigates a typical
341 problem of wood ash for soil application, high Cr availability.

342 **3.3 Environmental and agronomic benefits of biochar-ash** 343 **composites**

344 In this study, we demonstrated that the production and application of wood-ash-enhanced
345 biochar to soil has multiple benefits over pure biochar or pure wood ash application.

346 Wood ash application can result in significant changes in soil solution chemistry as the soil
347 exchange sites are not able to buffer the high load of cations. However, blending of wood ash
348 with wood, pelletizing and subsequent conversion into biochar effectively moderates the
349 release of cations and reduces the EC and available K significantly compared to pure wood
350 ash. Therefore, adverse effects in soil due to high salinity are less likely. Indeed, post-
351 production mixing of biochar and ash and application to plants reduced ash-related
352 phytotoxicity (Saletnik et al., 2016). Although this is different from the application of
353 composite materials as proposed in our study, the use of composites is likely to be even more
354 effective due to the close contact of biochar and ash. Furthermore, our results show reduced
355 availability and leaching of K which should result in a higher plant K use efficiency. The
356 availability of Cr, a key contaminant in wood ashes, is drastically reduced in biochar-ash
357 composites, minimising the risk for adverse plant effects. These are significant new findings.

358 Generally, biochar can improve the cation exchange capacity, water holding capacity and
359 structure of the soil, both, in the short and long-term (Glaser et al., 2002; Lehmann and
360 Joseph, 2015; Li et al., 2017) and pelletised biochar showed to be particularly beneficial.
361 Pelletised biochar applied in 14 t ha^{-1} increased the plant available water content and water
362 retention in soil (Andrenelli et al., 2016). Pellets made from biochar and wood flour applied
363 to growing media in 25% also increased the plant water availability (Dumroese et al., 2011).
364 Moreover, pelletising of biochar reduced the release of fine particles, and hence increased the
365 carbon sequestration potential of biochar and decreased the health risk due to dust formation
366 during biochar application (Maienza et al., 2017). We expect that our biochar-ash composite

367 has similar effects, which will be the focus of follow-up studies. Overall, the incorporation of
368 ash into pelletised biochar-ash composites makes it a superior product compared to
369 application of pure ash as it also adds a (stable) carbon fraction (biochar).

370 There are also multiple benefits of using biochar-ash composites over the production and use
371 of biochar from pure woody biomass. First, the biochar yield increases and therefore, less
372 biomass is needed to produce the same amount of biochar. This has economic and
373 environmental benefits; less CO₂ is released, and more carbon is available to be sequestered
374 in the ground as biochar. Secondly, the biochar is nutrient loaded, with K, Ca, Mg and P.

375 In practise, uncontaminated ash from biomass boilers and parts of the unburned wood (or saw
376 dust from timber industry or forestry residues) can be mixed and pelletized with existing
377 pelletizing equipment. Subsequently, the pellets can be pyrolysed at relatively low
378 temperatures (450-500°C) to create a nutrient-rich biochar with high surface functionality
379 (decreasing surface functionality with higher pyrolysis temperatures (Gai et al., 2014)). The
380 biochar-ash pellets can be easily spread on forest (or agricultural) soils with on-site
381 conversion and minimal transportation, closing the nutrient loop.

382 Wood ash provides the nutrients, such as K, Mg, Ca, P and micronutrients, while the organic
383 part of the biochar buffers and moderates the nutrient release, hence, increases the nutrient
384 use efficiency and brings further soil benefits (Li et al., 2017). In addition, charging this
385 biochar-ash composite with sources of available N could create a highly functional product
386 for improvement of soil properties and fertilization. The use of the biochar-ash composites as
387 fertilizer brings an immediate financial incentive and improves environmental sustainability,
388 while long-term positive effects are expected from soil improvements of biochar.

389 **4 Conclusion**

390 Expansion in the bioenergy sector makes it necessary to find a use for nutrient-rich wood ash
391 that can potentially cause detrimental soil effects. Here we present a strategy to address this
392 problem: mixing of wood ash with woody forestry residues and pyrolysis at relatively low
393 temperature. This results in a product which will change the soil solution less rapidly than
394 wood ash but for a longer time. It provides nutrients and changes the pH in a more controlled
395 way and demonstrates a significantly reduced available Cr concentration. This study clearly
396 demonstrates that biochar-ash composites are very promising as organo-mineral fertilizers,
397 opening a new field of research and applications for biomass ash in a circular economy.

398 **Acknowledgements**

399 The authors would like to acknowledge Bio4Energy (www.bio4energy.se), a strategic
400 research environment created by the Swedish government, for supporting this work. The
401 authors would also like to acknowledge Dr. Jan Mumme for his groundwork and help on this
402 project and thank John Morman and Dr. Laetitia Pichevin for lab work assistance.

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588 Table 1: Proximate analysis, biochar yields, pH and electric conductivity (EC) of feedstock and biochar produced in the auger reactor. Mean and
 589 one standard deviation for the proximate analysis (n = 3) are reported and single values for the biochar yield. The ash content was determined at
 590 500°C and 900°C in air. PSC, pyrolysed spruce cylinders; PPS, pelletised and pyrolysed spruce; NA, not applicable; % change, % change
 591 compared to the unamended biochar (PPS 0% 450°C).

	ash 500°C % dry	ash 900°C % dry	volatile matter % daf	fixed carbon % daf	char yield			pH	EC μS cm ⁻¹
					% dry	% daf biochar/ daf feed	% change		
wood ash	93.6 ± 0.3	84.4 ± 0.7	80.6 ± 3.7	19.4 ± 3.7	NA	NA	NA	12.75 ± 0.04	13250 ± 380
spruce	0.2 ± 0.2	0.9 ± 0.2	83.3 ± 0.5	16.7 ± 0.5	NA	NA	NA	10.09 ± 0.06	37.8 ± 10.7
PSC 0% 450°C	0.6 ± 0.2	3.1 ± 0.5	23.9 ± 0.3	76.1 ± 0.3	25.6	25.0	NA	8.78 ± 0.30	59.8 ± 12.9
PPS 0% 450°C	0.7 ± 0.4	2.0 ± 0.3	20.0 ± 0.6	80.0 ± 0.6	24.0	23.7	0.0	8.86 ± 0.05	53.0 ± 1.1
PPS 5% 450°C	16.5 ± 0.5	17.2 ± 0.7	22.3 ± 0.1	77.7 ± 0.1	31.4	27.5	16.1	10.43 ± 0.07	276 ± 1
PPS 10% 450°C	25.9 ± 1.4	23.1 ± 2.3	24.0 ± 0.5	76.0 ± 0.5	35.3	29.5	24.7	10.63 ± 0.04	444 ± 9
PPS 20% 450°C	42.7 ± 3.3	42.9 ± 0.9	32.5 ± 0.0	67.5 ± 0.0	40.4	27.9	17.9	11.60 ± 0.08	1185 ± 15
PPS 50% 450°C	68.7 ± 1.0	62.1 ± 0.7	47.8 ± 0.5	52.2 ± 0.5	65.8	42.1	78.1	12.07 ± 0.03	2765 ± 21

592 Table 2: Total and 0.01 M CaCl₂-extractable concentrations of nutrients in biochars and feedstocks as mean and one SD (n = 3). Only total
 593 concentration of Ca determined. PSC, pyrolysed spruce cylinders; PPS, pelletised and pyrolysed spruce.

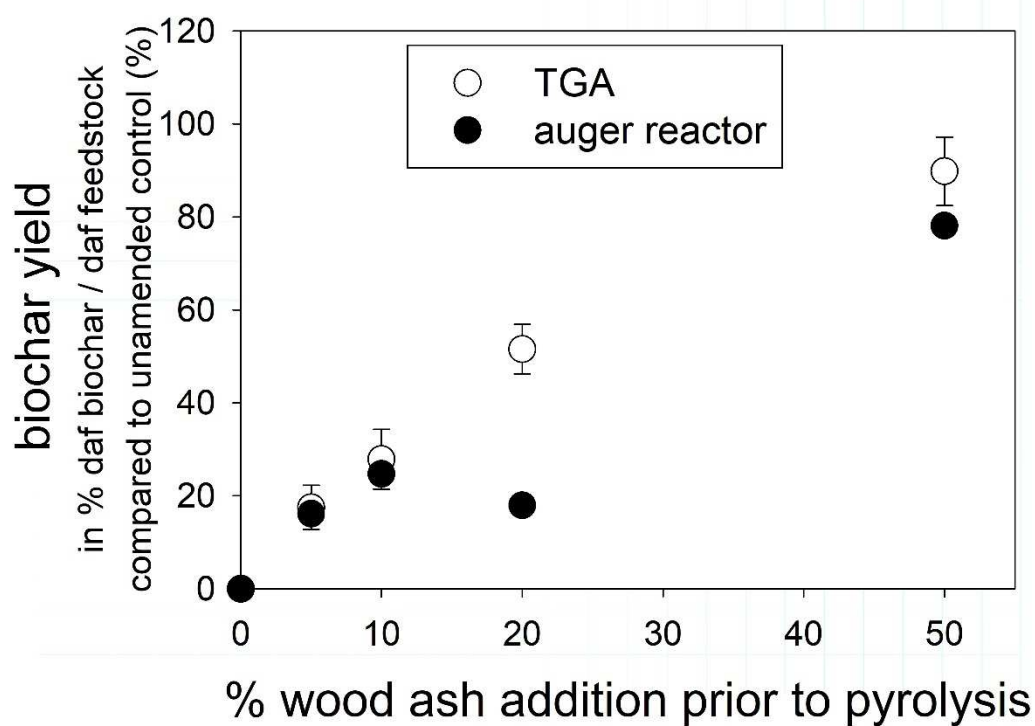
		K	Mg	Mn	B	P	Ca
available							
wood ash	mg kg ⁻¹	23200±1660	< 2.3	< 0.009	< 3.2	< 0.26	
spruce	mg kg ⁻¹	154±22	77.7±8.05	51.9±4.92	< 3.2	1.72 ± 1.17	
PSC 0% 450°C	mg kg ⁻¹	172±20	35.5±5.72	3.04±0.26	< 3.2	1.36 ± 0.23	
PPS 0% 450°C	mg kg ⁻¹	170±12	4.52±0.89	2.83±0.24	< 3.2	1.11 ± 0.30	
PPS 5% 450°C	mg kg ⁻¹	665±19	116±5.56	0.60±0.06	< 3.2	0.34 ± 0.15	
PPS 10% 450°C	mg kg ⁻¹	1070±61	102±3.64	< 0.009	< 3.2	< 0.26	
PPS 20% 450°C	mg kg ⁻¹	2090±22	80.6±1.25	1.08±0.08	< 3.2	< 0.26	
PPS 50% 450°C	mg kg ⁻¹	5170±127	< 2.3	0.26±0.16	< 3.2	< 0.26	
total							
wood ash	mg kg ⁻¹	38900±553	53600±998	32700±751	248±5.79	13700 ± 230	254000 ± 5150
spruce	mg kg ⁻¹	85.8±21.9	68.7±31.7	43.2±20.9	< 71.8	13.2 ± 6.51	390 ± 169
PSC 0% 450°C	mg kg ⁻¹	541±186	162±105	145±71.5	< 71.8	< 10.3	1490 ± 716
PPS 0% 450°C	mg kg ⁻¹	670±115	177±84.9	186±70.4	< 71.8	15.2 ± 7	1850 ± 631
PPS 5% 450°C	mg kg ⁻¹	4749±210	8690±448	5520±283	33.5±2.28	1980 ± 112	43000 ± 2170
PPS 10% 450°C	mg kg ⁻¹	7876±221	13600±794	8790±400	60.1±3.21	3000 ± 132	68600 ± 3260
PPS 20% 450°C	mg kg ⁻¹	14400±646	23000±2890	12500±1660	127±13.8	5080 ± 513	129000 ± 16200
PPS 50% 450°C	mg kg ⁻¹	21600±1150	36600±774	20100±333	223±3.16	11400 ± 213	206000 ± 4090

594

595 Table 3: Total and 0.01 M CaCl₂-extractable concentrations of PTEs in biochars and feedstocks as mean and one standard deviation (n = 3). As
 596 comparison, the following threshold values are from the German Federal Soil Protection Ordinance for protection of plant growth and crop
 597 quality based on NH₄NO₃-extractions: As 0.4 mg kg⁻¹, Cd 0.1 mg kg⁻¹, Cu 1 mg kg⁻¹, Ni 1.5 mg kg⁻¹, Pb 0.1 mg kg⁻¹, Zn 2 mg kg⁻¹ (German
 598 Federal Soil Protection and Contaminated Sites Ordinance, 1999). PSC, pyrolysed spruce cylinders; PPS, pelletised and pyrolysed spruce.

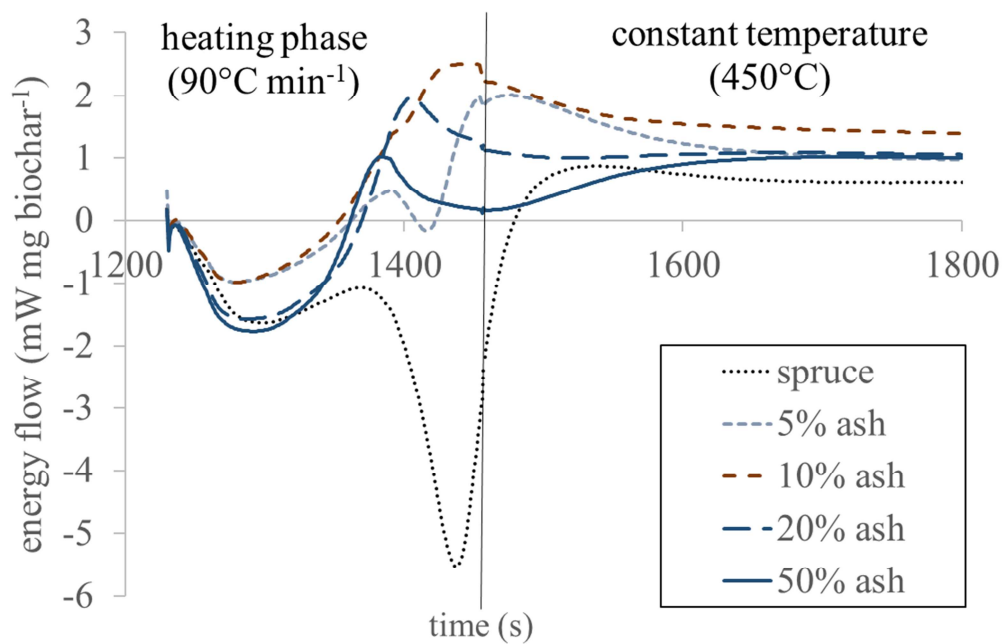
		As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Zn	
available												
	wood ash	mg kg ⁻¹	< 0.13	< 0.12	< 0.01	42.9±1.25	< 0.004	< 0.87	2.83±0.08	0.05±0.01	< 0.12	0.60±0.05
	spruce	mg kg ⁻¹	< 0.13	< 0.12	0.01±0.002	0.01±0.00	0.05±0.02	< 0.87 < 0.46		0.03±0.01	< 0.12	4.28±0.25
	PSC 0% 450°C	mg kg ⁻¹	< 0.13	< 0.12	< 0.01	< 0.002	0.02±0.01	< 0.87 < 0.46	< 0.009	< 0.12		0.13±0.03
	PPS 0% 450°C	mg kg ⁻¹	< 0.13	< 0.12	< 0.01	< 0.002	< 0.004	< 0.87 < 0.46		0.05±0.01	< 0.12	0.53±0.10
	PPS 5% 450°C	mg kg ⁻¹	< 0.13	< 0.12	< 0.01	0.14±0.00	< 0.004	< 0.87 < 0.46	< 0.009	< 0.12		< 0.01
	PPS 10% 450°C	mg kg ⁻¹	< 0.13	< 0.12	< 0.01	0.19±0.00	< 0.004	< 0.87 < 0.46	< 0.009	< 0.12		< 0.01
	PPS 20% 450°C	mg kg ⁻¹	< 0.13	< 0.12	< 0.01	0.11±0.00	0.02±0.00	< 0.87 < 0.46	< 0.009	< 0.12		< 0.01
	PPS 50% 450°C	mg kg ⁻¹	< 0.13	< 0.12	< 0.01	0.20±0.01	0.11±0.02	< 0.87 < 0.46	< 0.009	< 0.12		< 0.01
total												
	wood ash	mg kg ⁻¹	5.77±0.32	4.04±0.07	11.3±1.25	537±6.38	142±2.72	< 30.6	32.7±0.07	49.0±0.11	33.5±0.54	373±5.78
	spruce	mg kg ⁻¹	< 1.20	0.02±0.02	< 0.21	0.76±0.18	1.11±0.40	< 30.6 < 11.2		< 0.10	< 1.41	4.21±1.56
	PSC 0% 450°C	mg kg ⁻¹	< 1.20	0.02±0.02	< 0.21	< 0.13	2.94±0.75	< 30.6 < 11.2		0.38±0.08	0.63±0.44	17.6±7.81
	PPS 0% 450°C	mg kg ⁻¹	< 1.20	0.07±0.03	< 0.21	2.54±0.85	36.9±11.1	< 30.6 < 11.2		5.65±2.49	3.17±0.33	40.5±40.8
	PPS 5% 450°C	mg kg ⁻¹	< 1.20	0.31±0.02	2.31±0.12	91.9±5.48	33.0±4.41	< 30.6 < 11.2		14.9±2.36	6.60±0.67	101±5.20
	PPS 10% 450°C	mg kg ⁻¹	< 1.20	0.39±0.04	3.26±0.14	142±6.94	42.2±0.76	< 30.6 < 11.2		22.1±0.39	9.06±0.23	141±2.25
	PPS 20% 450°C	mg kg ⁻¹	2.94±0.79	1.75±0.21	4.59±0.23	226±16.6	69.9±6.23	< 30.6 < 11.2		26.8±2.16	9.80±0.33	192±13.1
	PPS 50% 450°C	mg kg ⁻¹	3.70±0.37	3.22±0.09	6.52±0.15	352±8.82	107±0.56	< 30.6 < 11.2		38.8±1.00	17.8±0.47	275±4.27

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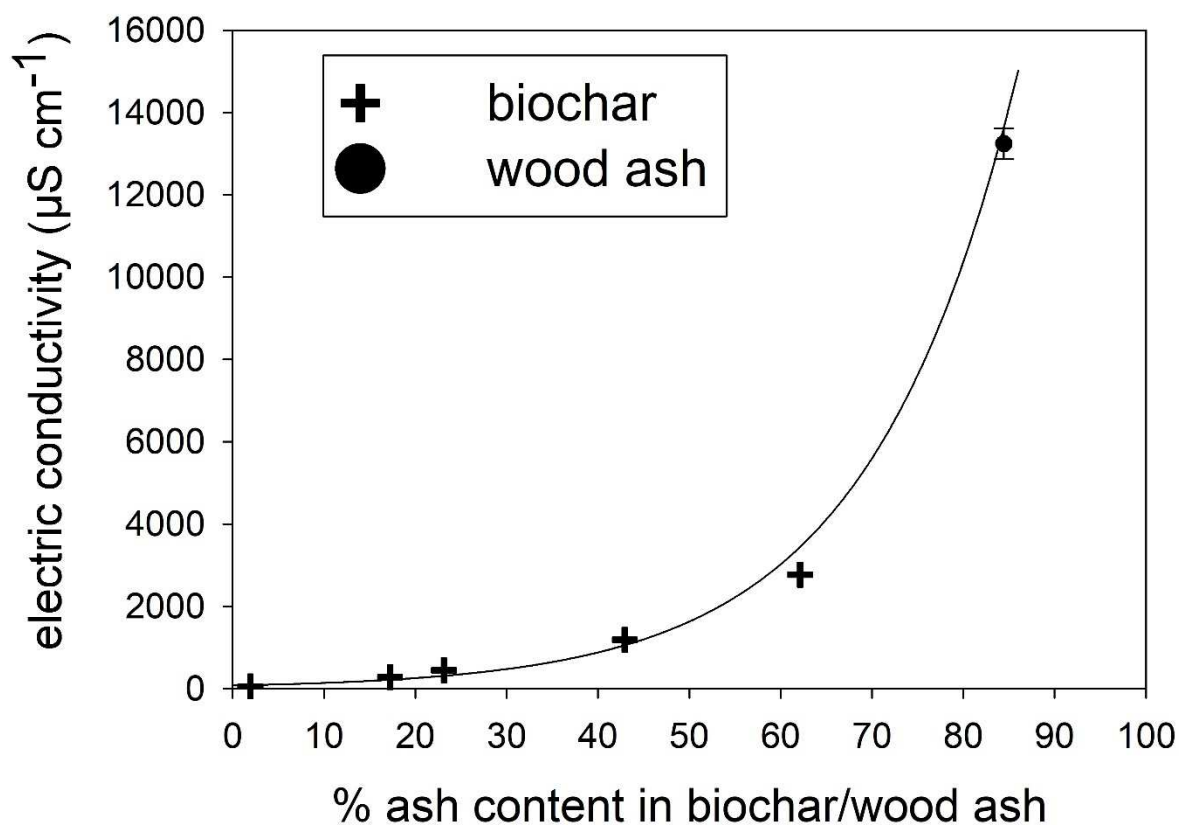
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601 Figure 1: Effect of wood ash addition on biochar yield (in % dry, ash-free biochar / dry, ash-
602 free feedstock) compared to the unamended control in % performed in a TGA (n = 3) and the
603 auger reactor (n = 1). No standard deviation shown here for auger reactor, raw values can be
604 found in Table 1 and SI Table 2.



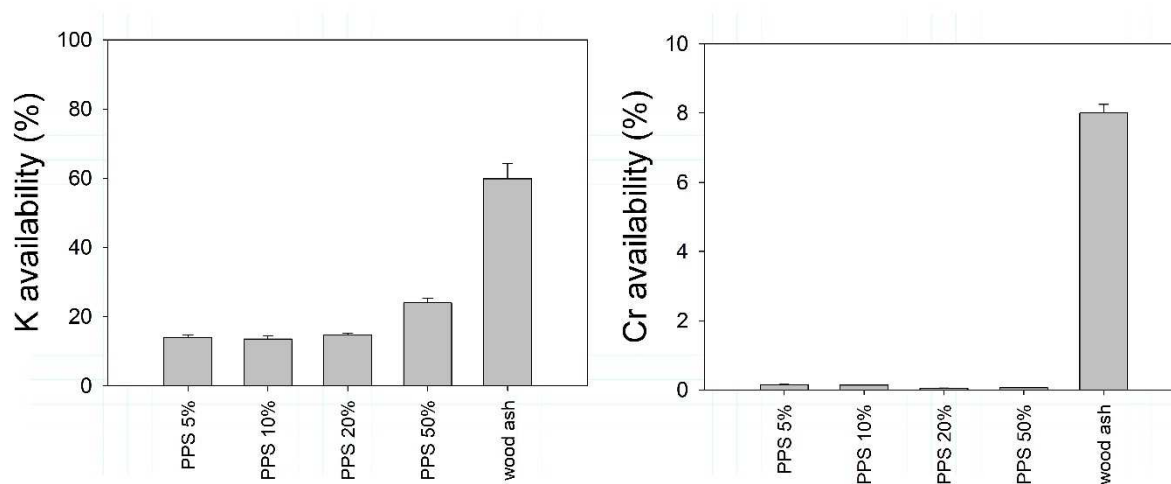
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606 Figure 2: DSC curve from pyrolysis of spruce in a TGA at 450°C with different percentages
 607 of wood ash additions. Initial stages of moisture removal at 110°C not shown, starting with
 608 heating phase at 90°C min⁻¹ heating, followed by an isothermal phase at 450°C for ~10 min.



609

610 Figure 3: Relationship between electric conductivity (EC) in biochar/pure wood ash with ash
 611 content in the materials. Ash contents determined via TGA through combustion in air at
 612 900°C (wood ash with ~16% residual carbon). An exponential curve of type $y = a * e^{bx}$ was
 613 fitted to the data. Mean EC values with standard deviation of duplicate analyses are shown.



614

615 Figure 4: Elemental availability of K and Cr as % 0.01 M CaCl₂ extractable of the total
616 elemental content in 450°C biochar with varying ash contents (%) and in pure wood ash.
617 PPS, pelletised and pyrolysed spruce 450°C.

Highlights

- Wood ash was mixed with pine wood and pyrolysed to create biochar-ash composites
- Biochar yield on ash-free basis was increased by 80-90% with 50% wood ash addition
- The percentage available of the total Cr content decreased by a factor of 50-160
- The EC and available K content of the biochar was also significantly reduced
- Biochar-ash composites are very promising organo-mineral fertilisers