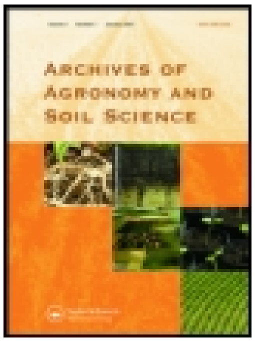

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Labile water soluble components govern the short-term microbial decay of hydrochar from sewage sludge

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Abstract

Due to higher proportions of labile carbon (C) compounds the suitability of biochar produced by hydrothermal carbonization (HTC) for C sequestration is questionable. We hypothesized that pre-treatment with water would reduce the biological decay of hydrochar from sewage sludge. Unwashed and washed feedstock and hydrochar were incubated in a short-term experiment. The kinetics of the biological decomposition of the materials was calculated on the basis of a double exponential model and the C sequestration potential using the CANDY Carbon Balance (CCB) model. Biological decomposition of the carbonized materials was governed by the percentage of labile C compounds. Mean residence time of a fast (MRT_{fast}) and slow decay pool (MRT_{slow}) of unwashed hydrochars varied clearly (MRT_{fast}: 0.8 – 5.0

months and the MRT_{slow}: 5.0 – 18.6 months). The pre-treatment with water removed labile hydrochar C and reduced the biological accessibility. MRT_{fast} and MRT_{slow} was increased by intensive washings (MRT_{fast}: 5.0 – 7.4 months and the MRT_{slow}: 14.9 months). High synthesis coefficients suggest that hydrochar C was humified and transferred into stabilized SOC. The results clearly show that once adsorbed components were eliminated, and as compared to pyrolysed biochar hydrochar from sewage sludge may also be useful for soil C sequestration.

Keywords: biochar; carbon sequestration; ccb model; hydrochar; respiration; sewage sludge

Introduction

The use of biochar as a soil amendment appears to be a promising option for restoring and maintaining soil quality (Lehmann & Joseph 2015). It can create a positive soil carbon (C) budget and provides significant agronomic benefits, while decreasing greenhouse gas emissions (Sänger et al. 2016). The effect of different biochars on soil-plant interactions can vary widely, since its overall properties depend on the type of the conversion processes (e.g. pyrolysis, hydrothermal carbonization - HTC) and specific process parameters. The advantage of the HTC process is that wet feedstock, such as sewage sludge, animal manure and human waste, can be converted into carbonaceous solids (hydrochar) without the need for an energy-intensive pre-drying process (Libra et al. 2014). Carbonaceous materials from sewage sludge for use as a soil amendment appear to be viable, both from an economic and an ecological standpoint (Breulmann et al. 2015), however, its suitability is yet to be investigated. Knowledge about the stability and the decomposition of hydrochar is fundamental to understanding their potential roles in the global soil C cycle. It has been shown that hydrochar contains a higher proportion of labile C compounds than pyrolysis biochar, suggesting that hydrochar may be less stable and less suitable for long-term C sequestration (Qayyum et al. 2012). The question whether this is also applicable to hydrochar produced from sewage sludge is still open. Elimination of adsorbed labile compounds by a specific pre-treatment led to varying effects on the mineralization of hydrochar C. Eibisch et al. (2013) found no significant effects on the total amount of mineralized C in washed hydrochar. In contrast, Naisse et al. (2015) showed that artificial physical weathering strongly decreased the biological utilization of one hydrochar produced from maize silage. We hypothesized that a pre-treatment with water would reduce the biological decomposition of hydrochars, but also of pyrolysis biochar from sewage sludge. Therefore, different unwashed and washed materials were used for a short-term incubation experiment. The respired carbon dioxide was used (i) to calculate the kinetics of the biological decay on the basis of a double exponential model and (ii) to model the C sequestration potential using the CANDY Carbon Balance model (CCB).

Materials and methods

Test materials

Eight materials were included in the study – three feedstocks, four hydrochars, and one pyrolysis biochar. The feedstocks were primary sludge (PS), activated surplus sludge, unstabilized (ASU) and activated sludge stabilized (ASS), differing in their overall C content (PS: 36.7%; ASU: 30.7%; ASS: 27.1%). The pyrolysis biochar was produced from ASU by thermocatalytic low temperature conversion (LTC) within 1 h at 400 °C. The four hydrochars were prepared by heating at different temperatures for different lengths of time. The hydrochars HTC I (4 h, 180 °C), HTC II (4 h, 200 °C) and HTC III (8 h, 200 °C) were produced from PS and HTC IV (4 h, 200 °C) from ASS. Further information on material characteristic can be found in the study of Breulmann et al. (2017).

Washing procedure

The materials were given intensive pre-treatment using cold water, three times for 60 min, to remove adsorbed labile components. A total of 10 g of material were mixed with 300 ml demineralized water and gently shaken (11 rpm) in an overhead shaker, decanting and renewing the aqueous solution between each washing. After centrifugation (15 min, 5000 *g*), all materials were homogenized, milled, and then dried at 70 °C.

General analysis

The total organic carbon (TOC) and nitrogen (TN) contents of the solid materials were analysed using a C/H/N analyzer (Vario El III, Elementar, Hanau, Germany). 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 analyzed for its total C (DOC) content, using an elemental analyzer for aqueous samples (Micro N/C and Multi N/C, Analytik Jena, Germany).

Respiration experiment

The respiration experiment was designed as a two-factorial study: Factor 1 – material; Factor 2 – washed/unwashed materials. The measurements of all treatments were replicated four times and included a control, resulting in a total of 68 experimental units. In order to exclusively reflect the pre-treatment effect on the materials and to avoid any potential matrix side effects, silica sand was chosen as carrier for the test materials. The air-dried, non-sterile silica sand was rewetted with water to 60% of its maximum water-holding capacity and pre-incubated for eight days. The experimental units consisted of polyethylene vessels containing a mix of 50 g of silica sand with test materials added on a 50 mg C basis. The sand/material mixtures were then incubated at 22 °C for 35 day in a Respicond V (Breulmann et al. 2014) and measurements of the CO_2 evolution were taken hourly by automatically recording changes in electrical conductivity induced by absorption of CO_2 in a KOH trap. To quantify the CO_2 produced during decomposition, the CO_2 originating from the carrier material was subtracted from the total CO_2 released from the material treatments. The results were not corrected for microbial resynthesis of CO_2 and thus only account for net mineralization.

Statistical analysis and modeling

Data were analyzed using the 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 in the tables. Results were evaluated statistically using analysis of variance (ANOVA) followed by a Tukey's post hoc test and by linear regression analysis. Data were fitted to a double exponential decay model and mean residence times (MRT) were calculated on the basis of the turnover rates as described by Knicker et al. (2013). A synthesis coefficient (η) and a first-order rate constant (k_0) of the materials were calculated on the basis of C input using the CCB model (Franko et al. 2011), which allows for the absolute quantification of SOC changes as an indicator of SOM levels (Brock et al. 2013). The scheme of CCB model and the functions of CCB to estimate the C decomposition in incubation experiments are presented in Figure 1. To estimate the fresh organic matter (FOM) decomposition of the different organic amendments the CCB model was used with the general parameters: $k_a = 0.00032\ d^{-1}$, $k_m = 0.00556\ d^{-1}$ and $k_s = 0.0009\ d^{-1}$ (turnover coefficients; Figure 1). At the beginning of the experiment beside the FOM pool all C pools (C_{rep}, C_A, C_S) were empty (zero). Using the observation values of CO_2 the parameter k_0 and η were estimated by solving the equations of CCB model. The CCB model is a simplified version of the CANDY model and describes the turnover of decomposable C in annual time steps. The η-coefficient describes the amount of C per unit of respired substrate C that is transformed into SOM, and can be used as a measure for the C sequestration potential of the materials; ŋ-coefficients equaling 1 imply that all C from the input material has remained in the soil. The k_0 parameter specifies the turnover rate for synthesized OM.

Results and discussion

The unwashed test materials differed in TOC (21.8% to 39.6%), TN (2.3% to 4.9%) and C/N ratios (6.6% to 16.6%) and intensive washings significantly decreased these concentrations (Table 1). In contrast to the fivefold washings for 2 minutes each by Eibisch et al. (2013), our threefold washings for 60 minutes significantly decreased the TOC and TN content of the solid fraction. The treatment resulted also in a significant elution of organic C. The respiration experiment revealed that the labile water soluble components of the test materials, calculated by $\mathrm{TOC}_{\mathrm{unwashed}} - \mathrm{TOC}_{\mathrm{washed}}$, correlated significantly with the amount of respired C from the washed materials (Figure 2). Unwashed hydrochar promoted the CO_2 production with increasing the temperature and duration of the HTC process (e.g. HTC I – HTC III), but no significant difference was observed (Figure 3). However, the amount of respired CO_2 depends also on the type of sewage sludge used as a feedstock. After 35 days of incubation 56.8% of the initial C of the unwashed PS was mineralized due to the significant higher organic content (Table 2). Additionally, significantly different respiration rates between the unwashed feedstock and the corresponding hydrochar were observed (Figure 3). Ones adsorbed labile compound were eliminated by a pre-treatment with water, the CO_2 production was significantly reduced as it was stated by Dicke et al. (2015). After pre-washings, the remaining C (%) from the feedstocks and the conversion products differed, depending on the conversion type (Figure 3). By using higher temperatures and longer process times (2–8h), more organic components were hydrolysed and, depending on the drying and filtering process, a larger amount of labile compounds could be adsorbed to the hydrochars' surface. It seems appropriate to spotlight that for the first time the respired CO_2 of hydrochar from sewage sludge was used to model the C sequestration potential. The pre-treatment with water almost prevented the biological decomposition of the fast decaying fraction of the feedstocks and the hydrochar, leading to an increase in half-life times for this pool (HLT_{fast}) by a factor of 1.5 to 6.8, and by a factor of 3 for the pyrolysis biochar LTC. In contrast to Jones et al. (2011) the total respired C of the pyrolysis biochar LTC was not affected at all. The MRT_{fast} of the unwashed feedstock varied from 1.5 to 5.0 months and was increased by intensive washings to 3.0 – 3.7 months (Table 2). Except of ASU, MRT_{slow} of the feedstocks was not affected by a washing. Furthermore, the MRT_{fast} and slow decay pool (MRT_{slow}) of unwashed hydrochars varied clearly (MRT_{fast}: 0.8 – 5.0 months and the MRT_{slow}: 5.0 – 18.6 months) and were significantly increased (MRT_{fast}: 5.0 – 7.4 months and the MRT_{slow}: 14.9 months) by intensive washings. For the unwashed LTC the MRT_{fast} was 3.8 years and increased by a pre-treatment to 11.4 years. However, the slow decay pool (MRT_{slow}) of LTC increased by a pre-treatment from 29.0 to 143.0 years. After the pre-treatment about 69.4% to 100% of the added C was not transformed. The η-coefficients ranged between 0.91 and 0.99, with a tendency for higher values relating to the washing of the hydrochar as compared to unwashed materials. The corresponding k_0 values of between 1.3 and 5.1 per year indicate the speed of the transformation process and tend to negatively correlate with the pre-treatment and η-coefficients. There was no biological utilization of the pyrolysis biochar LTC evident over 35 days of incubation, coupled with 100% remaining C from LTC at the end of the experiment and a η-coefficients equaling 1.0 of implying that all C from the feedstock has remained in the soil.

Conclusions

To conclude, the study showed that the biological decomposition of the carbonized materials depended on the type of feedstock and the type and conditions of the thermochemical carbonization processes. In addition, a pre-treatment of hydrochar with water eliminated superficially adsorbed labile components and significantly decreased their biological accessibility. Using the high η-coefficients as a measure of a differential humification coefficient, it can be assumed that some hydrochar C was transferred during biological degradation into more humified fractions. Washing of hydrochars can be an important pre-step for inducing changes in material properties in terms of their biological decay and might impact the C sequestration potential at decadal timescale. Lab and field scale respiration studies will give additional information on the interactions of abiotic parameters and biotic processes and the formation of mineral-organic associations for understanding C stabilization mechanisms of hydrochar in soils. However, due to their costs and expenditures extra washing processes may not be feasible for commercial hydrochar production.

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Figure Captions

Figure 1. Scheme and functions of the CCB model (adopted from Franko et al. 2011). η: synthesis coefficient; k_0: first-order rate constant of the CCB model; turnover coefficients: k_a: flux from C_S to C_A; k_s flux from C_A to C_S; k_m flux from C_A to CO_2; FOM: fresh organic matter

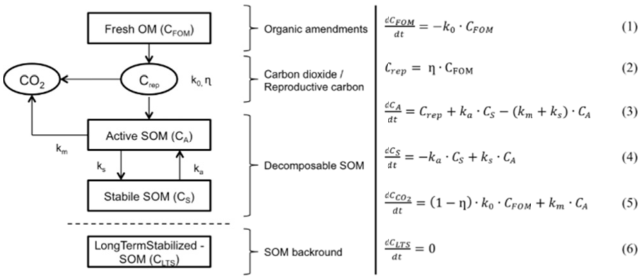

Figure 2. Relation of the total respired C of the washed materials to Δ total organic C content after 35 days of incubation. The Δ TOC of the individual materials was calculate by $TOC_{Unwashed} - TOC_{Washed}$.

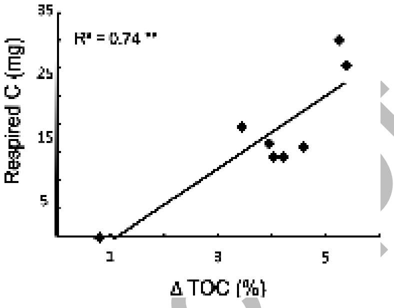

Figure 3. Remaining C in unwashed and washed materials after 35 days of incubation. Values are arithmetic means ± SE and values with the same letter are not significantly different at $p \leq 0.05$. PS: primary sludge; HTC: hydrothermal carbonisation; ASU: activated sludge unstabilised; ASS: activated sludge stabilised (ASS) and LTC: thermocatalytic low temperature conversion.

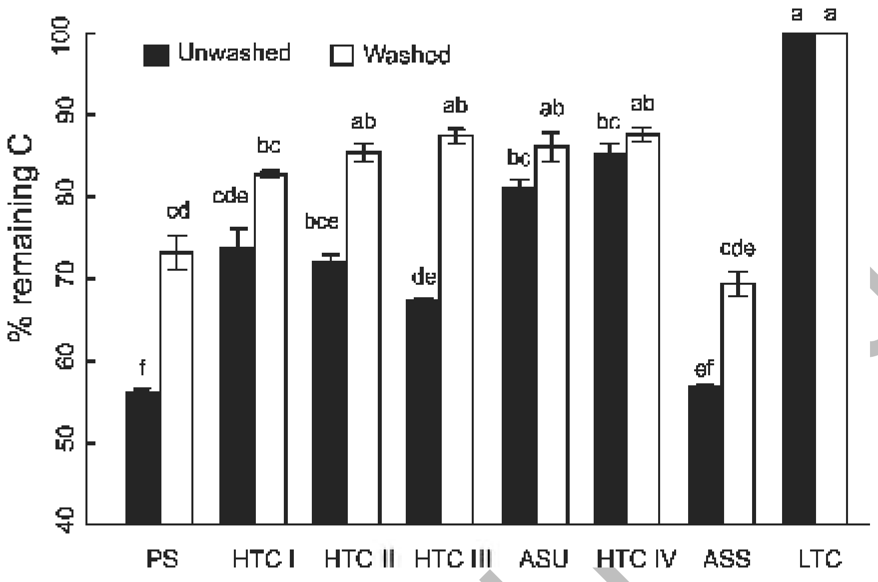

Table 1. Carbon and nitrogen content of unwashed and washed test materials and the dissolved organic C content. Significant effects were analysed between unwashed and washed materials. Values with the same letter are not significantly different at $p \leq 0.05$.

Material		TOC (%)		TN (%)		C/N		DOC (% of TOC)
PS	Unwashed	38.8	a	4.2	a	9.2	a	-
	Washed	33.5	b	2.7	b	12.4	b	14.0
HTC I	Unwashed	38.4	a	2.3	a	16.6	a	-
	Washed	35.0	b	1.6	b	21.6	b	8.6
HTC II	Unwashed	39.6	a	2.6	a	14.9	a	-
	Washed	35.6	b	1.7	b	21.0	b	14.8
HTC III	Unwashed	39.4	a	2.7	a	14.4	a	-
	Washed	35.3	b	1.7	a	21.2	b	10.9
ASU	Unwashed	32.5	a	4.4	a	7.3	a	-
	Washed	27.9	b	3.1	b	9.1	b	11.3
HTC IV	Unwashed	35.9	a	4.9	a	7.3	a	-
	Washed	31.8	b	3.7	b	8.6	b	15.6
ASS	Unwashed	29.3	a	4.5	a	6.6	a	-
	Washed	24.1	b	3.3	b	7.3	a	10.0
LTC	Unwashed	21.8	a	3.2	a	6.8	a	-
	Washed	21.0	a	2.9	a	7.4	a	0.7

PS: primary sludge; HTC: hydrothermal carbonisation; ASU: activated sludge unstabilised; ASS: activated sludge stabilised and LTC: thermocatalytic low temperature conversion; TOC: total organic carbon; TN: total nitrogen; DOC: dissolved organic carbon.

Table 2. Kinetics of the decay of unwashed and pre-treated materials calculated using a double exponential decay model and the CCB model. Significant effects were analysed between unwashed and washed materials. Values with the same letter are not significantly different at $p \leq 0.05$.

		Double exponential decay model							CCB Model	
		Fast pool			Slow pool					
Material	Treatment	k_1 (d^{-1})	HLT $_{fast}$ (d^{-1})	MRT_{fast} (months)	k_2 ($year^{-1}$)	HLT $_{slow}$ (d^{-1})	MRT_{slow} (months)	remaining C (%)	k_0 ($year^{-1}$)	synthesis coefficient (□)
PS	Unwashed	8.8 ^{a}	29 ^{a}	1.5 ^{a}	2.6 ^{a}	96 ^{a}	5.0 ^{a}	56.8 ^{a}	3.5 ^{a}	0.95 ^{a}
	Washed	3.5 ^{b}	72 ^{b}	3.7 ^{b}	2.6 ^{a}	96 ^{a}	5.0 ^{a}	73.1 ^{b}	1.5 ^{b}	0.93 ^{b}
HTC I	Unwashed	17.5 ^{a}	14 ^{a}	0.8 ^{a}	1.8 ^{a}	144 ^{a}	7.4 ^{a}	73.8 ^{a}	5.1 ^{a}	0.95 ^{a}
	Washed	2.6 ^{b}	96 ^{b}	5.0 ^{b}	0.9 ^{b}	289 ^{b}	14.9 ^{b}	82.7 ^{b}	1.4 ^{b}	0.96 ^{a}
HTC II	Unwashed	8.8 ^{a}	29 ^{a}	1.5 ^{a}	1.8 ^{a}	144 ^{a}	7.4 ^{a}	72.1 ^{a}	1.5 ^{a}	0.91 ^{a}
	Washed	1.8 ^{b}	144 ^{b}	7.4 ^{b}	0.9 ^{b}	289 ^{b}	14.9 ^{b}	85.4 ^{b}	1.4 ^{a}	0.98 ^{b}
HTC III	Unwashed	8.8 ^{a}	29 ^{a}	1.5 ^{a}	2.6 ^{a}	96 ^{a}	5.0 ^{a}	67.4 ^{a}	5.1 ^{a}	0.93 ^{a}
	Washed	2.6 ^{b}	96 ^{b}	5.0 ^{b}	0.9 ^{b}	289 ^{b}	14.9 ^{b}	87.4 ^{b}	3.4 ^{b}	0.99 ^{b}
ASU	Unwashed	2.6 ^{a}	96 ^{a}	5.0 ^{a}	1.8 ^{a}	144 ^{a}	7.4 ^{a}	80.9 ^{a}	1.4 ^{a}	0.92 ^{a}

	Washed	0.9 ^{b}	289 ^{b}	15.9 ^{b}	0.9 ^{b}	289 ^{b}	14.9 ^{b}	86.1 ^{b}	1.4 ^{a}	0.93 ^{a}
HTC IV	Un-washed	2.6 ^{a}	96 ^{a}	5.0 ^{a}	0.7 ^{a}	361 ^{a}	18.6 ^{a}	85.3 ^{a}	1.4 ^{a}	0.97 ^{a}
	Washed	1.8 ^{b}	144 ^{b}	7.4 ^{b}	0.9 ^{a}	289 ^{a}	14.9 ^{b}	87.6 ^{b}	1.4 ^{a}	0.99 ^{b}
ASS	Un-washed	8.8 ^{a}	29 ^{a}	1.5 ^{a}	1.8 ^{a}	144 ^{a}	7.4 ^{a}	55.8 ^{a}	1.4 ^{a}	0.96 ^{a}
	Washed	4.4 ^{b}	58 ^{b}	3.0 ^{b}	1.8 ^{a}	144 ^{a}	7.4 ^{a}	69.4 ^{b}	1.4 ^{a}	0.99 ^{b}
			(years)	(years)		(years)	(years)			
LTC	Fresh	0.3 ^{a}	2.6 ^{a}	3.8 ^{a}	0.0 ^{a}	20 ^{a}	29.0 ^{a}	100.0 ^{a}	1.3 ^{a}	1.00 ^{a}
	Washed	0.1 ^{b}	7.9 ^{b}	11.4 ^{b}	0.0 ^{a}	99 ^{b}	143.0 ^{b}	100.0 ^{a}	1.3 ^{a}	1.00 ^{a}

PS: primary sludge; HTC: hydrothermal carbonisation; ASU: activated sludge unstabilised; ASS: activated sludge stabilised and LTC: thermo-catalytic low temperature conversion; k_1 and k_2: first and second order mineralization rate constants for the fast and slow pool of the double exponential decay model; k_0: first-order rate constant of the CCB Model; MRT: mean residence time; HLT: halflife time and CCB: CANDY carbon balance model.