

This is the accepted manuscript version of the contribution published as:

Breulmann, M., Schulz, E., van Afferden, M., Müller, R.A., Fühner, C. (2018):
Hydrochars derived from sewage sludge: effects of pre-treatment with water on char properties, phytotoxicity and chemical structure
Arch. Agron. Soil Sci. **64** (6), 860 - 872

The publisher's version is available at:

<http://dx.doi.org/10.1080/03650340.2017.1396318>

Publisher: Taylor & Francis

Journal: *Archives of Agronomy and Soil Science*

DOI: 10.1080/03650340.2017.1396318

Hydrochars derived from sewage sludge: Effects of pre-treatment with water on char properties, phytotoxicity and chemical structure

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Abstract

- Large amounts of labile compounds are adsorbed to the surface of chars produced by hydrothermal carbonization (HTC). The aim of this study was to characterize the core and adsorbed fractions of hydrochars and to gain knowledge about the possibility to remove phytotoxic compounds by washings with water. Chars were produced by HTC of sewage sludge at different temperatures (180 – 200 °C) and over different periods of time (4 – 8 h). For comparison one pyrolysis char produced by thermocatalytic low temperature conversion (LTC) at 400 °C for 1 h was included in the study. The chars and their feedstocks were treated varying the duration (1 x 15, 1 x 30 and 1 x 60 min) and number (2 x 60 and 3 x 60 min) of washings. Physicochemical properties, including the molecular structure of the test materials, and their effects on germination and plant growth were analysed. Element concentrations and phytotoxic effects were

reduced (up to 90 % for total carbon and 61 % for total nitrogen), the number of washings had a stronger effect than their length of time. Intensive washings with water reduced the hydrochars' portion of biodegradable compounds significantly. However, also plant available nutrients were lost by washing with water, decreasing the value of hydrochars as a soil amendment.

Keywords: biochar; hydrochar; midDRIFTS peak area analysis; phytotoxicity, washing

Introduction

A promising option to mitigate anthropogenic climate change is to establish carbon sinks by applying biochars to the soil, where it can additionally increase soil fertility and crop yields (Lehmann 2007). By definition, biochar is the solid carbon-rich product of organic matter pyrolysis (Lehmann & Joseph 2015).

However, carbonized material can also be generated by hydrothermal carbonisation (HTC) and is then often referred to as hydrochar. Hydrothermal carbonisation is particularly suitable for converting wet biomass such as sewage sludge and human waste into carbonaceous solids since it supersedes energy-intensive drying processes (Libra et al. 2014). Converting sludge into carbonaceous material for use as a soil amendment is promising, both from an economic and ecological standpoint (Breulmann et al. 2015). During the HTC process pathogens are destroyed, and thermally labile pollutants can be degraded (Park & Jang 2011; Weiner et al. 2013). Furthermore, the process enables the recovery of plant mineral nutrients (Heilmann et al. 2014; Ro et al. 2016) and increases the dewaterability of sewage sludge (Kim et al. 2014). The overall properties of biochars and hydrochars can vary widely, depending on the process conditions under which they are produced and the feedstocks from which they are derived

(Lehmann & Joseph 2015). First steps in characterising hydrochar from sewage sludge are described by Breulmann et al. (2017), Danso-Boateng et al. (2015a; 2015b) and Zhang et al. (2014). However, information about the organic and inorganic functional groups of the reactive surface of hydrochar from sewage sludge is scarce (He et al. 2013; Zhang et al. 2015). Such functional groups can be characterised by vibrations at different wavenumbers and are visible as peaks in the mid-infrared spectrum (Demyan et al. 2012). Charred materials can show unwanted properties and effects including enhanced solubility of toxic trace elements in soils (Kloss et al. 2015). Pyrolysis can cause the formation of volatile organic compounds resulting from the re-condensation of liquid and gaseous products, can inhibit seed (Buss & Masek 2014). Furthermore, polycyclic aromatic hydrocarbons can be formed during pyrolysis (Schimmelpfennig & Glaser 2012). Hydrochars can cause the formation of long C-chain aliphatic compounds triggering toxic effects on plant growth (Jandl et al. 2013), the inhibition of germination processes (Busch et al. 2012) and priming effects of microbial mineralisation of soil organic matter (Zimmerman et al. 2011).

Breulmann et al. (2017) showed that a large amount of labile compounds are adsorbed to the hydrochars' surface. It is assumed that these labile components can be removed by washing the hydrochar with water. So far, there have been only few investigations with washed hydrochar. George et al. (2012), for instance, washed hydrochar with deionised water prior to a greenhouse experiment without comparing the effects of washed and unwashed materials. In the study by Eibisch et al. (2013), no significant differences on mineralization rates of unwashed and washed hydrochars were found. However, multiple very short washing steps of two minutes were carried out. Busch et al. (2013) showed that pre-treatment with hot water (100 °C) was successful in completely eliminating toxic effects of hydrochars in a greenhouse experiment and in enabling positive plant growth effects of hydrochars. To develop new

options for the conditioning and reuse of hydrochars there is the need for a comprehensive understanding of the physicochemical properties and behaviour of their core and adsorbed fractions. This particularly applies to hydrochars from sewage sludge, the most prominent feedstock for HTC. In order to show whether washing with water has similar effects on pyrolysis chars one biochar produced by thermocatalytic low temperature conversion was included in this study.

Given the above context, the aim of the study was: to understand how a pre-treatment with water alters hydrochars and biochars from sewage sludge; to gain knowledge about the washing process; to characterise the core and the adsorbed fraction of hydrochars and biochars and to investigate the effects of a pre-treatment on the elimination of potential phytotoxic effects. Four hydrochars, one pyrochar and their sewage sludge feedstocks were used to test the effect of the number and duration of water extractions on (1) the physicochemical properties, particularly (2) the molecular structure and (3) germination and plant biomass production of the test materials.

Material and methods

Char production

Eight materials were included in the analysis – three feedstocks, one pyrolysis biochar and four hydrochars. The feedstocks were primary sludge (PS), unstabilised activated sludge (ASU) and stabilised activated sludge (ASS). The pyrolysis biochar was produced within 1 h at 400 °C by thermocatalytic low temperature conversion (LTC). The four HTC hydrochars were prepared at temperatures of 180 – 200 °C in 4 – 8 h and are referred to as HTC I, HTC II, HTC III and HTC IV (Table 1). All materials were homogenised, milled and stored in closed plastic cups at room temperature until analysis. More detailed information about basic

physicochemical properties of the materials used can be found in the publication of Breulmann et al. (2017).

Washing procedure

For the pre-treatment with water 10 g of dried sewage sludge and chars were shaken three times for 60 minutes (3 x 60) with 300 ml of deionised water in an overhead shaker at 11 rpm, decanting and renewing the aqueous solution between each washing. To study the influence of (a) the duration and (b) the number of washings, the PS and HTC III were additionally washed: (i) once for 15 minutes (1 x 15), (ii) once for 30 minutes (1 x 30), (iii) once for 60 minutes (1 x 60) and (iv) twice for 60 minutes (2 x 60). After final centrifugation (15 min at 5000 g), the solid residues were dried at 70 °C. The water fractions were filtered using a RC 25 Minisart single-use syringe membrane filter (0.45 µm pore size; Sartorius AG, Göttingen, Germany) and stored at 4 °C until further analysis. The experimental design of the washing procedure is presented in Table 2. Each washing procedure was done in triplicates. However, in order to have enough material for all analysis, the material of the three replicates was pooled.

Basic analysis of solid materials and water extracts

In total, 24 solid materials, including the unwashed materials, and 10 water extracts were analysed. The total organic carbon (TOC) and nitrogen (TN) contents of the solid materials were assessed using dry combustion with a C/H/N analyser (Vario El III, Elementar, Hanau, Germany).

The pH and electrical conductivity (EC) were measured in the unfiltered water extracts.

Water-extractable fractions of ammonium-N (NH_4^+ -N) and nitrate-N (NO_3^- -N) were

quantified in the filtrates using a flow injection analyser (FIAstar 5000, Foss GmbH, Rellingen, Germany), total C and N concentrations (DOC, DON) with an elemental analyser for aqueous samples (Micro N/C and Multi N/C, Analytik Jena, Jena, Germany). The total phosphorous concentration (P_{tot}) was measured using ICP-OES and $\text{PO}_4^{3-}\text{-P}$ photometrically at 880 nm after formation of a molybdate complex (DIN ISO 15923-1).

MidDRIFTS analysis

Samples for Diffuse Reflectance Fourier Transform Spectroscopy (DRIFTS) analyses were post-dried overnight at 60 °C. Some 6 mg were then finely mixed with 194 mg KBr in a stainless steel ball mill (Retsch GmbH and Co. KG, Haan, Germany) at a vibration frequency of 30 Hz for 2 minutes. DRIFTS spectra of the sample KBr mixtures were then recorded using a PerkinElmer Spectrum One FTIR spectrometer (Ueberlingen, Germany) equipped with a DRIFT accessory. Three subsamples of each sample were scanned and the results averaged. The spectra were recorded in the mid-infrared range ($4000 - 400 \text{ cm}^{-1}$; midDRIFTS) by combining 100 individual scans at a resolution of 4 cm^{-1} . Spectral analysis included atmospheric correction for carbon dioxide (CO_2) and water, baseline correction and vector normalisation in order to compensate for slight variations in air humidity, temperature and CO_2 concentration at the time of measurement. Functional groups were quantified using SPECTRUM 5.1 software (PerkinElmer). Individual wave numbers were assigned as described by Whitman et al. (2013), Kloss et al. (2012), Demyan et al. (2012) and Chatterjee et al. (2012): 3200 cm^{-1} to O–H stretching in carboxylic acids, phenols and alcohols and hydrogen-bonded hydroxyl, 2923 cm^{-1} and 2853 cm^{-1} to aliphatic C–H stretching of CH_3 and CH_2 , 1645 cm^{-1} to aromatic C=C vibrations and stretching, 1550 cm^{-1} to aromatic C=C stretching, 1450 cm^{-1} to C–H deformation in lignin and carbohydrates, 1410 cm^{-1} to C–H stretching in cellulose and hemicellulose, 1030 cm^{-1} to C–O stretching in cellulose,

hemicellulose and lignocelluloses and 790 cm^{-1} to aromatic C–H bending. The following baselines were drawn: 3700 – 3000 for O–H stretching, 3000 – 2880 for aliphatic C–H stretching, 2880 – 2800 for aliphatic C–H stretching, 1800 – 1550 for aromatic C=O stretching, 1550 – 1490 for aromatic C=C stretching, 1490 – 1430 for C–H deformation in lignin and carbohydrates, 1430 – 1345 C–H stretching in cellulose and hemicellulose, 1230 – 930 for C–O stretching in cellulose, hemicellulose and lignocelluloses and 850–760 for aromatic C–H bending. For spectral comparisons and the quantification of changes in the appearance of functional groups, the relative absorbance (rA) at a given wavelength was calculated by dividing the corrected peak area of a distinct peak by the summed signal heights and areas of all peaks of interest and multiplied by 100 to give the relative peak area (rA %).

Germination and plant growth test with cress

Germination and plant growth tests were carried out in four replicates. The solid test materials were thoroughly mixed with quartz sand to a concentration of 1.5 % ($w_{\text{DW}}/w_{\text{DW}}$), 75 g of the sand/material mixture were filled in small plastic jars (7 x 10 cm) and adjusted to 100 % of the maximum water holding capacity. Twenty-five cress seeds (*Lepidium sativum* L.) were equally disseminated, the jars closed with a lid, which had 25 small holes to allow air exchange, and were randomly placed in a climatic chamber (Lichtthermostate Rumed®, Rubarth Apparte GmbH). Germination was evaluated 10 days after incubation at 25 °C and an air humidity of about 75 %. Finally, the plants were lifted, substrate material attached to the root surface was washed off with water and the plants dried at 105 °C, in order to determine their biomass.

Data analysis

Data were analysed using R Version 3.1.1 (R Development Core Team 2016). Distributions of data were tested for normality and homogeneity, and are presented as arithmetic means \pm standard errors (SE) in the tables and in the figures as box and whiskers plots. Results were evaluated statistically using analysis of variance (ANOVA) followed by a Tukey's post hoc test. Where the assumptions of the model were not fulfilled, a Box-Cox transformation was applied. Data for midDRIFTS peak area analysis were ln-transformed. Treatment effects were regarded as significant if $p \leq 0.05$.

Results

Washing effects on basic physicochemical parameters

Only the number of washings showed clear effects on basic parameters of the solids and the aqueous extracts (Table 3). Threefold washings for 60 minutes decreased the TOC and TN content of the PS and HTC III significantly (PS: TOC -8.7% , TN -27.0% ; HTC III: TOC -9.5% , TN -39.3% ; Table 3; Figure 1). The reduction of the mass fraction of P in the solid materials corresponded with a significant increase of P_{tot} in the washing solutions (Table 3). The duration of single washings showed no systematic effect (Table 3). A significant decrease was detected here only for the nitrogen fractions of the solid material extracted for 15 minutes (Figure 1).

midDRIFTS peak area analysis

In total, nine different midDRIFTS peak bands were identified, of which three were assigned to aromatic compounds (1645 , 1550 and 790 cm^{-1}).

Unwashed materials In general, the spectral bands at 3200 (O–H stretching in carboxylic acids, phenols and alcohols), 1645 (aromatic C=C vibrations) and 1030 cm^{-1} (C–O stretching

in cellulose, hemicellulose and lignocelluloses) contributed most to the total relative peak area of the unwashed feedstocks (Table 4a – d). The overall midDRIFTS peak spectra of the hydrochars depended on the feedstock used and the time and temperature of the HTC process. The proportion of 1645 cm^{-1} C=C aromatic groups increased with the process temperatures (PS: 9.6 % – HTC I: 11.5 % – HTC II: 12.9 % – HTC III: 13.5 %; Table 4a – d). The relative proportion of C=C aromatic bands was also increased by HTC IV and LTC (ASU: 9.0 % – HTC IV: 10.4 %) and the pyrolysis biochar LTC (ASS: 10.2 % – LTC: 11.7 %). In some cases, the HTC decreased the proportion of 1030 cm^{-1} C–O stretching of polysaccharides such as cellulose, hemicellulose and lignocellulose (ASU: 17.9 % – HTC IV: 15.4 % and ASS: 9.6 % – LTC: 4.8 %). In other cases, the proportion increased (PS: 21.1 % – HTC I: 21.6% – HTC II: 28.7 % – HTC III: 28.8 %). The proportions of 2923 cm^{-1} and 2853 cm^{-1} aliphatic C–H stretching of CH_3 and CH_4 increased as well (Table 4a – d). *Washed materials*

A pre-treatment with water had in general only a minor effect on the total relative peak areas of the feedstocks. Only for the primary sludge decreases of peak areas were detected at 1645 cm^{-1} by 9 % and at 1030 cm^{-1} by 23 %. At 1410 cm^{-1} , the response was completely eliminated by a threefold washing for 60 minutes (Table 4a). Further aromatic midDRIFTS peak bands (1550 and 790 cm^{-1}) for PS were not affected. For the ASU, an intensive washing of 3 x 60 minutes caused a reduction in the proportion of 2923 cm^{-1} aliphatic C–H (8 %), 1410 cm^{-1} cellulose and hemicellulose C–H (100 %) and 1030 cm^{-1} cellulose, hemicellulose and lignocellulose C–O groups (21 %, Table 4c). Aromatic midDRIFTS peak bands for the ASU were significantly increased (1645 cm^{-1} : 24 % and 790 cm^{-1} : 200 %) and decreased (1550 cm^{-1} : 50 %) by an intensive pre-treatment of 3 x 60 minute washings (Table 4c). Relative midDRIFTS peak areas for ASS were barely affected by an intensive washing of 3 x 60 minutes (Table 4d). The relative peak area for the ASS of the aromatic C=C stretching

(1645 cm^{-1}) was significantly positively influenced (22 %) and that of 3200 cm^{-1} and 1410 cm^{-1} negatively influenced by 4 % and 100 % respectively. A threefold washing for 60 minutes shows that most relative peak areas of the HTC I were increased (2923, 2853, 1450, 1410, 1030 cm^{-1}). The midDRIFTs peaks indicated that only aromatic groups at 1645 cm^{-1} were significantly reduced (20 %; Table 4a). The situation is different for HTC II and HTC III, where most relative peak areas decreased after the pre-treatment of 3 x 60 minutes washing. A significant increase was ascertained for both hydrochars for the proportion of 3200 cm^{-1} O–H stretching of carboxylic acids, phenols and alcohols (HTC II 17 %; HTC II: 5 %) and for 1450 cm^{-1} C–H deformation in lignin and carbohydrates (HTC II 64 %; HTC III: 70 %; Table 4b). Similar effects were found for HTC IV, however, on a different level. For the pyrolysis biochar LTC, an intensive washing of 3 x 60 minutes resulted in an elimination of the relative peak area of O–H stretching of carboxylic acids, phenols and alcohols (3200 cm^{-1} ; 10 %) and at the same time a significant increase in the signals for aromatic C=C (1645 cm^{-1} ; 7 %) and C–H (790 cm^{-1} ; 33 %) bending peak areas.

Germination and plant growth test with cress

Germination rate: Almost all seeds, equivalent to about 96 %, germinated in the control treatment. The addition of the unwashed solid material resulted in low mean germination rates for the feedstocks (PS 52 %, ASU 71 %, ASS 70 %; Table 5 and Figure 2a). Negative effects on plant germination were also documented for all unwashed biochars. A great variance of germination effects became apparent for the hydrochars. Mean germination rates varied between 64 % for HTC II (-33 %) and 81 % for HTC III (-16 %). Application of LTC biochar decreased the germination rate by 18 % compared to the control.

Threefold washings for 60 minutes decreased the negative effects of all test materials on plant germination, those of HTC I, HTC II and ASU significantly (Table 5). Other washing

procedures of PS and HTC III tended to have even slightly better effects. Single short washings of HTC III (1 x 15 min) resulted in an increase of the germination rate up to 90 %. An increase in the duration of single washings to 60 minutes resulted in germination rates of about 96 % for HTC III and 81 % for PS (Figure 2a).

Plant growth: In order to evaluate potential phytotoxic effects of unwashed and washed materials, total biomass production and total dry weight per plant were determined in addition to seed germination. In general, all unwashed test materials except the LTC biochar had negative effects on the individual plant dry weight (biomass per plant; Table 5). Mean plant weights were low, on average 56 % (PS), 66 % (ASU), 45 % (ASS), 57 % (HTC I), 53 % (HTC II), 48 % (HTC III), 41 % (HTC VI) compared to the control.. For the unwashed LTC biochar, no phytotoxic effects were seen, instead, there was a stimulation of plant growth (28 %). The mean dry biomass per plant increased but still showed no or negative response to 3 x 60 minutes washings of the test materials to 82 % (PS), 100 % (HTC I), 66 % (HTC II), 100 % (HTC III) and 87 % (HTC VI) compared to the control. Only for the LTC, a clear increase of biomass production by 38 % (LTC) was detected. However, effects of intensive washing were only significant for HTC I, HTC III and HTC IV. In general, with respect to the number and duration of PS and HTC III washing, there is a trend visible, being that by 2 x 60 minutes and 3 x 60 minutes treatments phytotoxic effects were eliminated (Figure 2b). However, increasing the duration of single washings of PS and HTC III tended to have a negative effect on the dry weight per plant. Evaluations based on the total biomasses of all seedlings are largely corresponding to these results.

Discussion

General properties

The results clearly show that a pre-treatment with water had a highly significant effect on physicochemical characteristics, which was apparent for all tested materials. However, the effects were visible only after multiple washings with an exchange of the solution. In contrast to fivefold washings of plant biomass derived hydrochars for 2 minutes each in the study by Eibisch et al. (2013), threefold washings of 60 minutes significantly decreased the TOC content of sewage sludge hydrochar, on average by 3 %. In particular, nitrogen and phosphorous were increasingly transferred to the water fraction when the number of washings was increased (2 x 60 and 3 x 60 min). Whether a nutrient-rich washing solution could be used as a liquid fertiliser has to be evaluated as it was done for HTC process water (Sun et al. 2014; Vozhdayev et al. 2015). Except for nitrogen, a onefold washing for 15, 30 and 60 minutes did not affect the element concentrations of the feedstock and hydrochar investigated. For characterising the hydrochar's core fraction, threefold washings of 3 x 60 minutes are strongly recommended.

midDRIFTS peak area analysis We used midDRIFTS peak area analysis of feedstocks and hydrochar to characterise the materials in relation to their potential stability and quality. As also reported by Zhang et al. (2014), no new functional groups are formed during the HTC process. Generally, the overall midDRIFTS peak spectra depend on the feedstock used and the HTC process conditions (time and temperature). The spectra of the primary sludge and HTC I were very similar, showing that HTC with short residence time of 2 hours and low a temperature of 180 °C causes only slight modifications of the molecular structures. The midDRIFTS peak areas of 1410, and 1030 cm^{-1} provide evidence of the presence of both cellulose and hemicellulose. As mentioned by Keiluweit et al. (2010), a heat-induced decomposition of hemicellulose and cellulose in the feedstock occurs rapidly at low temperatures, whereas that of complex molecules, such as lignin, happens over a broader

temperature range. In some cases, the thermochemical treatment reduces the proportion of 1030 cm^{-1} C–O stretching of polysaccharides such as cellulose, hemicellulose and lignocelluloses (ASU – HTC IV and ASS – LTC). In other cases, the proportion of the peak area around 1030 cm^{-1} increases (PS – HTC I – HTC II – HTC III). The same effect applies to the proportions of 2923 cm^{-1} and 2853 cm^{-1} aliphatic C–H stretching of CH_3 and CH_4 . This result clearly shows the dependency of the midDRFIFTs peak areas on the feedstock used for the HTC process. Feedstock with a high organic load, such as the primary sludge, contains aliphatic structures, which can be deduced from the midDRFIFTs peak areas at $3000 - 2800\text{ cm}^{-1}$, corresponding to stretching vibrations of aliphatic C–H. Furthermore, oligomers are hydrolysed into monomers, which undergo dehydration and fragmentation reactions leading to the formation of soluble products, such as 1,6-anhydroglucose, erythrose, furfural-like compounds, hydroxymethylfurfural-related 1,2,4- benzenetriol, acids and aldehydes (Sevilla & Fuertes 2009). If the organic load is high, such as for the unstabilised sewage sludge (ASU), midDRFIFTs peak areas of 1030 cm^{-1} are clearly decreased by the HTC. By increasing the residence time from 4 hours to 8 hours and the process temperature from $180\text{ }^{\circ}\text{C}$ to $230\text{ }^{\circ}\text{C}$, aromatic structures are generated by HTC. This is apparent from a steadily increasing proportion of aromatic C=C groups, indicated by the wavenumber 1645 cm^{-1} (e.g. HTC I – HTC II – HTC III). Increases in aromatic C=C stretching at about 1600 cm^{-1} were also described for pyrolysis chars (Kleber et al. 2015) and hydrochar from grass (Rohrdanz et al. 2016). Aromatic compounds may be produced by the condensation of molecules generated in the decomposition/ dehydration of oligosaccharides or monosaccharides (Li & Shahbazi 2015; Sevilla & Fuertes 2009).

It has been shown by Keiluweit et al. (2010) that the pyrolysis of wood at low temperatures of $230 - 400\text{ }^{\circ}\text{C}$ resulted in a rapid depolymerisation of polysaccharides, such as cellulose and hemicelluloses, whereas the decomposition of lignin occurs in a broader temperature range of

about 160 – 900 °C. We can support this hypothesis for our LTC biochar, where both midDRIFTS peak areas were clearly reduced. Keiluweit et al. (2010) showed that the feedstock undergoes dehydration and depolymerisation of biopolymers during pyrolysis, creating small volatile dissociation products. The decomposition of these monomers under HTC or multistep decomposition reactions under low temperature pyrolysis enable formation of organic acids (acetic, lactic, propeonic, levulinic and formic acids (Sevilla & Fuertes 2009) which could explain the increase in the midDRIFTS peak areas of O–H at 3200 cm⁻¹ for the pyrolysis char (Seshadri & Westmoreland 2012). A pre-treatment of the feedstock, hydrochar and LTC char with water resulted in a significant elimination of organic carbon, nitrogen and other macro-nutrients.

Phytotoxic effects

In our experiment, all unwashed sewage sludges and chars produced by HTC and LTC caused an inhibition of seed germination. We showed that negative effects of these materials on seed germination were significantly limited by pre-treatments with water. Single washings of 15 minutes significantly increased seed germination by HTC III completely and reduced it for PS. An intensive washing of 3 x 60 minutes did not further improve this effect, but even reversed it partially. Unlike other rapid test based studies of biochars and hydrochars (e.g. Bargmann et al. 2013; Gell et al. 2011; Rogovska et al. 2012), we also evaluated the effects of the test materials on the overall biomass production.

The results show that the unwashed materials negatively influenced not only seed germination but also the individual biomass. Varying the time and the number of the washings, PS and hydrochar showed very similar effects in the way, that the pre-treatment effects on seed germination and plant growth tended to be inverse. Short washings of 1 x 15 minutes did not alter the effect of the test materials on biomass production. Furthermore, washings of 1 x 30

and 1 x 60 minutes clearly decreased the dry weight per plant, whilst increasing the number of material washings was accompanied by a progressive removal of growth retardation effects.

The overall effect patterns of the test materials and the water pre-treatments on plant development is highly complex and cannot finally be explained by our experiments. It has been shown that mainly water-soluble compounds adsorbed to the surface of hydrochar and mobile volatile organic compounds can affect seed germination (Buss et al. 2015; Vozhdayev et al. 2015). By using higher temperatures and longer process times (2 – 8 h), more organic components are hydrolysed and, depending on the filtering and drying process, large amounts of labile and potentially plant toxic compounds can be adsorbed to the hydrochars' surface (Breulmann et al. 2017). In accordance with this, the results of our study show a trend, that increasing the temperature and time of the hydrothermal sewage sludge treatment (HTC I – III) raise the negative effects of the hydrochars on plant growth. Phytotoxic effects can also result from supraoptimal ammonia concentrations (Haden et al. 2011; Sun et al. 2014).

Therefore, we assume that negative effects on plant performance can be explained for the sewage sludges and the hydrochars partly by their high ammonium and DON concentrations. Only if the number of washings was increased (2 x 60 and 3 x 60 min), coupled with a change of the water, negative effects on the biomass production were eliminated. Since the nitrogen concentrations but also the plant biomass were significantly reduced during short washings also factors not included in our study must play a role in the plant growth effects of the test materials. Finally, opposite effects of increasing the time and the number of washings are suggesting, that the plant response is not only due to different effectors but also due to the mobility and localization of these substances on the surface or in the interior of the test materials.

Conclusions

Except for the TN content, the duration of the washing had only a negligible influence on the overall elemental composition of the solid materials. Only when the number of washings was increased, which was associated with an exchange of the water fraction, significant effects reductions of the element contents and phytotoxic effects became apparent. Our results showed that threefold washings of 60 minutes eliminated the adsorbed labile components of the hydrochar, allowing to characterize the hydrochars' core fraction and display its possible effects on plants. Intensive washing reduces the hydrochars' portion of biodegradable compounds significantly. However, also essential plant available nutrients are lost during a pre-washing procedure, decreasing their possible value as a soil amendment. An anaerobic digestion of HTC-treated sewage sludge before dewatering could be a valuable tool to substitute fossil fuels and to provide at the same time a more recalcitrant, nutrient rich material for carbon sequestration and soil amelioration. More research is needed to determine long-term effects of hydrochar amendment on soil properties and crop production under agricultural conditions.

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Figure Captions

Figure 1. Effect of different washing procedures of primary sludge and HTC III on a) the total organic carbon (TC) content and b) the total nitrogen (TN) content of the solid material. To display both washing parameters, two different colours are used: blue for the variation in the duration and green for the variation in the number of washings. Solid line, plus sign, boxes, and whiskers: median, mean, IQR and 1.5 x IQR, respectively. Values with the same letter are not significantly different at $p \leq 0.05$.

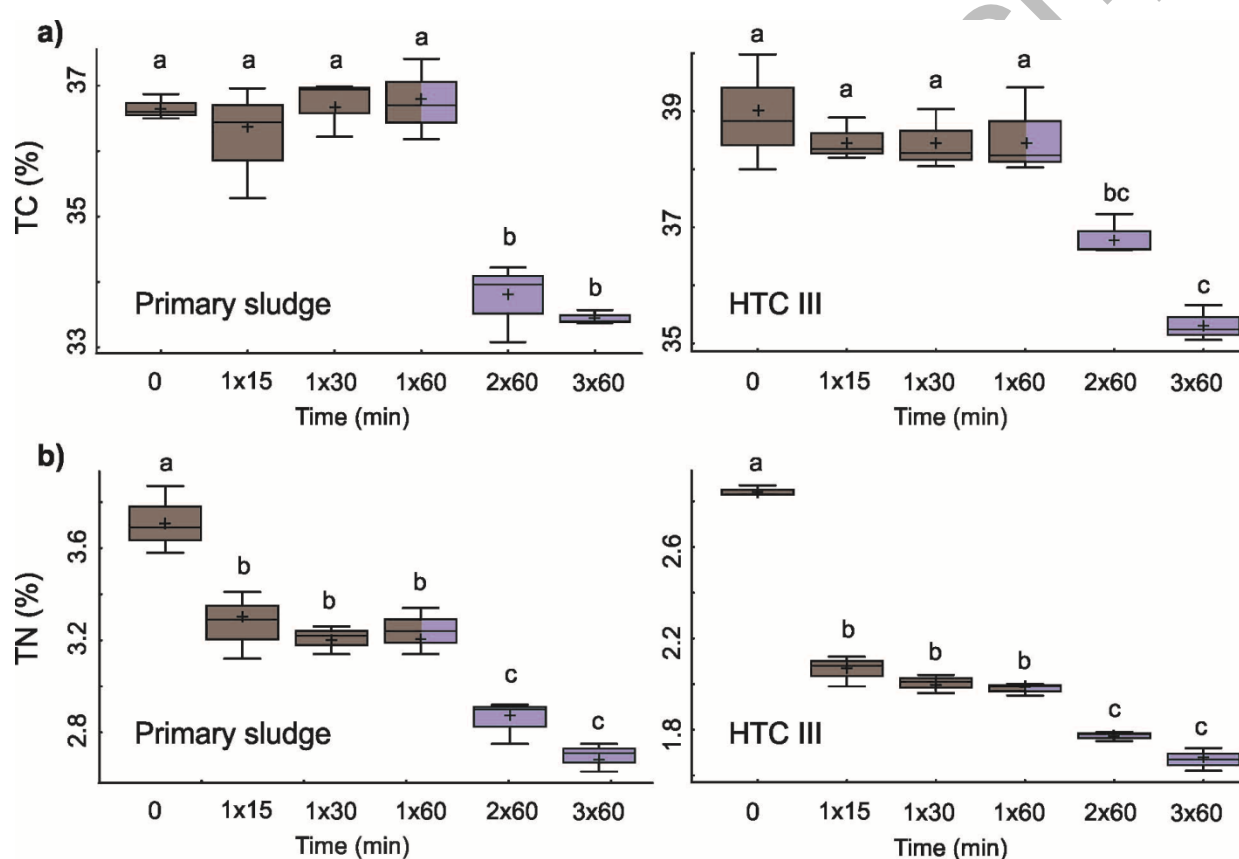


Figure 2. Effect of different washings of primary sludge (blue) and the HTC III (green) on a) germination and b) dry weight per cress plant. The dotted line represents the washing that includes a replacement of the water. Solid line, plus sign, boxes, and whiskers: median, mean, IQR and $1.5 \times \text{IQR}$, respectively. Values with the same letter are not significantly different at $p \leq 0.05$ and were analysed each for all treatments for PS and HTC III.

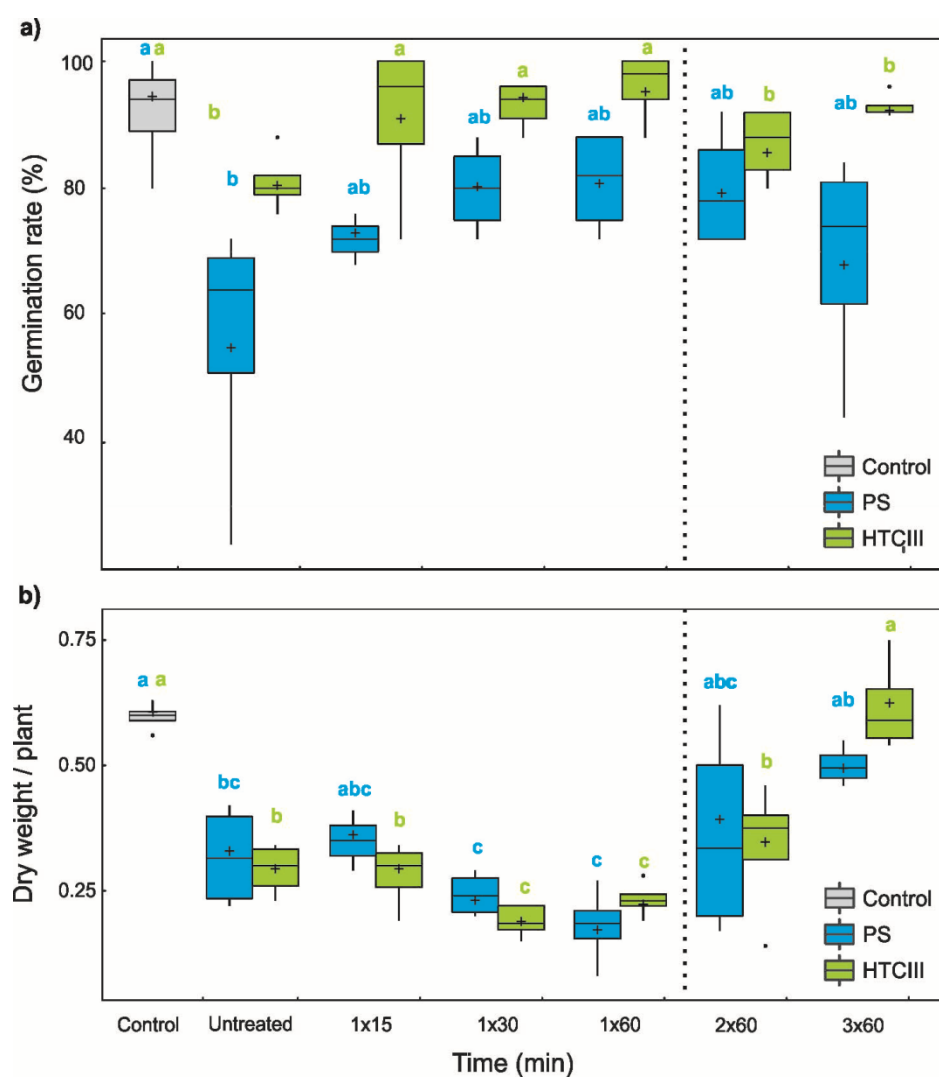


Table 1. Overview of feedstocks, type and process conditions of carbonized test materials.

Feedstock	Treatment type	t (h)	T (°C)	Label
Activated sludge stabilised (ASS)	Pyrolysis	1	400	LTC
Primary sludge (PS)	HTC	4	180	HTC I
	HTC	4	200	HTC II
	HTC	8	200	HTC III
Activated sludge unstabilised (ASU)	HTC	4	200	HTC IV

HTC: hydrothermal carbonisation and LTC: thermocatalytic low temperature conversion.

Table 2. Experimental design of the washing procedure.

		Factor 1: Number of washings			
		0 x	1 x	2 x	3 x
Factor 2: Duration of washings	0 min	■			
	15 min		□		
	30 min		□		
	60 min		□	□	■

PS: primary sludge and HTC: hydrothermal carbonization; closed symbols: all eight test materials; open symbols: only PS and HTC III.

Table 3. Effect of different washing procedures on basic parameters of the solid and dissolved fraction of primary sludge and HTC III. Values are arithmetic means \pm SE and values with the same letter are not significantly different at $p \leq 0.05$.

Material			Unwashed	1 x 15 min	1 x 30 min	1 x 60 min	2 x 60 min	3 x 60 min
Primary sludge	Solid fraction	TOC (% w/w)	36.7 \pm 0.1 ^a	36.3 \pm 0.5 ^a	36.7 \pm 0.3 ^a	36.8 \pm 0.4 ^a	33.8 \pm 0.3 ^b	33.5 \pm 0.1 ^b
		TN (% w/w)	3.7 \pm 0.1 ^a	3.3 \pm 0.0 ^b	3.2 \pm 0.0 ^b	3.2 \pm 0.0 ^b	2.9 \pm 0.1 ^c	2.7 \pm 0.0 ^c
	Liquid fraction	pH	-	6.4 \pm 0.0 ^a	6.4 \pm 0.0 ^a	6.5 \pm 0.0 ^a	6.7 \pm 0.1 ^b	6.8 \pm 0.1 ^b
		EC (mS)	-	1.5 \pm 0.0 ^a	1.5 \pm 0.0 ^a	1.6 \pm 0.0 ^b	0.4 \pm 0.0 ^c	0.1 \pm 0.0 ^d
		P _{tot} (mg l ⁻¹)	-	100.1 \pm 0.8 ^a	100.6 \pm 3.8 ^a	107.5 \pm 2.9 ^a	145.5 \pm 8.3 ^b	149.2 \pm 2.2 ^b
		PO ₄ ³⁻ (mg l ⁻¹)	-	34.2 \pm 0.8 ^a	34.7 \pm 1.3 ^a	37.6 \pm 0.9 ^a	49.5 \pm 2.2 ^b	49.6 \pm 0.8 ^b
		DOC (mg l ⁻¹)	-	1080 \pm 90 ^b	1213 \pm 20 ^b	1243 \pm 46 ^b	2400 \pm 19 ^a	3434 \pm 360 ^a
		DON (mg l ⁻¹)	-	334 \pm 24 ^b	394 \pm 19 ^b	401 \pm 17 ^b	765 \pm 18 ^a	1050 \pm 119 ^a
		NH ₄ ⁺ -N (mg l ⁻¹)	-	171 \pm 10 ^b	182 \pm 12 ^b	162 \pm 25 ^b	361 \pm 16 ^a	571 \pm 67 ^a
HTC III	Solid fraction	TOC (% w/w)	39.0 \pm 0.6 ^a	38.5 \pm 0.2 ^a	38.5 \pm 0.3 ^a	38.5 \pm 0.4 ^a	36.8 \pm 0.2 ^{bc}	35.3 \pm 0.2 ^c
		TN (% w/w)	2.8 \pm 0.0 ^a	2.1 \pm 0.0 ^b	2.0 \pm 0.0 ^b	2.0 \pm 0.0 ^b	1.8 \pm 0.0 ^c	1.7 \pm 0.0 ^c
	Liquid fraction	pH	-	5.8 \pm 0.0 ^a	5.7 \pm 0.0 ^a	5.9 \pm 0.0 ^a	6.3 \pm 0.1 ^b	6.6 \pm 0.1 ^c
		EC (mS)	-	0.7 \pm 0.0 ^a	0.7 \pm 0.0 ^a	0.8 \pm 0.0 ^a	0.1 \pm 0.0 ^c	0.1 \pm 0.0 ^c
		P _{tot} (mg l ⁻¹)	-	4.6 \pm 0.2 ^a	4.7 \pm 0.2 ^a	5.5 \pm 0.2 ^a	16.3 \pm 0.1 ^b	20.9 \pm 0.0 ^b
		PO ₄ ³⁻ (mg l ⁻¹)	-	4.6 \pm 0.1 ^a	5.2 \pm 0.1 ^{ab}	5.7 \pm 0.2 ^b	7.1 \pm 0.2 ^c	8.4 \pm 0.4 ^d
		DOC (mg l ⁻¹)	-	1175 \pm 55 ^b	1276 \pm 8.8 ^b	1327 \pm 29 ^{ab}	2367 \pm 59 ^a	3011 \pm 778 ^a
		DON (mg l ⁻¹)	-	295 \pm 9.1 ^b	315 \pm 0.5 ^b	329 \pm 6.5 ^b	590 \pm 15 ^a	757 \pm 232 ^a
		NH ₄ ⁺ -N (mg l ⁻¹)	-	55 \pm 6.5 ^b	49.5 \pm 4.3 ^b	70.7 \pm 3.6 ^{ab}	117.6 \pm 1.6 ^a	132.5 \pm 13.6 ^a

Washing procedure 2 x 60 min and 3 x 60 min: washing cycle that includes replacement of the water; Solid fraction - TOC: total carbon; TN: total nitrogen. Liquid fraction - EC: electrical conductivity; P_{tot} : total phosphorous, PO_4^{3-} : phosphate, DOC: dissolved organic carbon; DON: dissolved organic nitrogen; NH_4^+ -N: ammonium-N.

Table 4. Effects of threefold washings of 60 minutes of solid test materials on midDRIFTS peak areas. a) PS and HTC I, b) HTC II and HTC III, c) ASU and HTC IV and d) ASS and LTC. Values are arithmetic means \pm SE. Results of one-way ANOVA: n.s. $p > 0.05$, * $p \leq 0.05$, ** $p < 0.01$, *** $p < 0.001$.

b)

Relative peak area (%)					Relative peak area (%)				
Solid fraction	Peak	Unwashed	3x60 min		Solid fraction	Peak	Unwashed	3x60 min	
PS	3200	65.4 \pm 0.4	71.7 \pm 0.1	***	HTC II	3200	53.2 \pm 0.9	64.3 \pm 0.6	***
	2923	2.2 \pm 0.0	2.3 \pm 0.1	***		2923	3.6 \pm 0.0	3.3 \pm 0.1	n.s.
	2853	0.3 \pm 0.0	0.4 \pm 0.0	***		2853	0.8 \pm 0.0	0.7 \pm 0.0	n.s.
	1645	9.6 \pm 0.1	8.8 \pm 0.0	***		1645	12.9 \pm 0.2	10.5 \pm 0.0	***
	1550	0.4 \pm 0.1	0.2 \pm 0.0	n.s.		1550	n.d.	0.1 \pm 0.0	-
	1450	0.1 \pm 0.0	0.2 \pm 0.0	*		1450	0.6 \pm 0.1	1.7 \pm 0.1	***
	1410	0.6 \pm 0.0	n.d.	-		1410	0.1 \pm 0.0	0.0 \pm 0.0	*
	1030	21.1 \pm 0.4	16.2 \pm 0.1	***		1030	28.7 \pm 0.9	27.6 \pm 0.4	n.s.
	790	0.3 \pm 0.0	0.2 \pm 0.0	n.s.		790	0.0 \pm 0.0	0.1 \pm 0.0	**
HTC I	3200	74.5 \pm 0.1	59.6 \pm 0.9	***	HTC III	3200	52.6 \pm 1.2	55.5 \pm 0.7	***
	2923	1.7 \pm 0.0	3.9 \pm 0.2	***		2923	3.6 \pm 0.0	4.7 \pm 0.1	n.s.
	2853	0.3 \pm 0.0	0.8 \pm 0.0	***		2853	0.7 \pm 0.0	1.0 \pm 0.0	n.s.

			0.0	
	1645	11.5 ± 0.1	9.2 ± 0.1	***
	1550	0.0 ± 0.0	0.1 ± 0.0	n.s.
	1450	0.3 ± 0.0	1.6 ± 0.5	*
	1410	n.d.	0.0 ± 0.0	-
	1030	21.6 ± 0.1	24.7 ± 0.8	***
	790	0.1 ± 0.0	0.1 ± 0.0	n.s.

			0.0	
	1645	13.5 ± 0.2	8.8 ± 0.3	***
	1550	0.0 ± 0.0	0.1 ± 0.0	n.s.
	1450	0.6 ± 0.0	1.9 ± 0.6	***
	1410	0.1 ± 0.0	0.0 ± 0.0	*
	1030	28.8 ± 1.0	27.8 ± 0.1	***
	790	0.0 ± 0.0	0.1 ± 0.0	**

d)

Relative peak area (%)				
Solid fraction	Peak	Unwashed	3x60 min	
ASU	3200	70.3 ± 1.2	72.7 ± 0.9	*
	2923	1.3 ± 0.1	1.2 ± 0.0	*
	2853	0.1 ± 0.0	0.1 ± 0.1	n.s.
	1645	9.0 ± 0.0	11.2 ± 0.1	***
	1550	0.6 ± 0.0	0.3 ± 0.1	*
	1450	0.1 ± 0.0	0.2 ± 0.0	*

Relative peak area (%)				
Solid fraction	Peak	Unwashed	3x60 min	
ASS	3200	78.3 ± 1.1	75.3 ± 0.6	*
	2923	0.9 ± 0.1	1.1 ± 0.1	n.s.
	2853	0.1 ± 0.0	0.1 ± 0.0	n.s.
	1645	10.2 ± 0.5	12.4 ± 0.5	*
	1550	0.2 ± 0.0	0.2 ± 0.0	n.s.
	1450	0.2 ± 0.0	0.2 ± 0.0	n.s.

1410	0.6 ± 0.0	n.d.	-
1030	17.9 ± 1.0	14.2 ± 0.8	*
790	0.0 ± 0.0	0.2 ± 0.1	*

1410	0.2 ± 0.0	n.d.	-
1030	9.6 ± 1.3	10.1 ± 0.5	n.s.
790	0.4 ± 0.0	0.4 ± 0.0	n.s.

HTC IV	3200	71.5 ± 0.5	56.4 ± 8.2	*
	2923	1.4 ± 0.0	2.4 ± 0.7	*
	2853	0.2 ± 0.0	0.2 ± 0.1	*
	1645	10.4 ± 0.1	21.9 ± 4.5	*
	1550	0.3 ± 0.0	0.4 ± 0.1	n.s.
	1450	0.2 ± 0.0	0.4 ± 0.1	**
	1410	0.4 ± 0.0	n.d.	-
	1030	15.4 ± 0.4	18.2 ± 1.0	n.s.
	790	0.2 ± 0.0	0.1 ± 0.0	**

LTC	3200	83.1 ± 0.1	74.4 ± 0.9	***
	2923	0.1 ± 0.0	0.5 ± 0.0	***
	2853	0.0 ± 0.0	0.1 ± 0.0	n.s.
	1645	11.7 ± 0.2	12.5 ± 0.4	*
	1550	n.d.	n.d.	-
	1450	0.1 ± 0.0	0.3 ± 0.0	**
	1410	n.d.	n.d.	-
	1030	4.8 ± 0.2	11.9 ± 1.0	***
	790	0.2 ± 0.0	0.3 ± 0.0	*

PS: primary sludge; HTC: hydrothermal carbonisation; ASU: activated sludge unstabilised; ASS: activated sludge stabilised and LTC: thermocatalytic low temperature conversion; highlighted peak names: midDRIFTS peaks indicating aromatic functional groups; n.s.: not significant.

Table 5. Effects of threefold washings on a) the germination and b) the dry weight per cress plant. Values are arithmetic means \pm SE and values with the same letter are not significantly different at $p \leq 0.05$.

a)				b)			
Germination rate (%)				Dry weight / plant			
	Unwashed	3 x 60 min			Unwashed	3 x 60 min	
Control	96 \pm 2.3	-		Control	0.61 \pm 0.0	-	
PS	52 \pm 14.4	69 \pm 9.0	n.s.	PS	0.34 \pm 0.1	0.50 \pm 0.1	n.s.
HTC I	71 \pm 1.9	83 \pm 2.5	*	HTC I	0.35 \pm 0.0	0.61 \pm 0.1	*
HTC II	64 \pm 4.0	85 \pm 1.9	*	HTC II	0.32 \pm 0.0	0.40 \pm 0.1	n.s.
HTC III	81 \pm 2.5	93 \pm 1.0	n.s.	HTC III	0.29 \pm 0.0	0.61 \pm 0.0	*
ASU	71 \pm 1.0	83 \pm 4.4	*	ASU	0.40 \pm 0.0	0.35 \pm 0.0	n.s.
HTC IV	76 \pm 4.9	81 \pm 4.7	n.s.	HTC IV	0.25 \pm 0.0	0.53 \pm 0.1	*
ASS	70 \pm 4.8	85 \pm 4.4	n.s.	ASS	0.28 \pm 0.1	0.14 \pm 0.0	n.s.
LTC	79 \pm 1.3	88 \pm 5.9	n.s.	LTC	0.78 \pm 0.1	0.84 \pm 0.1	n.s.

PS: primary sludge; HTC: hydrothermal carbonisation; ASU: activated sludge unstabilised; ASS: activated sludge stabilised and LTC: thermocatalytic low temperature conversion; n.s.: not significant.