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# 1 **Effects of selected process conditions on the stability of hydrochar** 2 **in low-carbon sandy soil**

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## 10 **Abstract**

11 Biochars have been found to enhance soil properties and to reduce atmospheric  
12 greenhouse gases due to their stable carbon fractions. It is known that stable carbon  
13 fractions of pyrolysis-derived biochars usually exhibit mean residence times (MRT) of  
14 at least several hundred years. However, only a few studies exist on the stability of  
15 hydrochars, which are produced by hydrothermal carbonization (HTC).

16 This study examined the influence of two feedstock materials, straw digestate and  
17 poplar, and several processing and treatment parameters (carbonization temperature,  
18 washing of hydrochars and recirculating of process water) on the stability of hydrochars  
19 in a carbon-poor sandy soil. The results show that HTC leads to a product of variable  
20 carbon fractions with different stabilities as reflected in the different rates of CO<sub>2</sub>-C  
21 release from soil incubations within the first weeks. The carbon pool of the hydrochars

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22 could be classified into a readily available and a fast-cycling decade-scale fraction. No  
23 slow-cycling centennial-scale carbon fraction was observed in this 120-day study.  
24 Moreover, a high reaction temperature and enhanced recirculation rate of process liquor  
25 lead to higher stability of the hydrochars. Based on the two-pool model, the more stable  
26 carbon had an MRT of 4-15 y depending on the reaction temperature and an MRT of  
27 11-14 y for the recirculation of process liquor. The main hypothesis, that this short-term  
28 study of 120 days allows a reliable description of the long-term degradability of  
29 hydrochars, could not be confirmed.

### 30 **Keywords**

31 Biochar, hydrochar, hydrothermal carbonization, carbon degradation, char stability,  
32 carbon balance

### 33 **Abbreviations**

34 DAF: dry and ash free; DM: dry matter; FM: fresh matter; HTC: hydrothermal  
35 carbonization; LSM: least square method; MRT: mean residence time; ODM: organic  
36 dry matter; P: poplar; rec: recycled; Sd: straw digestate; SOM: Soil organic matter,  
37 unw: unwashed, VDLUFA: Verband Deutscher Landwirtschaftlicher Untersuchungs-  
38 und Forschungsanstalten e.V.; w: washed

## 39 **1. Introduction**

40 Biogas is recognized worldwide as a highly valuable renewable energy and it is  
41 produced and used extensively. In the ongoing search for new types of suitable  
42 feedstock, agricultural wastes and by-products such as manure and straw are receiving

43 more attention (Chen et al., 2014; Ribeiro and Raiher, 2013). However, the increased  
44 desire to put agricultural waste biomass to more complete use is not due to the demand  
45 for biogas production alone, but can be ascribed to the prosperous bio-based economy  
46 in general. On the one hand this can be a boon to the local economy, since new  
47 applications and higher prices for organic wastes add value to agricultural production  
48 and provide new business opportunities. On the other hand, higher withdrawal of  
49 biomass from the field can interfere with the soil's carbon balance and consequently  
50 threaten soil fertility (Thornley et al., 2014). A possible solution to this conflict of  
51 interest could be to stabilize organic wastes prior to their soil use, so that much less  
52 carbon needs to be returned. One of the options for stabilizing biomass is to convert it to  
53 biochar by pyrolysis. This has attracted considerable attention as a possible solution for  
54 both sequestering atmospheric carbon and simultaneously enhancing soil properties  
55 (Lehmann, 2007). Despite the large diversity in experimental results, pyrogenic carbon  
56 is assumed to have a high MRT, with turnover on a centennial scale (Singh et al., 2012).  
57 While pyrolysis is by far the most commonly used technology to produce biochar, in  
58 recent years interest has expanded to the HTC process, especially for organic waste  
59 treatment (Titirici et al., 2007). The use of HTC, which is a water-based process, can  
60 eliminate the energy-intensive drying step for wet feedstocks. One abundant type of  
61 water-rich biomass is the residue emerging from the biogas production unit after  
62 anaerobic digestion, called digestate. Digestate has been reported to contain 44.3-98.5  
63 % water, while its dry matter is largely organic (38.6-75.4 %) (Nkoa, 2014).

64 However, the solid products of HTC and dry pyrolysis do not have the same chemical  
65 composition due to the different reaction mechanisms that lead to carbonization (Falco  
66 et al., 2011b; Libra et al., 2011). Therefore, it is important to differentiate between the

67 two chars in terminology and in studies of potential applications. The term 'pyrochar' is  
68 used here to denote char produced by dry pyrolysis, whereas hydrothermally produced  
69 char is called 'hydrochar' (Libra et al., 2011). The authors point out that this terminology  
70 is irrespective of the chemical nature of the product and that a fraction of the hydrochar  
71 rather resembles 'coke' as defined by Fitzer et al. (1995), Antal and Grønli (2003) and  
72 Kruse et al. (2013). Indeed, the chars themselves may contain very heterogeneous  
73 structures or pools of carbon. As a consequence of this difference in chemical nature,  
74 there is still an urgent need to investigate whether the concepts proposed for pyrochar  
75 will also work with hydrochar. Since this paper deals exclusively with the stability of  
76 hydrochar, the dry poplar wood chips were also carbonized by HTC and not by  
77 pyrolysis for the purpose of comparison with the hydrochars produced from the wet  
78 feedstock straw digestate.

79 HTC is a well-known process for converting biomass to a product comparable with  
80 lignite. It has been used as a laboratory simulation method for natural coalification for  
81 decades and is often termed hydrous pyrolysis (Krevelen, 1993; Wilkins and George,  
82 2002). Practical applications of this conversion process existed to a limited extent for  
83 dewatering of lignite (Fohl et al., 1987) and peat beneficiation (Mensingher, 1980).  
84 Recently, HTC has been increasingly used for the production of carbonaceous  
85 nanocomposites and functionalized porous materials (Titirici et al., 2012; Wang et al.,  
86 2001). However, little is known about using the solid product from HTC in soils (Dicke  
87 et al., 2014; Eibisch et al., 2015; Libra et al., 2011). A strong influence of HTC reaction  
88 temperature on the MRT in soil has already been described (Gajić et al., 2012), but in  
89 general the stability of hydrochars in soil is lower than that of pyrochars (Bamminger et  
90 al., 2014; Steinbeiss et al., 2009).

91 The overall aim of this work is to determine to what extent HTC process conditions and  
92 post-treatments influence the stability of hydrochar in a carbon-poor sandy soil. It is  
93 hypothesized, that the lignin content of the biomass can be used as an indicator for the  
94 stability of hydrochars. The main hypothesis is that the long-term degradability of  
95 hydrochars can be described by fractioning the carbon pool in terms of biodegradability  
96 within this 120-day study.

## 97 **2. Materials and methods**

### 98 **2.1 Materials**

99 For this study, a carbon-poor soil with 0.62 % carbon (corresponding to 1.3 % DM soil  
100 organic matter (SOM)), a C/N ratio of 10.9 and a pH of 7.2 was used. The solum (0-30  
101 cm), taken at Leibniz-Institute of Vegetable and Ornamental Crops (IGZ) in  
102 Grossbeeren (Germany), south of Berlin, was determined as a pure sand (1.3 % clay, 7.9  
103 % silt and 90.8 % sand) according to DIN ISO 11277:2002-08 (2002). It represents a  
104 Cambisol, which is often found in Northeast Germany.

105 Two different kinds of biomass were used for the production of hydrochar: straw  
106 digestate (Sd) and poplar wood chips (P) (Table 1). The wet straw digestate was  
107 obtained from an upflow anaerobic solid-state reactor (Mumme et al., 2010) as residue  
108 of biomethane production at 55 °C (Pohl et al., 2012). Poplar wood was provided by the  
109 Saxon State Office for Environment, Agriculture and Geology (Germany). The hybrid  
110 poplars grew four to five years in a short-rotation coppice (N51°30'7.25", E13°7'20.28")  
111 up to February 2012. The wood from a mixture of several poplar trees was cut into

112 chips with a length of 2 mm (Pulverisette 19, Fritsch) and dried for 24 h at 105 °C.

113 Further information is given in Table 1.

## 114 **2.2 Hydrochar sample preparation**

115 Hydrochars were produced using a 1 L General Purpose Bench Top Reactor (Series  
116 4520 from Parr). The amounts of feedstocks in the respective production runs were 48 g  
117 of dried poplar wood chips (105 °C) or 300 g of fresh wet digestate. In order to achieve  
118 a dry matter content of 10 %, the reactor was filled each time with deionized water to  
119 reach a total mass of 480 g. Poplar was carbonized at 230 °C. For straw digestate, the  
120 reactor was heated to three different temperatures (210 °C, 230 °C and 250 °C) using a  
121 constant heating rate of 1.7 K min<sup>-1</sup>. The temperatures were maintained for six hours in  
122 each case.

123 All char samples were prepared in triplicate, except for the runs at 230 °C to study the  
124 effect of recirculating the process liquor. In this case, six hydrochars were produced at  
125 230 °C, and the process liquor from the previous run was recirculated. To study the last  
126 parameter, hydrochar samples with and without post-process washing were produced.  
127 The hydrochars were washed by adding 100 mL of deionized water to the filter cake six  
128 times. Before further use all the hydrochars were dried at 105 °C for at least 15 h.

## 129 **2.3 Determination of the carbon balance of the HTC-process**

130 From each run, solid hydrochar, process water and gas were collected, balanced and  
131 analyzed. To determine the carbon balance from the HTC-process, gas was collected in  
132 a bag and its volume was determined by using an eudiometer. The amounts of CO<sub>2</sub> and  
133 CH<sub>4</sub> were determined using the gas measuring equipment “Geotech GA2000”  
134 (Geotechnical Instruments).

135 Carbon partitioning between the phases was calculated using the following equations.

136 The amount of carbon in g C was determined for the biomass and hydrochars using

137 equation 1. Here,  $m_{\text{solids}}$  denotes the mass of biomass or hydrochar in g DM and

138  $x(\text{carbon})_{\text{solids}}$  denotes the measured percentage of carbon on a mass basis.

$$139 \quad m(\text{carbon})_{\text{solids}} = m_{\text{solids}} * x(\text{carbon})_{\text{solids}} / 100 \quad (1)$$

140 The amount of carbon (in g C) in process liquor or washing water was calculated as

141 follows:

$$142 \quad m(\text{carbon})_{\text{liquids}} = m_{\text{liquids}} * \text{TOC} / \rho \quad (2)$$

143 Here,  $m_{\text{liquids}}$  denotes the mass of process liquor or washing water in g, and TOC denotes

144 its measured total organic carbon.  $\rho$  is the density of process liquor or washing water.

145 The calculation of carbon in the gas was carried out as follows:

$$146 \quad m(\text{carbon})_{\text{gas}} = V * M(\text{C}) * ( x(\text{CO}_2)_{\text{Gas}} * \rho(\text{CO}_2)_{\text{Gas}} / M(\text{CO}_2)_{\text{Gas}} + x(\text{CH}_4)_{\text{Gas}} *$$

$$147 \quad \rho(\text{CH}_4)_{\text{Gas}} / M(\text{CH}_4)_{\text{Gas}} ) / 100 \quad (3)$$

148 The  $x$  describes the measured amounts of  $\text{CO}_2$  or  $\text{CH}_4$  in % on a volume basis,  $M$  is the

149 molecular mass for C,  $\text{CO}_2$  or  $\text{CH}_4$ ,  $\rho$  is the density of  $\text{CO}_2$  or  $\text{CH}_4$ , and  $V$  denotes the

150 measured gas volume. Subsequently, the percentage distribution of carbon was

151 determined.

## 152 **2.4 Chemical analyses**

153 The pH-value of soil and hydrochar was determined according to VDLUFA I A 5.1.1

154 (Methodenbuch Band I, 1991 comparable to DIN ISO 10390:2005-12, 2005), and for

155 biomasses DIN 38404-5:2009-07 (2009) was used. Cellulose, hemicellulose and lignin

156 contents of the biomasses were measured using the 'FilterBag' method according to the



157 German Handbook of Agricultural Experimental and Analytical Methods (VDLUFA  
158 III, Chap. 6.5.1 - 6.5.3, Methodenbuch Band III, 1976). Dry matter (DM) of biomasses  
159 and hydrochars was measured at 105°C in accordance with DIN EN 12880:2001-02  
160 (2001). The SOM was measured in accordance with DIN ISO 10694:1996-08 (1996) in  
161 contrast to the ODM of biomasses and hydrochars, which was determined in accordance  
162 with VDLUFA III Chap. 8.4. (Methodenbuch Band III, 1976). The elemental analysis  
163 of carbon, hydrogen, nitrogen and sulfur was performed with a Vario EL elemental  
164 analyzer (Table 2) according to VDLUFA III Chap. 4.1.2 (Methodenbuch Band III,  
165 1976 referring to DIN EN ISO 16634-1:2009-07, 2009); each sample was analyzed  
166 three times. Oxygen was calculated by difference: 100 % - percentage of C, H, N and S.  
167 The volatile matter from biomasses and hydrochars was determined in accordance with  
168 DIN 51720:2001-03 (2001). Statistical evaluation of the experimental data was  
169 conducted using Matlab R2012b (8.0.0.783). Built-in functions for ANOVA testing  
170 were used, followed by separation of means based on Tukey's honestly significant  
171 difference criterion ( $p < 0.05$ ). Total organic carbon (TOC) of the liquid phase was  
172 measured using a TOC Analyzer 5050A (Shimadzu Scientific Instruments, Columbia,  
173 MD, USA). All statistical analyses were conducted with a t-test. Significance levels  
174 were set at  $p = 0.001$ ,  $p = 0.01$  and  $p = 0.05$ .

## 175 **2.5 Incubation experiments**

176 The hydrochars were incubated for 120 d in 125 mL Boston Round Bottles. In total,  
177 10 g dry matter of soil and hydrochar was weighed into each vessel. In order to obtain  
178 equal conditions, the initial carbon content of the soil was topped up to the uniform  
179 value of 1.24 % (twice the soil's natural carbon content) by adding between 90 and 116  
180 mg hydrochar and 140 to 979 mg of the feedstock, respectively. Untreated soil was used

181 as a control. The maximum water-holding capacity of the mixtures was measured  
 182 according to Öhlinger (1996) and set to 50 %. Each varied parameter was present in two  
 183 to six repetitions (2x: samples from recirculated process liquor; 6x: soil control, each  
 184 biomass and washed hydrochar from digestate/poplar at 230 °C; 3x: all others). CO<sub>2</sub>  
 185 was measured by gas chromatography (CP-3800 from Varian, columns: Hayesep  
 186 N80/100 1mx1/8“ss and Porapak QS80/100 2mx1/8“ss, detectors: Flame Ionization  
 187 Detector and Electron Capture Detector, rate of flow: 30 ml/min). The measurements of  
 188 accumulated CO<sub>2</sub> were performed on days 0, 1, 4, 12, 22, 33, 43, 54, 64, 75, 85, 99 and  
 189 120 of incubation. The results were calculated using equations 4 and 5 and are given in  
 190 μg CO<sub>2</sub>-C per day and gram soil mixture on a dry basis (μg CO<sub>2</sub>-C g<sup>-1</sup> soil d<sup>-1</sup>):

$$191 \quad m_{(\mu\text{g CO}_2\text{-C g}^{-1} \text{ soil})} = V_{\text{vial}} * \beta(\text{CO}_2) / (10 * 3.67) \quad (4)$$

$$192 \quad m_{(\mu\text{g CO}_2\text{-C g}^{-1} \text{ soil d}^{-1})} = m_{(\mu\text{g CO}_2\text{-C g}^{-1} \text{ soil})} / \Delta d \quad (5)$$

193  $V_{\text{vial}}$ : volume of bottle in m<sup>3</sup>,

194  $\beta(\text{CO}_2)$ : measured mass concentration of CO<sub>2</sub> in μg m<sup>-3</sup>,

195 10: amount of soil per vial in g,

196 3.67: molecular conversion factor (CO<sub>2</sub>/C),

197  $\Delta d$ : time difference in days between two measurements.

198

199 The summarized values, after 120 days of incubation are given in mg CO<sub>2</sub>-C kg<sup>-1</sup> soil

200 (Table 3). Statistical evaluation of these data was performed with Matlab R2012b

201 (8.0.0.783). Built-in functions for ANOVA testing were used, followed by separation of

202 means based on Tukey's honestly significant difference criterion (p<0.05). The

203 degradation kinetics of the carbon fractions was determined using the gaseous carbon

204 losses. Possible priming effects as reported by Bamminger et al. (2014) have not been

205 considered in this study. Because of their simplicity and frequent use in SOM

206 degradation, two models for first-order kinetics were compared (McGill, 1996). The  
 207 one-fraction model treats the hydrochar as one carbon pool, while the two-fraction  
 208 model considers two pools with two rates of degradation. The experimental data of  
 209 initial C content as well as cumulative C content at specific time points were fitted to  
 210 the models with Matlab release R2013a, Method: Non-linear least squares, Toolbox:  
 211 Curve Fitting Toolbox:

212 Model 1:

$$213 \quad C(t) = C_0 * \exp^{-k_1 t} \quad (6)$$

214  $C(t)$ : Organic carbon at specific time,  $C_0$ : Initial organic carbon content of soil (control)  
 215 and soil biochar mixtures of the respective treatments,  $k_1 t$ : Decomposition rate of carbon  
 216 fractions at specific time

217 Model 2:

$$218 \quad C(t) = C_0 * (x * \exp^{-k_2 t} + (1-x) * \exp^{-k_3 t}) \quad (7)$$

219  $C(t)$ : Organic carbon at specific time,  $C_0$ : Organic carbon at the beginning of the 120 d  
 220 study,  $x$ : Readily available carbon fractions (MRT of several days),  $1-x$ : Fast-cycling  
 221 carbon fractions,  $k_2 t$ : Decomposition rate of readily available carbon fractions at specific  
 222 time,  $k_3 t$ : Decomposition rate of fast-cycling carbon fractions at specific time.

223 The Least square method was followed (LSM) to verify the model.

224 MRT ( $\tau$ ) was determined by calculating the reciprocal of the decomposition rate  
 225 constant:

$$226 \quad \tau = 1 / k \quad (8)$$

## 227 **3. Results**

### 228 **3.1 Effects of process conditions on the composition of hydrochars and the** 229 **liquid and gaseous phases**

230 An elemental analysis of the hydrochars produced shows a statistically significant  
231 increase in carbon and nitrogen with increasing process temperature (Table 2).

232 Differences were also found in the characteristics of the two feedstocks. So the initial  
233 carbon content was significantly higher for poplar compared with the straw digestate.

234 By contrast with this result, the carbon content of hydrochars from poplar was just one  
235 percentage point lower than that of straw digestate and did not differ significantly.

236 Another difference between the feedstocks is their ash content, which is higher in the  
237 case of wheat straw digestate. Its ash content after HTC is even higher in contrast to the  
238 decreased ash content for hydrochar of poplar. Other variations in sample preparation  
239 such as washing and recirculating of process water did not result in any significant  
240 difference in the composition of the hydrochar (Table 2).

241 Carbon balances reveal that between 60 and 74 % of the initial carbon is recovered with  
242 the solid product and that this recovery decreases with increasing reaction temperature  
243 (Figure 1). Between 18 and 24 % of the carbon input can be found in the process liquor  
244 and about 2 to 3 % of the initial carbon could be removed by subsequent washing with  
245 deionized water. Approximately 1 to 3 % of the carbon input was found in the gaseous  
246 phase. Furthermore, between 4 and 12 % of carbon could not be recovered in the mass  
247 balance.

## 248 **3.2 Carbon mineralization in incubation experiments**

249 The incubation of hydrochars resulted in significantly lower emission rates of CO<sub>2</sub>-C  
250 compared with the non-carbonized feedstocks, straw digestate and poplar (Figure 2a).  
251 After 120 d of incubation, the cumulative CO<sub>2</sub>-C-emissions from hydrochars were up to  
252 11.9 % and are significantly lower than the CO<sub>2</sub>-C-emissions of the untreated biomasses  
253 of poplar and straw digestate at 17.3 % and 22.1 %, respectively (Table 3).

### 254 **3.2.1 Effect of feedstock**

255 Comparing the CO<sub>2</sub>-C rates of hydrochars from digestate and poplar, it can be seen that  
256 the CO<sub>2</sub>-C rate of hydrochar from poplar is considerably higher up to the 64<sup>th</sup> day of  
257 incubation (Figure 2a). The same can be observed for the untreated poplar by  
258 comparison with straw digestate up to the fifth day of incubation. Obviously, poplar  
259 contains more readily available organic matter than straw digestate, because this  
260 fraction has been digested from the straw feedstock to a certain extent during the  
261 anaerobic digestion process. This observation is also reflected in the higher amount of  
262 volatile matter in poplar compared with straw digestate, both in the biomass and in the  
263 hydrochar produced (Table 3). At the end of incubation after 120 d, the decomposed  
264 carbon already totals 4.31 % for the mix of soil and hydrochar from poplar by contrast  
265 with 3.94 % for hydrochar from straw digestate in soil (Table 3 and Supplemental Table  
266 1).

### 267 **3.2.2 Effect of process temperature**

268 As shown in section 3.1 the process temperature has the largest influence on the  
269 elemental carbon content of hydrochars. On the other side, the higher the process  
270 temperature, the lower the CO<sub>2</sub>-C emission rates from the hydrochar/soil mixtures are,

271 pointing to higher stability (Figure 2b). Even after 120 d of incubation, these differences  
272 are still present as reflected by significantly lower emissions of CO<sub>2</sub>-C at 230 °C  
273 compared with 210 °C. This corresponds with an enhanced degree of stabilization,  
274 which is higher than that between 230 and 250 °C. The hydrochar produced at 230 °C  
275 emits 60 % less CO<sub>2</sub>-C compared with the 210 °C hydrochar, whereas that produced at  
276 250 °C emits 28 % less CO<sub>2</sub>-C than the 230 °C hydrochar.

277 Furthermore, the volatile matter reflects the degree of degradability. This decreases with  
278 increasing process temperature from 70.3 % at 210 °C to 50.5 % at 250 °C (Table 3).  
279 That indicates less readily available carbon with increasing process temperatures and  
280 thus less degradation by microorganisms resulting in lower CO<sub>2</sub>-C emission rates.

### 281 **3.2.3 Effect of char washing**

282 Washing the hydrochars significantly affected the CO<sub>2</sub>-C emission. Especially during  
283 the first days of incubation, the washed hydrochars emitted less CO<sub>2</sub>-C than their  
284 unwashed counterparts. However, after a maximum of 54 days of incubation, no  
285 statistically significant differences between the various treatments could be identified  
286 anymore. Only one hydrochar, produced at 210 °C, emitted significantly less CO<sub>2</sub>-C  
287 also after 120 days of incubation (Figure 2b).

### 288 **3.2.4 Effect of recirculating the process water**

289 Significant differences in CO<sub>2</sub>-C emission can only be seen in the hydrochar of the  
290 fivefold-recirculated process liquor by comparison with the control without  
291 recirculation. This significance persists up to the 43<sup>rd</sup> day of incubation (Figure 2c).

292 Although not reflected in the carbon content of the hydrochar under study, each step of  
293 recirculating the process water reduces the volatile matter by up to four percentage

294 points in the fivefold-recirculated hydrochar (Table 3). This leads to an accumulation of  
295 organic carbon in the process water of about 35 % compared with process water without  
296 recirculation.

### 297 **3.3 One- and two-pool degradation kinetics**

298 As reflected in the cumulative amount of gaseous carbon after 120 d of incubation,  
299 poplar was less degraded than straw digestate (17.32 and 22.11 % decomposed carbon,  
300 Table 3 and Supplemental Table 1). The MRT of the one-fraction model seems to  
301 confirm this observation with MRTs of 1.6 and 1.1 y, respectively (Table 4). The two-  
302 fraction model, however, delivers better results than the one-fraction model, as can be  
303 seen from the comparison of the goodness of fit for the two models expressed by the  
304 LSM (Table 4). With this two-fraction model, which includes a readily available and a  
305 fast-cycling carbon fraction, there are differences in the MRT of the two biomasses  
306 regarding the readily available fraction. In contrast, the MRT of the fast cycling fraction  
307 is almost identical.

308 The fast-cycling carbon pool of the hydrochar is characterized by an MRT ranging  
309 between 3.4 and 14.8 y (Table 4). Apart from this carbon pool, no slow cycling carbon  
310 pool was found during the 120 d of measurements, such as is known for pyrolysis chars.  
311 Instead, a readily available carbon fraction was found in the hydrochars with very short  
312 MRTs between 9 and 26 d (Table 4).

## 313 **4. Discussion**

### 314 **4.1 Impact of feedstock and process temperature on the composition and stability** 315 **of hydrochars**

#### 316 **4.1.1 Impact of feedstock on the stability of hydrochars**

317 The amount of CO<sub>2</sub> released in incubation experiments reflects the mineralization of  
318 char compounds. Generally it is accepted that the kind of feedstock influences the rate  
319 of mineralization and thus the degree of stability of char products (Singh et al. 2012;  
320 Zimmerman et al. 2011; Eibisch et al. 2013). In our study the difference in carbon  
321 content between feedstock and hydrochar was higher for wheat straw than for poplar.  
322 This means that the carbonization of poplar was less intense compared with that of  
323 wheat straw. Reaction conditions of HTC tend to degrade primarily hemicellulose and  
324 cellulose by hydrolysis, whereas lignin remains fairly stable (Kruse et al., 2013; Liu and  
325 Guo, 2015). Feedstock fiber analysis shows that poplar wood has a higher lignin content  
326 than the straw digestate (Table 1), which also explains the lower degree of  
327 carbonization. This higher lignin content of the biomass is also reflected in the  
328 incubation studies, because the poplar biomass sample emits significantly less CO<sub>2</sub> after  
329 120 d than the straw digestate. This behavior changes after HTC and it is observed that  
330 hydrochar from poplar decomposes more than that from straw digestate under the same  
331 process conditions. Even this difference is not significant (Table 3). Similar results have  
332 been reported for lignin-containing wood powder and holocellulose (cellulose +  
333 hemicellulose) by Liu and Guo (2015). This indicates that the products from  
334 hydrothermal treatment, more specifically the polymerization products from  
335 carbohydrate hydrolysis, are characterized by a higher stability than lignin. One  
336 explanation is that cross-linked phenylpropane units of the lignin polymer have been  
337 detached from the cellulose chain at a temperature of 230° C, becoming degradable  
338 themselves and making cellulose and hemicellulose deriving from the lignin polymer  
339 amenable for microbial degradation. However, further investigations are required to  
340 validate these preliminary observations.



341 **4.1.2 Impact of HTC process temperature on the composition and stability of**  
342 **hydrochars**

343 The increase in carbon content with rising process temperature is a well-known  
344 correlation for HTC (Funke and Ziegler, 2010). The effect of reaction conditions on  
345 elements other than carbon, hydrogen and oxygen is less well investigated. In this study  
346 it can be observed that the nitrogen content of the hydrochars also increases with  
347 temperature. This supports observations of an earlier study on the behavior of nitrogen  
348 during HTC (Funke et al., 2013a). In another study it was observed that the nitrogen  
349 content of hydrochars obtained from microalgae was lower than that of the original feed  
350 (Heilmann et al., 2010). This, however, may be explained by the high nitrogen content  
351 of 7-12 % in the microalgae, which in part was probably lost to the gas phase during the  
352 HTC process.

353 The content of other elements represented by the ash content accumulates in the  
354 hydrochar after HTC of straw digestate and increases further with the process  
355 temperature. The solubility of salts in water decreases rapidly towards the critical point  
356 facilitating their recovery with the solid product. Both, accumulation and leaching of  
357 ash by HTC have been reported in literature, the former being observed as a tendency  
358 for high-ash starting materials (Zhao et al., 2014; Liu et al., 2014; Parshetti et al., 2013).  
359 This is supported by the present study because the hydrochar of the low-ash poplar is  
360 characterized by lower ash content than its starting material.

361 Notably, the ash content of hydrochar from straw digestate is reduced by washing with  
362 de-ionized water. This can be explained by easily leached minerals such as potassium.

363 As expected, hydrochars show an increase in stability compared with the untreated  
364 biomass in soil. One reason for the increasing stability with increasing temperature is

365 the intensified protonation of the OH groups during dehydration and the reaction of  
366 monomers to polymers by resolution of their multiple bonds (Funke and Ziegler, 2010).  
367 Furthermore, the polymers are strongly aromatized with increasing temperature (Falco  
368 et al. 2011a, 2011b), which results in a higher degree of carbonization (compare the H/C  
369 and O/C ratios in Table 2), leading to lower CO<sub>2</sub>-C-rates. Recently Liu and Guo (2015)  
370 found a threshold range of HTC temperature between 210 and 220 °C, above which the  
371 resistance to degradation increased clearly. It could be shown that in this temperature  
372 range the crystalline structure of cellulose started to disintegrate during HTC.  
373 Delignified substrates such as holocellulose were degraded much more easily compared  
374 with wood powder of poplar well protected by lignin. This is in good accordance with  
375 our results for straw digestate and poplar wood chips. Also, Bai et al. (2013) observed  
376 significantly different cumulative carbon degradation over a time period of 200 days  
377 after treating Miscanthus with HTC at 200 °C. Similar effects of HTC reaction  
378 temperature on the degradability of the hydrochar produced have been published  
379 previously and show consistence (Ramke and Hendricks, 2011; Gajic et al., 2012). It  
380 should be noted that hydrochar is produced at relatively low temperatures as compared  
381 to dry pyrolysis. Consequently, hydrochar is degraded to a certain extent and it was  
382 shown elsewhere that it even stimulates microbial activity in soil (Bargmann et al.,  
383 2014).

384

## 385 **4.2 Impact of post-treatments on hydrochar stability**

### 386 **4.2.1 Washing**

387 The results of the washing experiment show that water-soluble organics, which are  
388 easily mineralized by microorganisms, are removed by washing. It is known that several

389 organic acids are byproducts of HTC, such as e.g. acetic, formic and glycolic acid  
390 (Berge et al., 2011; Reza et al., 2014; Stemann and Ziegler, 2011; Yan et al., 2010). As  
391 a minimum, calculated from Table 3, they represent 0.35 % - 2.32 % of the initial  
392 carbon and have to be regarded as readily available. These byproducts affect the  
393 measured stability of the hydrochar negatively, although they cannot be considered part  
394 of the solid product. As shown by recent studies, there is a need to distinguish clearly  
395 between the mineralization of labile byproducts and that of the hydrochar in order to  
396 increase the validity of the results (Dicke et al., 2014; Eibisch et al., 2013).

#### 397 **4.2.2 Recirculation of process water**

398 An accumulation of organic carbon in the process water by consecutive recirculation  
399 has been previously reported and explained by an enhanced concentration of organic  
400 acids, which accumulate in the process liquor (Stemann and Ziegler, 2011). In this  
401 investigation, there is no significant change in the carbon content of the hydrochar,  
402 which contradicts the aforementioned experiments. However, in that case the process  
403 water was recirculated up to twenty times (Stemann et al., 2013). Recirculation of  
404 process water leads both to an increased residence time and to a drop in initial pH due to  
405 the accumulation of organic acids. This circumstance facilitates hydrolysis (Bobleter,  
406 1994; Lu et al., 2014), the decisive first step of HTC (Kruse et al., 2013). In  
407 consequence, it is to be expected that carbonization is enhanced by recirculation of  
408 process water. While this is not reflected in the carbon content of the hydrochar under  
409 study, the decrease in volatile matter supports this hypothesis (Table 3).

410

#### 411 **4.3 Degradation kinetics**

412 The mineralization of organic matter in soils is often described by a single or double  
413 exponential decay model reflecting a one-pool and a two-pool approach, respectively  
414 (Wieder and Lang, 1982). In recent years, application of these simple models has also  
415 been discussed for biochar produced by dry pyrolysis (Lehmann et al., 2009; Singh et  
416 al., 2012). Results from a meta-analysis of 16 studies on the decay of pyrogenic carbon  
417 are interpreted as a fast-cycling pool with an average MRT of 3 y and a slow-cycling  
418 pool with an average MRT of 870 y (Singh et al., 2012). In the present study, both  
419 models have been applied for the results of the incubation experiments. It has been  
420 shown that the two-fraction model describes the degradation of hydrochar in soil better  
421 than the one-fraction model, which is in accordance with other studies on hydrochars  
422 (Dicke et al., 2014; Gajić et al., 2012; Qayyum et al., 2012) and biochars from pyrolysis  
423 (Foereid et al., 2011). However, it must be questioned whether it really describes all  
424 carbon fractions of the hydrochar.

425 The fast-cycling carbon pool was much smaller in this study compared with studies of  
426 pyrolysis chars, but it was up to seven times more stable than untreated straw digestate  
427 or poplar wood in sandy soil. These results correspond well with previously published  
428 incubation studies with hydrochar, where MRTs of 4 to 29 y and no slow-cycling  
429 carbon pool with an MRT in centennial scales were reported (Gajić et al., 2012;  
430 Steinbeiss et al., 2009).

431 The second carbon fraction represents between 0.7 and 3.0 % of the overall carbon pool  
432 depending on the process conditions. It represents readily available organic compounds  
433 due to its low MRT of several days. It is hypothesized that this carbon derived from  
434 volatile organic compounds that are adsorbed on the solid hydrochar. Despite this small  
435 amount, the result affects the calculation of the MRT in a one-pool model. Therefore,

436 this carbon fraction deserves more attention in future incubation experiments with  
437 hydrochar in order to improve the predictability of char stability.

438 Finally it has to be pointed out that due to the existing readily available carbon pool,  
439 models derived from short-term incubation studies of hydrochar cannot be regarded as  
440 reliable for describing a slow-cycling carbon pool. The readily available carbon pool  
441 represents a significant fraction for the determination of a double exponential decay  
442 model (Gajić et al., 2012). Therefore, much longer incubation studies are required in  
443 order to determine the long-term degradability of hydrochars in more detail.

444

#### 445 **4.4 Carbon recovery**

446 The carbon recovery found in the solid, the liquid and the gaseous phase of the HTC  
447 process (Figure 1) is in good agreement with results reported earlier (Berge et al., 2011;  
448 Heilmann et al., 2010, 2011; Hoekman et al., 2011; Inoue et al., 2002; Sevilla and  
449 Fuertes, 2009; Stemann and Ziegler, 2011; Wiedner et al., 2013; Yan et al., 2010). The  
450 carbon recovery with the hydrochar is in the lower range of these literature results due  
451 to the low solids content used for sample preparation. Increasing the solids content leads  
452 to higher carbon recovery with the solid product (Funke et al., 2013b ; Heilmann et al.,  
453 2010, 2011).

454 In our study, the carbon content of hydrochar increased with reaction severity (i.e.  
455 increasing temperature), while the mass loss increased simultaneously. As a  
456 consequence, the carbon yield does not change significantly and no trend can be  
457 observed.

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458 The combined measurement of the carbon recovery after HTC and the subsequent  
459 incubation studies allows a rough assessment of the suitability of HTC for sequestering  
460 carbon. Comparison of the remaining carbon after 120 d incubation shows that 77.9 %  
461 is left in the case of the straw digestate, and 96.1 % in the case of the hydrothermally  
462 carbonized digestate at 230 °C (Table 3). However, for the hydrochar, 32.9 % of the  
463 carbon is already lost during HTC due to losses associated with gaseous and liquid  
464 byproducts (Figure 1). Therefore, the residual carbon content is lower compared with  
465 that of the non-carbonized straw digestate after 120 d of incubation (Figure 3). This  
466 shows that although the stability and thus the MRT of biomass is increased by HTC, the  
467 carbon efficiency in a carbon balance can be negatively affected by the conversion  
468 process. This is true for the relatively short incubation and balance periods in this study.  
469 Longer incubation periods of at least 3 y as reported by Kuzyakov et al. (2014) would  
470 shift this picture due to longer MRTs of the hydrochar-soil mixtures.

---

## 471 **5. Conclusions**

472 The reaction temperature of the HTC process, particularly the temperature range  
473 between 210 and 230 °C, has been identified as one key factor influencing the stability  
474 of hydrochar. A significant increase in the stability of the produced char was also  
475 obtained by repeated recirculation of process liquor. The hypothesis that the stability of  
476 hydrochar correlates with the lignin content could not be confirmed, however.  
477 By applying a double exponential model, two carbon pools for the hydrochars under  
478 study could be distinguished. There is a fast-cycling pool with an MRT of up to 15  
479 years and a readily available carbon pool, which degraded within days. This fraction  
480 affects the calculated MRT of a one-pool model considerably and deserves more

481 attention in further studies. A slow-cycling carbon fraction could not be observed in this  
482 120-day study and thus our hypothesis that the long-term degradability of hydrochars  
483 can be determined within 120 days of our study could not be confirmed.

484 It is suggested that the incubation period be extended ( $> 3$  y) to obtain more reliable  
485 information about the long-term degradability of hydrochars and the carbon efficiency  
486 of the HTC process.

487 It has also to be taken into consideration that our incubation experiment was restricted  
488 to the laboratory, which does not allow extrapolation to field conditions. The influence  
489 of factors such as dry periods, varying ambient temperature and the presence of soil  
490 biota may greatly affect the stability of hydrochars. Therefore, long-term experiments in  
491 the lab and in the field must be pursued to assess the long-term stability of carbon  
492 compounds after application of hydrochars to the soil.

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500

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**700 Figure captions**

701 Table 1: Characterization of feedstock

702 Table 2: Elemental analysis of feedstock and hydrochars

703 Table 3: Cumulative amounts of CO<sub>2</sub>-C and proportion of total carbon mineralized after  
704 120 days of incubation

705 Table 4: Fitting parameters of exponential models for one-fraction:  $C(t)=C_0 \cdot \exp(-k_1t)$

706 and two-fractions:  $C(t)=C_0 \cdot (x \cdot \exp(-k_2t) + (1-x) \cdot \exp(-k_3t))$

707

708 Figure 1: Carbon balance of HTC of straw digestate as a function of process  
709 temperature (6 h, 10 % dry solids)

710 Figure 2: Mineralization rates from (a) poplar, straw digestate and their hydrochars, (b)  
711 washed compared to unwashed hydrochars at different temperatures and (c) hydrochars  
712 after 1 to 5 steps of recirculating the process water during 120 days of incubation in soil

713 Figure 3: Carbon losses after 120 d of incubation including losses due to the conversion  
714 process (left: untreated straw digestate, right: hydrochar from straw digestate (230 °C,  
715 washed)

716

717 Supplemental Table 1: Degradation of initial carbon across different treatments