THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Effects of selected process conditions on the stability of hydrochar in low-carbon sandy soil

Citation for published version:

Schulze, M, Mumme, J, Funke, A & Kern, J 2016, 'Effects of selected process conditions on the stability of hydrochar in low-carbon sandy soil', *Geoderma*, vol. 267, pp. 137-145.
<https://doi.org/10.1016/j.geoderma.2015.12.018>

Digital Object Identifier (DOI):

[10.1016/j.geoderma.2015.12.018](https://doi.org/10.1016/j.geoderma.2015.12.018)

Link:

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

Document Version:

Peer reviewed version

Published In:

Geoderma

Publisher Rights Statement:

Copyright © 2015 Elsevier B.V. All rights reserved.

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

Effects of selected process conditions on the stability of hydrochar in low-carbon sandy soil

M. Schulze^a, J. Mumme^{a,b}, A. Funke^{a,c}, J. Kern^{a,*}

^a Leibniz Institute for Agricultural Engineering Potsdam-Bornim, Max-Eyth-Allee 100,
14469 Potsdam, Germany

^b UK Biochar Research Center, School of GeoSciences, University of Edinburgh, Crew
Building, King's Buildings, Edinburgh, EH9 3JN, U.K.

^c Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, Building 727,
76344 Eggenstein-Leopoldshafen, Germany

Abstract

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

This study examined the influence of two feedstock materials, straw digestate and poplar, and several processing and treatment parameters (carbonization temperature, washing of hydrochars and recirculating of process water) on the stability of hydrochars in a carbon-poor sandy soil. The results show that HTC leads to a product of variable carbon fractions with different stabilities as reflected in the different rates of CO₂-C release from soil incubations within the first weeks. The carbon pool of the hydrochars

*Corresponding author. Tel.: +49 (0) 331 5699-123. E-Mail address: jkern@atb-potsdam.de

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

Keywords

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

Abbreviations

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

1. Introduction

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

more attention (Chen et al., 2014; Ribeiro and Raiher, 2013). However, the increased desire to put agricultural waste biomass to more complete use is not due to the demand for biogas production alone, but can be ascribed to the prosperous bio-based economy in general. On the one hand this can be a boon to the local economy, since new applications and higher prices for organic wastes add value to agricultural production and provide new business opportunities. On the other hand, higher withdrawal of biomass from the field can interfere with the soil's carbon balance and consequently threaten soil fertility (Thornley et al., 2014). A possible solution to this conflict of interest could be to stabilize organic wastes prior to their soil use, so that much less carbon needs to be returned. One of the options for stabilizing biomass is to convert it to biochar by pyrolysis. This has attracted considerable attention as a possible solution for both sequestering atmospheric carbon and simultaneously enhancing soil properties (Lehmann, 2007). Despite the large diversity in experimental results, pyrogenic carbon is assumed to have a high MRT, with turnover on a centennial scale (Singh et al., 2012). While pyrolysis is by far the most commonly used technology to produce biochar, in recent years interest has expanded to the HTC process, especially for organic waste treatment (Titirici et al., 2007). The use of HTC, which is a water-based process, can eliminate the energy-intensive drying step for wet feedstocks. One abundant type of water-rich biomass is the residue emerging from the biogas production unit after anaerobic digestion, called digestate. Digestate has been reported to contain 44.3-98.5 % water, while its dry matter is largely organic (38.6-75.4 %) (Nkoa, 2014). However, the solid products of HTC and dry pyrolysis do not have the same chemical composition due to the different reaction mechanisms that lead to carbonization (Falco et al., 2011b; Libra et al., 2011). Therefore, it is important to differentiate between the

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

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

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

2. Materials and methods

2.1 Materials

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

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

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

Further information is given in Table 1.

2.2 Hydrochar sample preparation

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

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

2.3 Determination of the carbon balance of the HTC-process

From each run, solid hydrochar, process water and gas were collected, balanced and analyzed. To determine the carbon balance from the HTC-process, gas was collected in a bag and its volume was determined by using an eudiometer. The amounts of CO₂ and CH₄ were determined using the gas measuring equipment “Geotech GA2000” (Geotechnical Instruments).

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

The amount of carbon in g C was determined for the biomass and hydrochars using equation 1. Here, m_{solids} denotes the mass of biomass or hydrochar in g DM and $x(\text{carbon})_{\text{solids}}$ denotes the measured percentage of carbon on a mass basis.

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

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

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

Here, m_{liquids} denotes the mass of process liquor or washing water in g, and TOC denotes its measured total organic carbon. ρ is the density of process liquor or washing water.

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

$$m(\text{carbon})_{\text{gas}} = V * M(\text{C}) * (x(\text{CO}_2)_{\text{Gas}} * \rho(\text{CO}_2)_{\text{Gas}} / M(\text{CO}_2)_{\text{Gas}} + x(\text{CH}_4)_{\text{Gas}} * \rho(\text{CH}_4)_{\text{Gas}} / M(\text{CH}_4)_{\text{Gas}}) / 100 \quad (3)$$

The x describes the measured amounts of CO_2 or CH_4 in % on a volume basis, M is the molecular mass for C, CO_2 or CH_4 , ρ is the density of CO_2 or CH_4 , and V denotes the measured gas volume. Subsequently, the percentage distribution of carbon was determined.

2.4 Chemical analyses

The pH-value of soil and hydrochar was determined according to VDLUFA I A 5.1.1 (Methodenbuch Band I, 1991 comparable to DIN ISO 10390:2005-12, 2005), and for biomasses DIN 38404-5:2009-07 (2009) was used. Cellulose, hemicellulose and lignin contents of the biomasses were measured using the 'FilterBag' method according to the

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

2.5 Incubation experiments

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

as a control. The maximum water-holding capacity of the mixtures was measured according to Öhlinger (1996) and set to 50 %. Each varied parameter was present in two to six repetitions (2x: samples from recirculated process liquor; 6x: soil control, each biomass and washed hydrochar from digestate/poplar at 230 °C; 3x: all others). CO₂ was measured by gas chromatography (CP-3800 from Varian, columns: Hayesep N80/100 1mx1/8“ss and Porapak QS80/100 2mx1/8“ss, detectors: Flame Ionization Detector and Electron Capture Detector, rate of flow: 30 ml/min). The measurements of accumulated CO₂ were performed on days 0, 1, 4, 12, 22, 33, 43, 54, 64, 75, 85, 99 and 120 of incubation. The results were calculated using equations 4 and 5 and are given in µg CO₂-C per day and gram soil mixture on a dry basis (µg CO₂-C g⁻¹ soil d⁻¹):

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

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

V_{vial} : volume of bottle in m³,

$\beta(\text{CO}_2)$: measured mass concentration of CO₂ in µg m⁻³,

10: amount of soil per vial in g,

3.67: molecular conversion factor (CO₂/C),

Δd : time difference in days between two measurements.

The summarized values, after 120 days of incubation are given in mg CO₂-C kg⁻¹ soil

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

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

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

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

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

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

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

Model 1:

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

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

Model 2:

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

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

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

MRT (τ) was determined by calculating the reciprocal of the decomposition rate constant:

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

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.

3.2 Carbon mineralization in incubation experiments

The incubation of hydrochars resulted in significantly lower emission rates of CO₂-C compared with the non-carbonized feedstocks, straw digestate and poplar (Figure 2a). After 120 d of incubation, the cumulative CO₂-C-emissions from hydrochars were up to 11.9 % and are significantly lower than the CO₂-C-emissions of the untreated biomasses of poplar and straw digestate at 17.3 % and 22.1 %, respectively (Table 3).

3.2.1 Effect of feedstock

Comparing the CO₂-C rates of hydrochars from digestate and poplar, it can be seen that the CO₂-C rate of hydrochar from poplar is considerably higher up to the 64th day of incubation (Figure 2a). The same can be observed for the untreated poplar by comparison with straw digestate up to the fifth day of incubation. Obviously, poplar contains more readily available organic matter than straw digestate, because this fraction has been digested from the straw feedstock to a certain extent during the anaerobic digestion process. This observation is also reflected in the higher amount of volatile matter in poplar compared with straw digestate, both in the biomass and in the hydrochar produced (Table 3). At the end of incubation after 120 d, the decomposed carbon already totals 4.31 % for the mix of soil and hydrochar from poplar by contrast with 3.94 % for hydrochar from straw digestate in soil (Table 3 and Supplemental Table 1).

3.2.2 Effect of process temperature

As shown in section 3.1 the process temperature has the largest influence on the elemental carbon content of hydrochars. On the other side, the higher the process temperature, the lower the CO₂-C emission rates from the hydrochar/soil mixtures are,

pointing to higher stability (Figure 2b). Even after 120 d of incubation, these differences are still present as reflected by significantly lower emissions of CO₂-C at 230 °C compared with 210 °C. This corresponds with an enhanced degree of stabilization, which is higher than that between 230 and 250 °C. The hydrochar produced at 230 °C emits 60 % less CO₂-C compared with the 210 °C hydrochar, whereas that produced at 250 °C emits 28 % less CO₂-C than the 230 °C hydrochar.

Furthermore, the volatile matter reflects the degree of degradability. This decreases with increasing process temperature from 70.3 % at 210 °C to 50.5 % at 250 °C (Table 3). That indicates less readily available carbon with increasing process temperatures and thus less degradation by microorganisms resulting in lower CO₂-C emission rates.

3.2.3 Effect of char washing

Washing the hydrochars significantly affected the CO₂-C emission. Especially during the first days of incubation, the washed hydrochars emitted less CO₂-C than their unwashed counterparts. However, after a maximum of 54 days of incubation, no statistically significant differences between the various treatments could be identified anymore. Only one hydrochar, produced at 210 °C, emitted significantly less CO₂-C also after 120 days of incubation (Figure 2b).

3.2.4 Effect of recirculating the process water

Significant differences in CO₂-C emission can only be seen in the hydrochar of the fivefold-recirculated process liquor by comparison with the control without recirculation. This significance persists up to the 43rd day of incubation (Figure 2c).

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

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

3.3 One- and two-pool degradation kinetics

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

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

4. Discussion

4.1 Impact of feedstock and process temperature on the composition and stability of hydrochars

4.1.1 Impact of feedstock on the stability of hydrochars

The amount of CO₂ released in incubation experiments reflects the mineralization of char compounds. Generally it is accepted that the kind of feedstock influences the rate of mineralization and thus the degree of stability of char products (Singh et al. 2012; Zimmerman et al. 2011; Eibisch et al. 2013). In our study the difference in carbon content between feedstock and hydrochar was higher for wheat straw than for poplar. This means that the carbonization of poplar was less intense compared with that of wheat straw. Reaction conditions of HTC tend to degrade primarily hemicellulose and cellulose by hydrolysis, whereas lignin remains fairly stable (Kruse et al., 2013; Liu and Guo, 2015). Feedstock fiber analysis shows that poplar wood has a higher lignin content than the straw digestate (Table 1), which also explains the lower degree of carbonization. This higher lignin content of the biomass is also reflected in the incubation studies, because the poplar biomass sample emits significantly less CO₂ after 120 d than the straw digestate. This behavior changes after HTC and it is observed that hydrochar from poplar decomposes more than that from straw digestate under the same process conditions. Even this difference is not significant (Table 3). Similar results have been reported for lignin-containing wood powder and holocellulose (cellulose + hemicellulose) by Liu and Guo (2015). This indicates that the products from hydrothermal treatment, more specifically the polymerization products from carbohydrate hydrolysis, are characterized by a higher stability than lignin. One explanation is that cross-linked phenylpropane units of the lignin polymer have been detached from the cellulose chain at a temperature of 230° C, becoming degradable themselves and making cellulose and hemicellulose deriving from the lignin polymer amenable for microbial degradation. However, further investigations are required to validate these preliminary observations.

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

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

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

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

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

the intensified protonation of the OH groups during dehydration and the reaction of monomers to polymers by resolution of their multiple bonds (Funke and Ziegler, 2010). Furthermore, the polymers are strongly aromatized with increasing temperature (Falco et al. 2011a, 2011b), which results in a higher degree of carbonization (compare the H/C and O/C ratios in Table 2), leading to lower CO₂-C-rates. Recently Liu and Guo (2015) found a threshold range of HTC temperature between 210 and 220 °C, above which the resistance to degradation increased clearly. It could be shown that in this temperature range the crystalline structure of cellulose started to disintegrate during HTC. Delignified substrates such as holocellulose were degraded much more easily compared with wood powder of poplar well protected by lignin. This is in good accordance with our results for straw digestate and poplar wood chips. Also, Bai et al. (2013) observed significantly different cumulative carbon degradation over a time period of 200 days after treating *Miscanthus* with HTC at 200 °C. Similar effects of HTC reaction temperature on the degradability of the hydrochar produced have been published previously and show consistence (Ramke and Hendricks, 2011; Gajic et al., 2012). It should be noted that hydrochar is produced at relatively low temperatures as compared to dry pyrolysis. Consequently, hydrochar is degraded to a certain extent and it was shown elsewhere that it even stimulates microbial activity in soil (Bargmann et al., 2014).

4.2 Impact of post-treatments on hydrochar stability

4.2.1 Washing

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

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

4.2.2 Recirculation of process water

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

4.3 Degradation kinetics

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

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

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

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

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

4.4 Carbon recovery

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

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

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

5. Conclusions

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

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

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

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

Acknowledgements

The research was supported by grants from the German Federal Ministry of Research and Education administered by Project Management Jülich (PtJ). The authors thank Laureen Herklotz, Mandy Jäkel, Mandy Meckelburg, Jonas Nekat, Amrei Schmutzler and Markus Schleusener for their support in chemical analyses. Furthermore we acknowledge two anonymous reviews and the final proofreading by Judy Libra and Linda Golding.

501 **References**

- 502 Antal, M.J., Grønli, M., 2003. The art, science, and technology of charcoal production.
503 Ind. Eng. Chem. Res. 42, 1619–1640.
- 504 Bai, M., Wilske, B., Buegger, F., Esperschutz, J., Kammann, C.I., Eckhardt, C.,
505 Koestler, M., Kraft, P., Bach, M., Frede, H.G., Breuer, L., 2013. Degradation
506 kinetics of biochar from pyrolysis and hydrothermal carbonization in temperate
507 soils. Plant Soil 37, 375–387.
- 508 Bamminger, C., Marschner, B., Jüschke, E., 2014. An incubation study on the stability
509 and biological effects of pyrogenic and hydrothermal biochar in two soils, Eur.
510 J. Soil Sci. 65, 72–82.
- 511 Bargmann, I., Martens, R., Rillig, M.C., Kruse, A., Kucke, M., 2014. Hydrochar
512 amendment promotes microbial immobilization of mineral nitrogen. J. Plant
513 Nutr. Soil Sci. 177(1), 59–67.
- 514 Berge, N.D., Ro, K.S., Mao, J., Flora, J.R.V., Chappell, M.A., Bae, S., 2011.
515 Hydrothermal carbonization of municipal waste streams. Environ. Sci. Technol.
516 45, 5696–5703.
- 517 Bobleter, O., 1994. Hydrothermal degradation of polymers derived from plants. Prog.
518 Polym. Sci. 19, 797–841.
- 519 Chen, X., Gu, Y., Zhou, X., Zhang, Y., 2014. Asparagus stem as a new lignocellulosic
520 biomass feedstock for anaerobic digestion: increasing hydrolysis rate, methane
521 production and biodegradability by alkaline pretreatment. Bioresour. Technol.
522 164, 78–85. doi:10.1016/j.biortech.2014.04.070
- 523 Dicke, C., Lanza, G., Mumme, J., Ellerbrock, R., Kern, J., 2014. Effect of
524 hydrothermally carbonized char application on trace gas emissions from two

- 525 sandy soil horizons. J. Environ. Qual. 43, 1790–1798.
526 doi:10.2134/jeq2013.12.0513
- 527 DIN 38404-5:2009-07, 2009, German standard methods for the examination of water,
528 waste water and sludge - Physical and physico-chemical characteristics (group
529 C) - Part 5: Determination of pH value (C 5), Beuth, Berlin.
- 530 DIN 51720:2001-03, 2001, Testing of solid fuels - Determination of volatile matter
531 content, Beuth, Berlin.
- 532 DIN EN 12880:2001-02, 2001, Characterization of sludges - Determination of dry
533 residue and water content; German version EN 12880:2000, Beuth, Berlin.
- 534 DIN EN ISO 16634-1:2009-07, 2009, Food products - Determination of the total
535 nitrogen content by combustion according to the Dumas principle and
536 calculation of the crude protein content - Part 1: Oilseeds and animal feeding
537 stuffs (ISO 16634-1:2008); German version EN ISO 16634-1:2008, Beuth,
538 Berlin.
- 539 DIN ISO 10390:2005-12, 2005, Soil quality - Determination of pH (ISO 10390:2005),
540 Beuth, Berlin.
- 541 DIN ISO 10694:1996-08, 1996, Soil quality - Determination of organic and total carbon
542 after dry combustion (elementary analysis) (ISO 10694:1995), Beuth, Berlin.
- 543 DIN ISO 11277:2002-08, 2002, Soil quality - Determination of particle size distribution
544 in mineral soil material - Method by sieving and sedimentation (ISO 11277:1998
545 + ISO 11277:1998 Corrigendum 1:2002), Beuth, Berlin.
- 546 Eibisch, N., Helfrich, M., Don, A., Mikutta, R., Kruse, A., Ellerbrock, R., Flessa, H.,
547 2013. Properties and degradability of hydrothermal carbonization products. J.
548 Environ. Qual. 42, 1565–1573. doi:10.2134/jeq2013.02.0045

- 549 Eibisch, N., Durner, W., Bechtold, M., Fuß, R., Mikutta, R., Woche, S.K., Helfrich, M.,
550 2015. Does water repellency of pyrochars and hydrochars counter their positive
551 effects on soil hydraulic properties? *Geoderma* 245–246, 31–39.
- 552 Falco, C., Baccile, N., Titirici, M.-M., 2011a. Morphological and structural differences
553 between glucose, cellulose and lignocellulosic biomass derived hydrothermal
554 carbons. *Green Chem.* 13, 3273–3281. doi:10.1039/C1GC15742F
- 555 Falco, C., Perez Caballero, F., Babonneau, F., Gervais, C., Laurent, G., Titirici, M.-M.,
556 Baccile, N., 2011b. Hydrothermal carbon from biomass: Structural differences
557 between hydrothermal and pyrolyzed carbons via ¹³C solid state NMR.
558 *Langmuir* 27, 14460–14471. doi:10.1021/la202361p
- 559 Fitzer, E., Kochling, K.-H., Boehm, H.P., Marsh, H., 1995. Recommended terminology
560 for the description of carbon as a solid (IUPAC Recommendations 1995). *Pure*
561 *Appl. Chem.* 67, 473–506.
- 562 Foereid, B., Lehmann, J., Major, J., 2011. Modeling black carbon degradation and
563 movement in soil. *Plant Soil* 345, 223–236. doi:10.1007/s11104-011-0773-3
- 564 Fohl, J., Lugscheider, W., Tessmer, G., Wallner, F., 1987. Entfernen von Wasser aus
565 der Braunkohle. II: Thermische Entwässerungsverfahren. *Braunkohle* 39, 78–87.
- 566 Funke, A., Ziegler, F., 2010. Hydrothermal carbonization of biomass: A summary and
567 discussion of chemical mechanisms for process engineering. *Biofuels, Bioprod.*
568 *Biorefin.* 4, 160–177.
- 569 Funke, A. Mumme, J., Koon, M., Diakité, M., 2013a. Cascaded production of biogas
570 and hydrochar from wheat straw: energetic potential and recovery of carbon and
571 plant nutrients. *Biomass Bioenergy* 58: 229–237.

- 572 Funke, A., Reeb, F., Kruse, A., 2013b. Experimental comparison of hydrothermal and
573 vapothermal carbonization. *Fuel Process. Technol.* 115, 261–269.
574 doi:10.1016/j.fuproc.2013.04.020
- 575 Gajić, A., Ramke, H.-G., Hendricks, A., Koch, H.-J., 2012. Microcosm study on the
576 decomposability of hydrochars in a Cambisol. *Biomass Bioenerg.* 47, 250–259.
- 577 Heilmann, S.M., Davis, H.T., Jader, L.R., Lefebvre, P.A., Sadowsky, M.J., Schendel,
578 F.J., von Keitz, M.G., Valentas, K.J., 2010. Hydrothermal carbonization of
579 microalgae. *Biomass Bioenerg.* 34, 875–882.
- 580 Heilmann, S.M., Jader, L.R., Sadowsky, M.J., Schendel, F.J., von Keitz, M.G.,
581 Valentas, K.J., 2011. Hydrothermal carbonization of distiller's grains. *Biomass*
582 *Bioenerg.* 35, 2526–2533.
- 583 Hoekman, S.K., Broch, A., Robbins, C., 2011. Hydrothermal carbonization (HTC) of
584 lignocellulosic biomass. *Energ. Fuel.* 25, 1802–1810.
- 585 Inoue, S., Hanaoka, T., Minowa, T., 2002. Hot compressed water treatment for
586 production of charcoal from wood. *J. Chem. Eng. Jpn.* 35, 1020–1023.
- 587 Krevelen, D.W., 1993. *Coal: Typology, Physics, Chemistry, Constitution*. 3rd ed.
588 Elsevier, Amsterdam.
- 589 Kruse, A., Funke, A., Titirici, M.-M., 2013. Hydrothermal conversion of biomass to
590 fuels and energetic materials. *Current opinion in chemical biology, Next*
591 *generation therapeutics.* *Energy* 17, 515–521. doi:10.1016/j.cbpa.2013.05.004
- 592 Kuzyakov, Y., Bogomolova, I., Glaser, B., 2014. Biochar stability in soil:
593 Decomposition during eight years and transformation as assessed by compound-
594 specific ¹⁴C analysis. *Soil Biol. Biochem.* 70, 229–236.
- 595 Lehmann, J., 2007. A handful of carbon. *Nature* 447, 143–144. doi:10.1038/447143a

- 596 Lehmann, J., Czimczik, C., Laird, D., Sohi, S., 2009. Stability of biochar in soil.
597 Biochar for environmental management: science and technology. Earthscan,
598 London, pp. 183–205.
- 599 Libra, J.A., Ro, K.S., Kammann, C., Funke, A., Berge, N.D., Neubauer, Y., Titirici,
600 M.M., Fühner, C., Bens, O., Kern, J., Emmerich, K., 2011. Hydrothermal
601 carbonization of biomass residuals: a comparative review of the chemistry,
602 processes and applications of wet and dry pyrolysis. *Biofuels* 2, 71–106.
- 603 Liu, F., Guo, M., 2015. Comparison of the characteristics of hydrothermal carbons
604 derived from holocellulose and crude biomass. *J. Mater. Sci.* 50, 1624–1631.
- 605 Liu, Z.G., Quek, A., Balasubramanian, R., 2014. Preparation and characterization of
606 fuel pellets from woody biomass, agro-residues and their corresponding
607 hydrochars. *App. Energy*. 113, 1315–1322.
- 608 Lu, X., Flora, J.R.V., Berge, N.D., 2014. Influence of process water quality on
609 hydrothermal carbonization of cellulose. *Bioresour. Technol.* 154, 229–239.
- 610 McGill, W.B., 1996. Review and Classification of Ten Soil Organic Matter (SOM)
611 Models, in: Powelson, D.S., Smith, P., Smith, J.U. (Eds.), *Evaluation of Soil*
612 *Organic Matter Models*, NATO ASI Series. Springer Berlin Heidelberg, pp.
613 111–132.
- 614 Mensinger, M.C., 1980. Wet carbonization of peat: state-of-the-art review, symposium
615 proceedings: peat as an energy alternative. Chicago, III., USA: IGT, pp. 249–
616 280.
- 617 Mumme, J., Linke, B., Tölle, R., 2010. Novel upflow anaerobic solid-state (UASS)
618 reactor. *Bioresour. Technol.* 101, 592–599. doi:10.1016/j.biortech.2009.08.073

- 619 Nkoa, R., 2014. Agricultural benefits and environmental risks of soil fertilization with
620 anaerobic digestates: a review. *Agron. Sustain. Dev.* 34, 473–492.
621 doi:10.1007/s13593-013-0196-z
- 622 Öhlinger R., 1996. Methods in soil physics: Maximum water-holding capacity, in:
623 Schinner F., Öhlinger R., Kandeler E., Margesin R., *Methods in soil biology.*
624 Springer, Berlin, pp. 385–386.
- 625 Parshetti, G.K., Hoekman, S.K., Balasubramanian, R., 2013. Chemical, structural and
626 combustion characteristics of carbonaceous products obtained by hydrothermal
627 carbonization of palm empty fruit bunches. *Bioresour. Technol.* 135, 683–689.
- 628 Pohl, M., Mumme, J., Heeg, K., Nettmann, E., 2012. Thermo- and mesophilic anaerobic
629 digestion of wheat straw by the upflow anaerobic solid-state (UASS) process.
630 *Bioresour. Technol.* 124, 321–327. doi:10.1016/j.biortech.2012.08.063
- 631 Qayyum, M.F., Steffens, D., Reisenauer, H.P., Schubert, S., 2012. Kinetics of carbon
632 mineralization of biochars compared with wheat straw in three soils. *J. Environ.*
633 *Qual.* 41, 1210–1220. doi:10.2134/jeq2011.0058
- 634 Ramke, H.G., Hendricks, A., 2011. Charakterisierung von HTC-Biokohle für die
635 Nutzung als Bodenhilfsstoff. *Hydrothermale Carbonisierung von Biomasse -*
636 *Ergebnisse und Perspektiven*, Osnabrück, Germany, Erich Schmidt Verlag.
- 637 Reza, M.T., Wirth, B., Lüder, U., Werner, M., 2014. Behavior of selected hydrolyzed
638 and dehydrated products during hydrothermal carbonization of biomass.
639 *Bioresour. Technol.* 169, 352–361. doi:10.1016/j.biortech.2014.07.010
- 640 Ribeiro, M. de F. dos S., Raiher, A.P., 2013. Potentialities of energy generation from
641 waste and feedstock produced by the agricultural sector in Brazil: The case of
642 the State of Paraná. *Energ. Policy* 60, 208–216. doi:10.1016/j.enpol.2013.05.004

- 643 Sevilla, M., Fuertes, A.B., 2009. The production of carbon materials by hydrothermal
644 carbonization of cellulose. *Carbon* 47, 2281–2289.
- 645 Singh, N., Abiven, S., Torn, M.S., Schmidt, M.W.I., 2012. Fire-derived organic carbon
646 in soil turns over on a centennial scale. *Biogeosciences* 9, 2847–2857.
- 647 Singh, B.P., Cowie, A.L., Smernik, R.J., 2012. Biochar carbon stability in a clayey soil
648 as a function of feedstock and pyrolysis temperature. *Environ. Sci. Technol.* 46(21),
649 11770–11778. DOI:10.1021/es302545b
- 650 Steinbeiss, S., Gleixner, G., Antonietti, M., 2009. Effect of biochar amendment on soil
651 carbon balance and soil microbial activity. *Soil Biol. Biochem.* 41, 1301–1310.
652 10.1016/j.soilbio.2009.03.016
- 653 Stemann, J., Putschew, A., Ziegler, F., 2013. Hydrothermal carbonization: Process
654 water characterization and effects of water recirculation. *Bioresour. Technol.*
655 143, 139–146. doi:10.1016/j.biortech.2013.05.098
- 656 Stemann, J., Ziegler, F., 2011. Hydrothermal Carbonisation (HTC): Recycling of
657 Process Water, in: 19th European Biomass Conference and Exhibition, Berlin,
658 Germany, 6-10 June 2011.
- 659 Thornley, P., Chong, K., Bridgwater, T., 2014. European biorefineries: Implications for
660 land, trade and employment. *Environ. Sci. Policy* 37, 255–265.
661 doi:10.1016/j.envsci.2013.09.004
- 662 Titirici, M.-M., Thomas, A., Antonietti, M., 2007. Back in the black: hydrothermal
663 carbonization of plant material as an efficient chemical process to treat the CO₂
664 problem? *New J. Chem.* 31, 787–789. doi:10.1039/B616045J

- 665 Titirici, M.-M., White, R.J., Falco, C., Sevilla, M., 2012. Black perspectives for a green
666 future: hydrothermal carbons for environment protection and energy storage.
667 Energy Environ. Sci. 5, 6796–6822. doi:10.1039/C2EE21166A
- 668 VDLUFA I A 5.1.1, 1991. Bestimmung von Bodenazidität und Kalkzustand, in:
669 Methodenbuch Band I Die Untersuchung von Böden, VDLUFA-Verlag,
670 Darmstadt.
- 671 VDLUFA III 4.1.2, 1976. Stickstoffverbindungen, in: Methodenbuch Band III Die
672 chemische Untersuchung von Futtermitteln, VDLUFA-Verlag, Darmstadt.
- 673 VDLUFA III 6.5.1-6.5.3, 1976. Pflanzliche Gerüstsubstanzen, in: Methodenbuch Band
674 III Die chemische Untersuchung von Futtermitteln, VDLUFA-Verlag,
675 Darmstadt.
- 676 VDLUFA III 8.4, 1976. Rohasche bei Mineralfuttermittel, in: Methodenbuch Band III
677 Die chemische Untersuchung von Futtermitteln, VDLUFA-Verlag, Darmstadt.
- 678 Wang, Q., Li, H., Chen, L., Huang, X., 2001. Monodispersed hard carbon spherules
679 with uniform nanopores. Carbon 39, 2211–2214.
- 680 Wieder, R.K., Lang, G.E., 1982. A critique of the analytical methods used in examining
681 decomposition data obtained from litter bags. Ecology 63, 1636–1642.
- 682 Wiedner, K., Naisse, C., Rumpel, C., Pozzi, A., Wieczorek, P., Glaser, B., 2013.
683 Chemical modification of biomass residues during hydrothermal carbonization –
684 What makes the difference, temperature or feedstock? Org. Geochem. 54, 91–
685 100. doi:10.1016/j.orggeochem.2012.10.006
- 686 Wilkins, R.W., George, S.C., 2002. Coal as a source rock for oil: a review. Int. J. Coal
687 Geol. 50, 317–361.

- 688 Yan, W., Hastings, J.T., Acharjee, T.C., Coronella, C.J., Vásquez, V., 2010. Mass and
689 energy balances of wet torrefaction of lignocellulosic biomass. *Energ. Fuel.* 24,
690 4738–4742.
- 691 Zhao, P., Shen, Y., Ge, S., Yoshikawa, K., 2014. Energy recycling from sewage sludge
692 by producing solid biofuel with hydrothermal carbonization. *Energ. Con.*
693 *Manage.* 78, 815–821.
- 694 Zimmerman, A.R., Gao, B., Ahn, M.Y., 2011. Positive and negative carbon
695 mineralization priming effects among a variety of biochar-amended soils. *Soil Biol.*
696 *Biochem.* 43(6), 1169–1179. DOI:10.1016/j.soilbio.2011.02.005
- 697
- 698
- 699

Figure captions

Table 1: Characterization of feedstock

Table 2: Elemental analysis of feedstock and hydrochars

Table 3: Cumulative amounts of CO₂-C and proportion of total carbon mineralized after 120 days of incubation

Table 4: Fitting parameters of exponential models for one-fraction: $C(t)=C_0 \cdot \exp(-k_1 t)$ and two-fractions: $C(t)=C_0 \cdot (x \cdot \exp(-k_2 t) + (1-x) \cdot \exp(-k_3 t))$

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

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

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

Supplemental Table 1: Degradation of initial carbon across different treatments