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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_2-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 (Mensinger, 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

6

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^{-1}. 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_2 and

133   CH_4 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_{solids} denotes the mass of biomass or hydrochar in g DM and

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

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

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

141   follows:

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

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

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

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

146    $m(carbon)_{gas} = V * M(C) * (x(CO_2)_{Gas} * \rho(CO_2)_{Gas} / M(CO_2)_{Gas} + x(CH_4)_{Gas} *$

147    $\rho(CH_4)_{Gas} / M(CH_4)_{Gas}) / 100$ (3)

148   The x describes the measured amounts of CO_2 or CH_4 in % on a volume basis, M is the

149   molecular mass for C, CO_2 or CH_4, ρ is the density of CO_2 or 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_2

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_2 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_2-C per day and gram soil mixture on a dry basis (µg CO_2-C g^{-1} soil d^{-1}):

191    $m_{(\mu g\ CO_2\text{-}C\ g^{-1}\ soil)} = V_{vial} * \beta(CO_2) / (10 * 3.67)$ (4)

192    $m_{(\mu g\ CO_2\text{-}C\ g^{-1}\ soil\ d^{-1})} = m_{(\mu g\ CO_2\text{-}C\ g^{-1}\ soil)} / \Delta_d$ (5)

193   V_{vial}: volume of bottle in m^3,

194    $\beta_{(CO_2)}$: measured mass concentration of CO_2 in µg m^{-3},

195   10: amount of soil per vial in g,

196   3.67: molecular conversion factor (CO_2/C),

197   Δ_d: time difference in days between two measurements.

198

199   The summarized values, after 120 days of incubation are given in mg CO_2-C kg^{-1} 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    $C(t) = C_0 * \exp^{-k_1 t}$ (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    $C(t) = C_0 * (x * \exp^{-k_2 t} + (1-x) * \exp^{-k_3 t})$ (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 (τ) was determined by calculating the reciprocal of the decomposition rate

225   constant:

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

3. Results

3.1 Effects of process conditions on the composition of hydrochars and the liquid and gaseous phases

An elemental analysis of the hydrochars produced shows a statistically significant increase in carbon and nitrogen with increasing process temperature (Table 2). Differences were also found in the characteristics of the two feedstocks. So the initial carbon content was significantly higher for poplar compared with the straw digestate. By contrast with this result, the carbon content of hydrochars from poplar was just one percentage point lower than that of straw digestate and did not differ significantly. Another difference between the feedstocks is their ash content, which is higher in the case of wheat straw digestate. Its ash content after HTC is even higher in contrast to the decreased ash content for hydrochar of poplar. Other variations in sample preparation such as washing and recirculating of process water did not result in any significant difference in the composition of the hydrochar (Table 2).

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

248   **3.2 Carbon mineralization in incubation experiments**

249   The incubation of hydrochars resulted in significantly lower emission rates of CO_2-C

250   compared with the non-carbonized feedstocks, straw digestate and poplar (Figure 2a).

251   After 120 d of incubation, the cumulative CO_2-C-emissions from hydrochars were up to

252   11.9 % and are significantly lower than the CO_2-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_2-C rates of hydrochars from digestate and poplar, it can be seen that

256   the CO_2-C rate of hydrochar from poplar is considerably higher up to the 64th 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_2-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_2-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_2-C compared with the 210 °C hydrochar, whereas that produced at

276   250 °C emits 28 % less CO_2-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_2-C emission rates.

281   **3.2.3 Effect of char washing**

282   Washing the hydrochars significantly affected the CO_2-C emission. Especially during

283   the first days of incubation, the washed hydrochars emitted less CO_2-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_2-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_2-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 43rd 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_2 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_2 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_2-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.

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.

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.

500

23

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Figure captions

701 Table 1: Characterization of feedstock

702 Table 2: Elemental analysis of feedstock and hydrochars

703 Table 3: Cumulative amounts of CO_2–C and proportion of total carbon mineralized after

704 120 days of incubation

705 Table 4: Fitting parameters of exponential models for one-fraction: $C(t)=C_0 \cdot exp(-k_1 t)$

706 and two-fractions: $C(t)=C_0 \cdot (x \cdot exp(-k_2 t) + (1-x) \cdot exp(-k_3 t))$

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