



Effect of biochar amendment on compost organic matter composition following aerobic composting of manure



Nikolas Hagemann ^{a,*}, Edison Subdiaga ^b, Silvia Orsetti ^b, José María de la Rosa ^c, Heike Knicker ^c, Hans-Peter Schmidt ^d, Andreas Kappler ^a, Sebastian Behrens ^{e,f,**}

^a Geomicrobiology, Center for Applied Geoscience, University of Tuebingen, Sigwartstrasse 10, 72076 Tuebingen, Germany

^b Environmental Mineralogy and Chemistry, Center for Applied Geoscience, University of Tuebingen, Sigwartstrasse 10, 72076 Tuebingen, Germany

^c Instituto de Recursos Naturales Agrobiología de Sevilla (IRNAS-CSIC), Av. Reina Mercedes, 10, 41012 Seville, Spain

^d Ithaka Institute for Carbon Strategies, Ancienne Eglise 9, Arbaz 1974, Switzerland

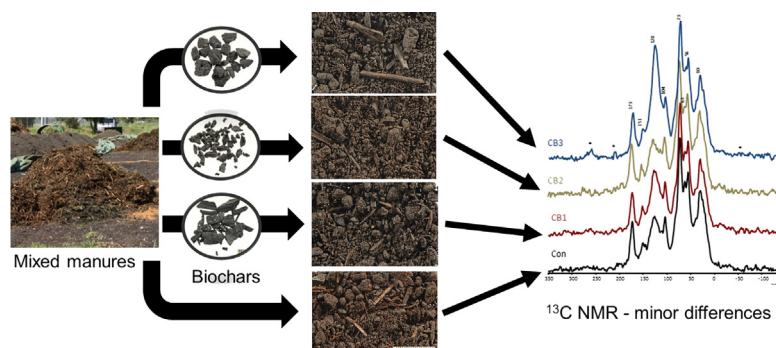
^e Department for Civil, Environmental, and Geo-Engineering, University of Minnesota, MN, United States

^f BioTechnology Institute, University of Minnesota, MN, United States

HIGHLIGHTS

- Overall, biochar had minor impacts on organic matter speciation after optimized aerobic composting.
- ¹³C NMR does not reveal biochar-induced changes in compost bulk C speciation.
- Just FT-IR suggests that compost feedstock decomposition decreased in the presence of biochar.
- Sewage sludge biochar reduced concentrations of dissolved organic carbon in compost.
- Higher total organic carbon content can be widely explained by the added biochar-C.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 16 March 2017

Received in revised form 15 August 2017

Accepted 15 August 2017

Available online xxx

Editor: D. Barcelo

Keywords:

Pyrogenic organic carbon

FTIR

NMR

Humic substances

Amazonian Dark Earth

Sewages sludge char

ABSTRACT

Biochar, a material defined as charred organic matter applied in agriculture, is suggested as a beneficial additive and bulking agent in composting. Biochar addition to the composting feedstock was shown to reduce greenhouse gas emissions and nutrient leaching during the composting process, and to result in a fertilizer and plant growth medium that is superior to non-amended composts. However, the impact of biochar on the quality and carbon speciation of the organic matter in bulk compost has so far not been the focus of systematic analyses, although these parameters are key to determine the long-term stability and carbon sequestration potential of biochar-amended composts in soil. In this study, we used different spectroscopic techniques to compare the organic carbon speciation of manure compost amended with three different biochars. A non-biochar-amended compost served as control. Based on Fourier-transformed infrared (FTIR) and ¹³C nuclear magnetic resonance (NMR) spectroscopy we did not observe any differences in carbon speciation of the bulk compost independent of biochar type, despite a change in the FTIR absorbance ratio $2925\text{ cm}^{-1}/1034\text{ cm}^{-1}$, that is suggested as an indicator for compost maturity. Specific UV absorbance (SUVA) and emission-excitation matrixes (EEM) revealed minor differences in the extractable carbon fractions, which only accounted for ~2–3% of total organic carbon. Increased

* Corresponding author.

** Correspondence to: S. Behrens, Department for Civil, Environmental, and Geo-Engineering, University of Minnesota, MN, United States.

E-mail addresses: nikolas.hagemann@agroscope.admin.ch (N. Hagemann), sbehrens@umn.edu (S. Behrens).

¹ Present address: Agroscope, Environmental Analytics, Reckenholzstrasse 191, 8046 Zurich, Switzerland.

EEM
Electron exchange capacity
Farmyard manure

total organic carbon content of biochar-amended composts was only due to the addition of biochar-C and not enhanced preservation of compost feedstock-C. Our results suggest that biochars do not alter the carbon speciation in compost organic matter under conditions optimized for aerobic decomposition of compost feedstock. Considering the effects of biochar on compost nutrient retention, mitigation of greenhouse gas emissions and carbon sequestration, biochar addition during aerobic composting of manure might be an attractive strategy to produce a sustainable, slow release fertilizer.

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1. Introduction

Biochar is defined as charred organic matter produced by pyrolysis that has multiple uses in agriculture and is eventually applied as a soil amendment (EBC, 2012; Lehmann and Joseph, 2009). Its use as a soil amendment is motivated by the global historic use of charcoal that led to the formation of anthropogenic soils including the Amazonian Dark Earths in the Amazon basin (“Terra Preta do Indio”, Glaser, 2007). Amazonian Dark Earths and similar soils worldwide have a higher agronomic value and a higher content of organic matter than their adjacent, non-anthropogenic soils that have not received an anthropogenic input of pyrogenic carbon (Lehmann et al., 2003; Wiedner and Glaser, 2015). However, the addition of pure biochar to soil combined with conventional agricultural practices, especially the application of inorganic fertilizers, does not necessarily increase soil quality and crop yields (Crane-Droesch et al., 2013; Hagemann et al., 2017a; Jeffery et al., 2015). The combination of biochar with organic amendments, such as compost, has recently received increasing attention due to promising results in both pot and field experiments (Kammann et al., 2016; Schmidt et al., 2015; Schulz et al., 2013).

Biochar amendment was further shown to have desired effects on the composting process, including the reduction of N₂O emissions (C. Wang et al., 2013) and the reduction of nitrogen leaching (Steiner et al., 2010). Increases in crop yield by biochar-amended composts have been explained by the slow nutrient release from co-composted biochar and its improved properties as organic fertilizer (Kammann et al., 2015b). Biochar pieces that were manually picked from compost following a co-composting process have been shown to have an increased cation exchange capacity and a higher number of oxidized carbon functional groups on their surface than the original (Khan et al., 2016; Wiedner et al., 2015).

In practice, co-composted biochar is not applied to soil after separation from the compost, but as a biochar-amended compost. Thus, there is the need to also understand the composition of this complex organic material mix as a whole. This includes the impact of biochar on the quality of non-pyrogenic organic matter of the mature biochar-amended compost, which has so far only been the subject of a few studies. Jindo et al. (2012) found an increased stability of biochar-amended manure + organic waste compost assessed by thermogravimetric analysis. In this study the authors did not observe any considerable changes in ¹³C nuclear magnetic resonance (NMR) spectra of the bulk compost beyond a general increase in aromatic carbon structures. Since this increase in aromatic carbon is a direct consequence of the biochar addition (Jindo et al., 2012), the authors argued for the need of a selective analysis of the non-biochar organic matter of biochar-amended compost, i.e. to separate biochar and compost for analysis. Other studies have focused only on the humic substances instead of the bulk compost (Jindo et al., 2016; Wang et al., 2014) or focused on biochar-amended sewage sludge compost (Zhang et al., 2014).

In the present study, we conducted a farmyard manure composting experiment at a sub-industrial scale. Mixed manure was composted as a non-amended control as well as after addition of three different biochars at 4.3% (w/w). After maturation, we analyzed and compared the organic matter of the four different biochar compost treatments using elemental analysis, extractions with 0.1 M KCl, and spectroscopic techniques applied to bulk compost. Prior spectroscopy on the bulk compost

samples, we manually removed biochar particles to focus our data analyses on the non-biochar fraction of the composts.

2. Materials and methods

2.1. Biochars and aerobic composting of manure

Aerobic co-composting of biochar was conducted from August to October 2014 on an outdoor composting facility at the Ithaka Institute in St. Léonard, VS, Switzerland. The composting feedstock comprised mixed manures (farmyard manure) and green plant materials. The feedstock was mixed and split into four windrows of 20 m³ each. Three windrows were amended with different biochars (B1, B2, B3) at a rate of 4.3% (dry matter w/w) resulting in biochar-amended composts CB1, CB2, CB3. One windrow was composted without amendment as a control (Con).

Mixed woody waste biochar: B1 (700 °C, Pyreg® process, Sehn et al., 2010), sewage sludge char: B2 (650 °C, Pyreg® process) and wood waste/pruning residue biochar: B3 quenched with water (700 °C, flame curtain pyrolysis in a Kon-Tiki, cf. Cornelissen et al., 2016; Schmidt and Taylor, 2014) were analyzed according to the requirements of European Biochar Certificate (EBC, 2012) by Eurofins Umwelt Ost GmbH, Halsbrücke-Tuttendorf, Germany. The physical and chemical properties of the three biochars are listed in Table 1. While B1 and B3 fulfill the “basic” criteria of the European Biochar Certificate, sewage sludge char B2 had elevated concentrations of Cu and Zn and a carbon content below 50%. Therefore, B2 would not be considered a biochar according to EBC (2012). However, to facilitate reading this text, we will also refer to B2 as a biochar.

Compost windrows were mechanically turned for aeration every day during the first three weeks of composting and every third day thereafter, for 6 weeks. Between turning events, windrows were covered with a felt to reduce evaporation and heat loss. These procedures promote an aerobic process of decomposition and allow the development of elevated (“thermophilic”) decomposition temperatures (Kammann et al., 2016). Temperatures reached 60 °C and remained at about 60 °C for the first two to three weeks. Thereafter, temperatures decreased gradually to ambient outdoor temperatures (18–25 °C) in the following seven weeks. When the ammonium concentration in the four compost windrows reached <10 mg NH₄⁺-N kg⁻¹ the composts were considered mature and were packed in open plastic bags and stored frost-protected.

2.2. Elemental analysis of composts

Samples of mature control compost and biochar-amended composts CB1, CB2 and CB3 were freeze-dried and powdered in an agate mortar. Total organic carbon (TOC) was measured in a CN elemental analyzer (Vario EL, Elementar, Hanau, Germany). For inductively coupled plasma optical emission spectrometry (ICP-OES; DV 5300, Perkin Elmer, Waltham MA, USA), a modified aqua regia (nitrohydrochloric acid) microwave extraction/digestion protocol was used as suggested by the manufacturer (Start 1500, MLS, Leutkirch, Germany).

Exchangeable ions, including nutrients, were extracted from moist compost with a calcium-acetate-lactate extraction (“CAL” extraction, Kießling et al., 2008) and quantified by ICP-OES (DV 5300, Perkin

Table 1
Origin of the three biochars and their physical and chemical characteristics measured according to the requirements of the European Biochar Certificate. Numbers in bold exceed the EBC set threshold for the respective parameter (in B2 only).

	EBC basic threshold	B1	B2	B3
Manufacturer		SwissBiochar GmbH, Belmont-sur-Lausanne (VD), Switzerland	Pyreg GmbH, Bingen, Germany	Ithaka institute, Arbaz (VS), Switzerland
Technology		Pyreg®	Pyreg®	KonTiki – flame curtain pyrolysis
Feedstock		Mixed woody waste materials	Sewage sludge	Vine wood
HTT ^a [°C]		700	650	750
BET surface [m ² g ⁻¹]		200	60	252
Ash 550 °C [% w/w]		18.2	76.5	18.4
Elemental composition				
H		2.13	0.68	1.45
C	>50	74.5	21.3	76.8
N		0.68	1.70	0.75
O		4.5	-2.7 ^c	2.5
S		0.04	2.43	0.07
Molar ratios				
H/C	<0.6	0.34	0.38	0.22
H/C _{org}	<0.7	0.34	0.38	0.23
O/C	<0.4	0.045	-0.01	0.024
pH	<10	8.3	7.2	8.5
Salt [g kg ⁻¹]		3.83	8.41	4.71
Trace elements [mg kg ⁻¹]				
Pb	<150	3	27	4
Cd	<1.5	<0.2	0.6	<0.2
Cu	<100	13	610	86
Ni	<50	5	65	6
Hg	<1	<0.07	<0.07	<0.07
Zn	<400	52	1290	200
Cr	<90	6	110	9
B		24	74	41
Mn		190	1140	160
Nutrients [mg kg ⁻¹]				
P		870	87,000	2100
Mg		2700	16,000	4200
Ca		37,000	100,000	40,000
K		5800	7200	4800
Na		740	6500	740
Fe		3900	130,000	3700
Si		28,000	36,000	21,000
S		230	230,000	550
PAH [mg kg ⁻¹] ^b	<12	4.60	2.40	6.90

^a HTT: Highest Treatment Temperature.

^b PAHs are given as the sum of 16 polycyclic aromatic hydrocarbons as suggested by the US Environmental Protection Agency (16 EPA PAH), extracted with toluene as recommended by the EBC, 2012 and Hilber et al., 2012.

^c Oxygen content is calculated after thermal oxidation as follows: [O] = 100% - [C] - [H] - [N] - [S] - [ash]. Negative oxygen values are the result of both CO₂ precipitated as carbonate in the ash or reduced inorganic components of the biochar. The oxygen bound in oxides after ashing increases the mass of the ash (pers. comm. Eurofins Umwelt Ost GmbH and EBC, 2012).

Elmer, Waltham, USA), ion chromatography (IC, DX-120, Dionex, Sunnyvale, CA, USA) and colorimetric flow injection analysis for phosphate (SEAL Analytical, Germany).

2.3. Separation of biochar from biochar-amended composts for FTIR and ¹³C NMR

To avoid influence of the biochar on FTIR and ¹³C NMR spectra, biochar was removed from compost aliquots by manual picking of biochar pieces from each compost until no pieces were visible to the naked eye. After separation, we weighed the picked biochar and the now “biochar-

free” compost samples. Aliquots were used to determine dry matter content of composts and biochar in triplicates after drying at 105 °C for 48 h. The non-amended control compost and three composts from which biochar particles have been removed were freeze-dried and powdered in an agate mortar. The expected TOC (TOC_{Exp}) content of biochar-amended composts were calculated according to Eq. (1),

$$\text{TOC}_{\text{Exp}} = A \cdot C_{\text{Biochar}} + (1-A) \cdot C_{\text{Compost}}, \quad (1)$$

in which A is the biochar content of the biochar-amended compost [%], C_{Biochar} is the carbon content of biochar (Table 1) and C_{Compost} is the carbon (TOC) content of the control compost (Table 2) [g C kg⁻¹]. We quantified A_{empiric} gravimetrically by separating biochar and compost. In addition, for A_{theoretic} we used 8.6% for all biochar-amended composts because biochars were added at a rate of 4.3% to the compost feedstock and we assumed a feedstock mass loss during composting of ~50% (Kammann et al., 2016). We therefore report TOC_{Exp} as a range of values based on calculations using both A_{empiric} and A_{theoretic}.

2.4. Fourier transformed infrared spectroscopy

Freeze-dried and powdered compost after biochar removal were mixed in triplicates with water-free KBr (1 mg + 250 mg). The mixtures were ground in an agate mortar to homogenize the sample and the powders were pelleted. IR transmission absorption spectra were obtained on a Vertex 80v (Bruker Corporation, Billerica, MA, USA) as average of 128 scans (1.93 cm⁻¹ resolution, 368.4–4497.7 cm⁻¹).

2.5. ¹³C nuclear magnetic resonance spectroscopy

Freeze-dried and powdered compost after biochar removal was also subject to solid state ¹³C nuclear magnetic resonance (NMR) spectroscopy. Spectra were obtained with a Bruker Avance 400 MHz using zirconium rotors of 4 mm OD with KEL-F-caps. The cross polarization magic angle spinning (CPMAS) technique was applied during magic-angle spinning of the rotor at 14 kHz. A ramped ¹H-pulse was applied during the 1 ms contact time to circumvent Hartmann-Hahn mismatches, and a pulse delay of 300 ms was employed. Over 10,000 scans were accumulated for each sample, and line broadenings of 75 Hz were applied. The ¹³C chemical shifts were calibrated relative to tetramethylsilane (0 ppm) with glycine (COOH at 176.08 ppm). The spectra were quantified by integration of the following chemical shift regions as described in Knicker (2011): alkyl C (0–45 ppm); N-alkyl/methoxyl C (45–60 ppm); O-alkyl C (60–110 ppm); aromatic C and phenol C (110–160 ppm); carboxyl/amide C and carbonyl C (160–245 ppm).

Table 2

Characteristics of the 0.1 M KCl extract of biochar-amended composts. Compost (Con) and three different biochar-amended composts (CB1, CB2, CB3) were produced from the same composting feedstock (mixed manures and green plant material). Data provided as means of duplicates (bulk TOC: triplicates) ± standard deviation. Superscript lower case letters indicate significant differences according to an ANOVA and Tukey test.

	Control	CB1	CB2	CB3
DOC [g C kg ⁻¹]	5.3 ± 0.8 ^{ab}	6.0 ± 0.6 ^a	3.6 ± 0.1 ^b	6.1 ± 0.1 ^a
DOC [% TOC]	2.8 ± 0.4	2.6 ± 0.3	1.7 ± 0.1	2.2 ± 0.1
Bulk TOC ¹ [g C kg ⁻¹]	188 ± 4 ^b	227 ± 9 ^{ab}	207 ± 16 ^b	272 ± 7 ^a
Expected TOC ² [g C kg ⁻¹]		232–248	189–201	234–239
pH ³	6.7	6.8	7.0	6.7
pH (cor) ⁴	8.7	8.8	8.8	8.7
SUVA ₂₅₄	5.0 ± 0.5	4.0 ± 0.3	4.6 ± 0.3	4.3 ± 0.1
E ₂ /E ₃	3.7 ± 0.1	3.8 ± 0.0	3.6 ± 0.1	3.7 ± 0.1

¹ Bulk TOC refers to the total organic carbon of the bulk, solid compost.

² Expected TOC an estimate of the TOC of biochar-amended composts based on the TOC of the control and the TOC of the biochars (Table 1).

³ pH was measured prior to EEM and SUVA determination, i.e. after dilution by 100 (control, CB1, CB3) and 60 (CB2), respectively.

⁴ pH (cor) is corrected for the dilution of protons.

The spinning speed of 14 kHz was not sufficient for complete removal of the chemical shift anisotropy, thus spinning side bands occurred at both sides of the parent material at a distance of the spinning speed (here between 275 and 225 ppm and between 0 and 45 ppm). Their intensities were added to that of the parent signal between 160 and 90 ppm.

2.6. Dissolved organic matter extraction for UV-vis, EEM and redox properties

Moist aliquots of Control, CB1, CB2 and CB3 were extracted with 0.1 M KCl for 70 h (1:10) on an overhead shaker at 10 rounds per minute (no removal of biochar) to obtain a dissolved organic matter (DOM) extract. We chose this elongated extraction time of 70 h, as DOM sorbed to biochar was shown to be released only during long extractions (Kammann et al., 2015b). However, this procedure probably resulted in considerable mechanical stress and thus potentially increased the amount of dissolved matter by abrasion, which should be investigated in future studies. The extracts were filtered through a 0.45 µm membrane filter after centrifugation at 5000g for 15 min. Content of organic carbon (dissolved organic carbon – DOC) was determined after acidification with HCl to remove dissolved carbonate on a Vario Cube (Elementar, Hanau, Germany).

2.7. UV-vis absorption

UV-vis absorption spectra were acquired in 1 cm cuvettes in a Multiskan GO (Thermo Fischer Scientific, Waltham, MA USA). $SUVA_{254}$ (specific ultraviolet absorbance at $\lambda = 254$ nm, Weishaar et al., 2003) was calculated as the absorption at $\lambda = 254$ nm divided by the concentration of organic carbon multiplied by 100 to obtain the unit [$L\ mg^{-1}\ m^{-1}$]. The E_2/E_3 ratio was calculated as the ratio of absorbance at $\lambda = 250$ and $\lambda = 365$ nm (De Haan and De Boer, 1987; He et al., 2011).

2.8. Excitation-emission-matrix

Excitation-emission-matrix (EEM) fluorescence spectra of the compost extracts were acquired using a Fluoromax4 (Horiba, Jobin-Yvon, Kyoto, Japan) spectrofluorometer. Extracts were diluted until the absorbance at 254 nm was 0.3. EEM fluorescence spectra were recorded over a range of excitation wavelength (300–500 nm) and emission wavelength (400–600 nm) relevant for natural organic matter (Chen et al., 2003a).

2.9. Redox properties

The redox properties of the compost extracts, i.e. electron accepting (EAC) and donating (EDC) capacities of the compost extracts were determined by Mediated Electrochemical Reduction (MER) and Oxidation (MEO) following established procedures (Aeschbacher et al., 2010; Kluepfel et al., 2014a). In brief, the electrochemical system consists of a glassy carbon cell (Sigradur G, HTW, Germany) as working electrode, a Ag/AgCl as reference electrode (Bioanalytical systems Inc., USA) and a platinum wire (0.5 mm, 99.9%, Sigma-Aldrich Co., USA) attached to a platinum gauze (52 mesh, 99.9%, Sigma-Aldrich Co., USA) as auxiliary electrode. The applied potential was measured against Ag/AgCl electrode but is reported against the Standard Hydrogen Electrode potential ($EH = -0.49$ V in MER and $EH = +0.61$ V in MEO). Electron transfer mediators were used during the measurements to ensure a fast electron transfer between the electrodes and the analyte (Aeschbacher et al., 2010); diquat-dibromide monohydrate (DQ, Sigma-Aldrich Co., USA) was used for MER and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS, Sigma-Aldrich Co., USA) for MEO. EAC and EDC are calculated from the measured reductive and oxidative currents considering normalization to carbon content ($\mu\text{mol e}^-/\text{mmol C}$,

Kluepfel et al., 2014a). The total electron exchange capacity (EEC) is the sum of the individual accepting and donating capacities ($EEC = EAC + EDC$).

2.10. Statistical analyzes

Data obtained from elemental analysis were normalized to the dry matter content of the composts and presented as the average of triplicate extraction \pm standard error if not stated differently. Statistical analysis was conducted in ORIGIN PRO 8 (OriginLab, Northampton, MA, USA). Differences between the different composts were tested with one-way-ANOVAs and Tukey test.

3. Results

3.1. Biochar separation and analysis of elemental composition and nutrient content

We quantified the carbon content and various additional elements of both the bulk composts and extractable fractions. Visually, the composts are brown in color (Fig. 1) and composts amended with wood biochar (CB1, CB3) appear considerably darker than the control. The compost amended with sewage sludge biochar (CB2) was almost the same color as the non-amended control. CB1 and CB3 showed a significantly higher total organic carbon (TOC) than control and CB2 (Table 2), whereas CB2 had only a slightly higher TOC content (not significant) compared to the non-amended control compost. Manual removal of the biochar from biochar-amended composts revealed a biochar content of 11% (w/w dry matter) in CB1, 3% in CB2 and 8% in CB3. Initially, compost feedstock was amended with 4.3% of the respective biochar. The relative biochar content in the different composts most likely increased with composting due to degradation of organic matter to final concentrations of up to 8–10% (Kammann et al., 2016). Particles of B2 biochar were too small to be picked out. All biochars showed a wide distribution of particle sizes (Fig. 1) suggesting that small pieces of biochar remained in the sample and that the manual picking was not complete, but this was especially evident in B2. This means that we most likely underestimated the biochar content following this protocol. Using both experimentally determined and theoretically expected biochar contents, we calculated a range of the expected TOC contents of the biochar-amended composts, based on the TOC of the control and the biochars. The expected TOC content matched the measured TOC in CB1 and CB2, while the measured TOC was higher than the expected TOC values for CB3 (Table 2).

In order to characterize the potentially “least-stable” fraction of the compost OM, we analyzed the dissolved organic matter (DOM) fractions of each compost. DOM of CB2 showed a significantly lower carbon content compared to the control, CB1 and CB3; while all other three composts showed a similar dissolved organic carbon (DOC) content. However, this fraction represented only ~2–3% of TOC. The contribution of DOC to TOC was reduced in all biochar-amended composts, especially in B2 (Table 2).

The presence of biochar barely affected the content of nutrient and trace elements in compost according to both aqua regia (estimation of total content) and CAL (estimation of plant available fraction) extractions (Tables 3–6), except for K and P/PO_4^{3-} . All biochars, especially B1, reduced the total and plant-available contents of K in compost. Biochar-amended composts also showed reduced amounts of plant-available phosphate. All composts meet the criteria on heavy metals in bio-waste fertilizers according to German regulations (“Bioabfallverordnung”, Section 4 BioAbfV).

3.2. Fourier-transformed infrared spectroscopy

The FTIR spectra of the four different composts (Fig. 2) showed very similar peak patterns. The dominant band at 1030 cm^{-1} can be assigned

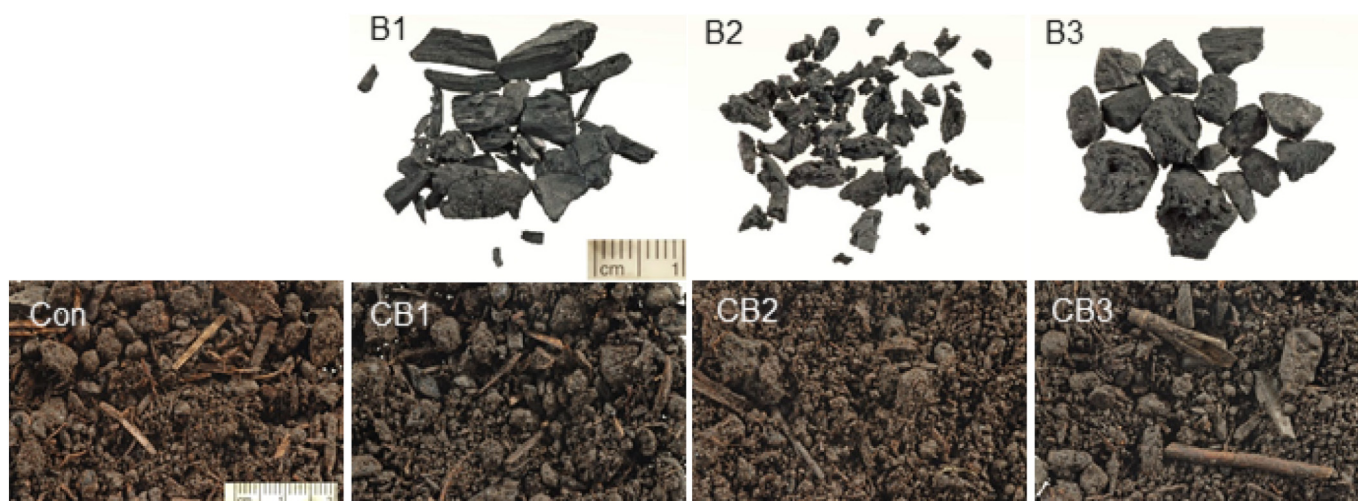


Fig. 1. Photographs of biochars B1, B2, B3, control compost Con and biochar-amended composts CB1, CB2, CB3. All photographs of biochar and composts were taken with exact same light conditions and camera settings to obtain a representative color reproduction. Scale bars in images B1 and CB1 apply to all biochar and compost photos, respectively.

to silica (Si—O stretching, Smidt et al., 2002), as the manure contains a considerable amount of straw, which was used as bedding in the cowshed. Wheat straw has a silica content of ~7% (Pan and Sano, 2005). However, C—O stretching of polysaccharides and carbohydrate ($1000\text{--}1100\text{ cm}^{-1}$, Grube et al., 2006) can also contribute to the bands between 1030 and 1080 cm^{-1} . Various bands in the range of $700\text{--}900\text{ cm}^{-1}$ include absorption by alkanes, alkenes, and alcohols. Two minor bands are present at 2900 cm^{-1} and 2840 cm^{-1} , these match the absorption of carboxylic O—H or aliphatic carbon moieties (Reusch, 1999). They may be interpreted as deriving from lipids, as has previously been reported for biogenic wastes (Grube et al., 2006). A broad band from ~ 3100 to 3600 cm^{-1} can be assigned to O—H stretching of H-bonded OH groups ($3200\text{--}3550\text{ cm}^{-1}$, Reusch, 1999), most likely from carbohydrates. This broad band includes a rather sharp band at 3626 cm^{-1} , which refers to free (as the opposite of H-bonded) O—H stretching (Reusch, 1999), while Smidt et al., 2002 assigned this specifically to silanol (SiO—H stretching, 3620 cm^{-1}).

The bands typically assigned to aromatic carbon species are barely visible. These include 1690 cm^{-1} (aromatic C=C bending and alkene C=C stretching in biochar, de la Rosa et al., 2014), and 1500 cm^{-1} and 1600 cm^{-1} (aromatic C=C stretching, Reusch, 1999). The sharp band for nitrate at 1384 cm^{-1} is consistent with the high nitrate content found in these composts ($\sim 1.0\text{--}1.2\text{ g NO}_3^- \text{N kg}^{-1}$; Hagemann et al., 2017b).

Smidt et al. (2002) proposed the calculation of an intensity ratio of absorbance bands for methylene groups of aliphatics (decrease during composting) and silica (relative increase during composting) as a tool to evaluate the maturation of composts. The absorption ratio $2925\text{ cm}^{-1}/1034\text{ cm}^{-1}$ (band of methylene groups of aliphatics normalized to the band of silica) is lower for the control compost (0.24 ± 0.00) compared CB1 (0.34 ± 0.02), CB2 (0.32 ± 0.05) and CB3 (0.36 ± 0.06). Thus, FTIR suggests that the presence of biochar led to a lower degree of organic matter decomposition in the amended composts.

3.3. ^{13}C nuclear magnetic resonance

The solid-state ^{13}C NMR spectra (Fig. 3, Table 7) of all composts were dominated by signals in the *O*-alkyl C region ($110\text{--}60\text{ ppm}$; ~34% of the total ^{13}C intensity) and the alkyl C region ($45\text{--}0\text{ ppm}$; ~22%). *O*-alkyl C is most likely derived from carbohydrates, alkyl C occurs in lipids and peptides. The signals between 160 and 145 ppm are typical for *O*- and *N*-substituted aryl C and may derive from partially degraded lignin, furfurals or *N*-hetero-aromatic structures (Knicker et al., 2005). Methoxyl C of lignin and *N*-alkyl C cause signals in the chemical shift region between 60 and 45 ppm accounting for $10\text{--}12\%$ of the total ^{13}C intensity. According to the *O*-alkyl/alkyl C ratio (Jindo et al., 2012), the presence of biochars had no major impact on the organic matter degradation of the compost.

^{13}C NMR spectra of CB1 and CB3 showed an increased relative intensity in the chemical shift region of aryl C ($160\text{--}110\text{ ppm}$). Of all the samples, CB1 exhibits the highest aromaticity (~31% of the total ^{13}C intensity), while CB2 does not contain any additional aromatic structures compared to the control. Higher aryl C revealed for CB1 and CB3, are most likely biochar residues that were not removed by manual picking. The absence of additional aromatic C in CB2, may be explained by the fact that due to the low organic carbon content of B2, any residual particles that have not been removed did not contribute to the total C of the samples and had no noticeable impact on the intensity distribution of the ^{13}C NMR spectrum.

3.4. UV-vis absorption

The DOM extracts were analyzed to obtain information on their aromaticity and molecular size. SUVA_{254} was similar for the control and CB2, but was significantly lower for CB1 and CB3 (Table 2). SUVA_{254} is an indicator for the aromaticity of DOC. It was originally used for freshwater samples (Weishaar et al., 2003), but also for composts. The values

Table 3
Elemental composition (major elements $>1\text{ g kg}^{-1}$) of compost (Con) and three different biochar-amended composts (CB1, CB2, CB3) according to ICP-OES after a modified aqua regia (nitrohydrochloric acid) extraction/digestion [g kg^{-1}]. Letters indicate statistical differences (0.05 level) according to one-way ANOVA and Tukey Test.

	Ca	K	Fe	Mg	P	S	Si
Con	$42.7 \pm 0.7\text{ab}$	$19.2 \pm 0.6\text{a}$	$16.4 \pm 0.5\text{b}$	$6.7 \pm 0.1\text{a}$	$3.4 \pm 0.1\text{b}$	$2.4 \pm 0.1\text{b}$	$1.2 \pm 0.0\text{c}$
CB1	$48.8 \pm 3.0\text{a}$	$15.2 \pm 0.2\text{bc}$	$15.6 \pm 0.1\text{bc}$	$6.1 \pm 0.1\text{b}$	$2.6 \pm 0.0\text{c}$	$1.9 \pm 0.0\text{a}$	$1.4 \pm 0.0\text{a}$
CB2	$44.9 \pm 0.9\text{ab}$	$16.5 \pm 0.4\text{c}$	$22.8 \pm 0.2\text{a}$	$6.9 \pm 0.1\text{a}$	$8.5 \pm 0.1\text{a}$	$3.6 \pm 0.1\text{c}$	$1.2 \pm 0.0\text{c}$
CB3	$39.5 \pm 1.2\text{b}$	$17.1 \pm 0.4\text{d}$	$14.9 \pm 0.2\text{c}$	$6.0 \pm 0.2\text{b}$	$3.1 \pm 0.1\text{b}$	$2.2 \pm 0.0\text{b}$	$1.3 \pm 0.0\text{b}$

Table 4

Elemental composition (minor elements <1 g kg⁻¹) of compost (Con) and three different biochar-amended composts (CB1, CB2, CB3) according to ICP-OES after a modified aqua regia (nitrohydrochloric acid) extraction/digestion [mg kg⁻¹]. Cd, Cu were below detection limit. Letters indicate statistical differences (0.05 level) according to one-way ANOVA and Tukey Test.

	Mn	Na ^a	Zn	Ni	Cr	Mo	Pb
Con	368 ± 10ab	113 ± 5a	107 ± 4b	25 ± 1ab	28 ± 1b	24 ± 1a	14 ± 1
CB1	348 ± 3b	90 ± 1b	99 ± 7b	24 ± 1ab	24 ± 0b	18 ± 0b	13 ± 0
CB2	390 ± 1a	124 ± 5a	168 ± 2a	26 ± 0a	36 ± 2a	20 ± 2ab	14 ± 0
CB3	341 ± 8b	91 ± 2b	104 ± 4b	23 ± 0b	23 ± 1b	17 ± 1b	13 ± 0

^a Please note that an aqua regia extraction does not dissolve the compost matrix completely, which might explain the inconsistent results for Na (higher Na⁺ in CAL extract compared to Na in the aqua regia extract).

shown in Table 2 are well within the range of other studies on composts (He et al., 2011; Zhang et al., 2016).

E₂/E₃ (ratio of absorbance at λ = 250 and λ = 365 nm) is suggested as an indicator for the molecular size of DOM. The E₂/E₃ ratio is negatively correlated with molecular size of organic matter (De Haan and De Boer, 1987). E₂/E₃ ratios were not affected by the presence of biochar and were slightly lower than values obtained in previous studies on municipal waste compost or sewage sludge compost (He et al., 2011; Soriano-Disla et al., 2010), i.e. manure compost potentially contains larger molecules in the fraction of dissolved organic matter (DOM).

Because all composts had a high content of nitrate (up to ~1.0–1.2 g NO₃⁻-N kg⁻¹, with control > CB1 = CB3 > CB2, Hagemann et al., 2017b), the tail of the absorption peak of nitrate (222 nm) could have affected the measurements by increasing the absorption at λ = 254 nm and λ = 250 nm (Weishaar et al., 2003).

3.5. EEM fluorescence

Three dimensional fluorescence spectra (EEM – excitation emission matrix) can provide information on composition and C speciation of dissolved OM and have been used to follow organic matter degradation during composting (Chen et al., 2003b; K. Wang et al., 2013). In our study, EEM spectra did not reveal any considerable differences of the DOM extract comparing Con and the biochar-amended composts (Fig. S1).

3.6. Redox properties

Redox properties of the compost extracts were quantified as the electron exchange capacity (EEC, Fig. 4), i.e. the number of electrons that can be accepted or donated when the sample is added to an electrochemical cell with reducing or oxidizing conditions (Kluepfel et al., 2014b). Typically, EEC is reported normalized to the amount of carbon in the sample (DOC, Fig. 4a). However, in this study the method did not reveal any differences between the control and the biochar-amended composts. Thus, the redox reactivity of the DOM was not altered by the addition of biochar to manure compost. However, when EEC is normalized to the respective amount of compost (bulk dry matter, Fig. 4b), we find a lower EEC per g compost for CB2. This is due to the lower DOC content of CB2, as EEC is by definition determined on the dissolved fraction (<0.45 μm) of organic carbon (Kluepfel et al.,

Table 5

CAL-extractable ions of compost (Con) and three different biochar-amended composts (CB1, CB2, CB3) according to IC (PO₄³⁻: colorimetric measurement in flow injection analysis) [g kg⁻¹]. Letters indicate statistical differences (0.05 level) according to one-way ANOVA and Tukey Test.

	K ⁺	Mg ²⁺	Na ⁺	PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻
Con	17 ± 2.6a	3 ± 0	0.9 ± 0.1a	3.8 ± 0.2a	2.7 ± 0.2ab	2.4 ± 0.4a
CB1	10 ± 0.2b	2 ± 0	0.5 ± 0.0b	2.7 ± 0.0b	2.3 ± 0.0b	1.3 ± 0.0b
CB2	12 ± 0.9ab	2 ± 0	0.6 ± 0.0ab	3.4 ± 0.1ac	3.1 ± 0.1a	1.6 ± 0.1ab
CB3	11 ± 1.1ab	2 ± 0	0.5 ± 0.1ab	3.1 ± 0.1bc	2.1 ± 0.2b	1.5 ± 0.2ab

2014b). Electron accepting capacities (EAC) were ~3 times higher than electron donating capacities (EDC).

4. Discussion

This study elucidates on the impact of three different biochars on the quality of manure compost as characterized by elemental composition and carbon speciation. For a holistic assessment of the carbon speciation, we combined analysis of the bulk compost after manual removal of biochar with the analysis of dissolved organic matter.

4.1. Content of nutrients and trace metals

Addition of biochar did not significantly alter both the total and extractable content of nutrients and trace metals in the four composts. However, minor differences between composts were observed for the amount of extractable and potentially bioavailable phosphorous (P) and the potassium (K) content.

The amount of extractable and potentially plant available phosphate was reduced by biochar amendment. However, Kammann et al. (2015a) showed that biochar effectively sorbs nutrients during composting that are only slowly released during extractions. Thus, the 1.5 h extraction time in this study potentially underestimated the content of phosphate in the biochar-amended samples. However, CB1 also showed a significantly reduced total content of P according to the aqua regia extraction, which indicates a loss of P during composting, e.g. by leaching as the compost windrows were exposed to precipitation, although they were covered with a felt. CB2 had a significantly higher total P content due to the high P content of biochar B2 produced from sewage sludge. Sewage sludge is known to have a high content of phosphorus, but also contains organic contaminants as well as relatively high levels of heavy metals (Adam et al., 2009; Smith, 2009). Accordingly, also the sewage sludge biochar did contain considerable amounts of heavy metals (Table 1). However, these metals do not seem to be bioavailable, because CAL extracts of CB2 did not show higher concentrations of heavy metals compared to control, CB1 and CB3. This observation is in agreement with previously reported results from the application of sewage sludge char to soil (Hossain et al., 2010). Previous studies also found that the addition of sewage sludge char promoted plant growth and increased soil P concentrations (Hossain et al., 2010; Sousa and Figueiredo, 2016). In contrast to these findings, CB2 did not have a higher content of extractable P than the control. However, P bioavailability would need to be investigated in more detail by plant growth experiments in either pot or field experiments with the composts used in this study.

The content of potassium decreased for all biochar-amended composts according to both the aqua regia and CAL extractions. This can be explained by a dilution-effect due to the lower content of K in all biochars (Table 1).

4.2. Analysis of bulk compost organic matter

Addition of biochar to compost changes the bulk carbon speciation of the compost, simply because of the distinct carbon speciation of biochar that is enriched in aromatic moieties (Lehmann and Joseph, 2009). Thus, Jindo et al. (2012) highlighted the need for a selective analysis of the non-biochar OM of biochar-amended composts. We attempted this in this study by manual separation of compost and biochar after compost maturation. However, this approach was dependent on the particle size of biochar. Very small biochar particles were hard to identify and pick. Therefore, our results were most likely affected by an undefined amount of small biochar residues in the analyzed compost samples that could not be removed completely. However, to the best of our knowledge, no other techniques have been proposed so far when the biochars were mixed directly with the compost feedstock instead of being physically separated e.g. with mesh bags (Prost et al., 2013).

Table 6
CAL-extractable ions of compost (Con) and three different biochar-amended composts (CB1, CB2, CB3) according to ICP-OES [mg kg^{-1}]. Cd was below detection limit. Letters indicate statistical differences (0.05 level) according to one-way ANOVA and Tukey Test.

	Mn	Fe	Si	Zn	Cu	Cr	Ni
Control	143 ± 14	44 ± 14 ^b	13.5 ± 5.9	12.7 ± 2.9	0.3 ± 0.2	0.2 ± 0.1	0.2 ± 0.0
CB1	142 ± 3	83 ± 5 ^a	15.2 ± 6.5	14.1 ± 0.3	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.0
CB2	150 ± 2	70 ± 1 ^{ab}	14.9 ± 12.2	17.8 ± 0.2	0.0 ± 0.0	0.1 ± 0.0	0.3 ± 0.0
CB3	143 ± 2	64 ± 4 ^{ab}	26.8 ± 3.2	18.8 ± 1.5	0.2 ± 0.0	0.2 ± 0.0	0.2 ± 0.0

After separation, we used FTIR and ^{13}C NMR to characterize the bulk C speciation in the obtained composts. Qualitative comparison of the FTIR spectra did not reveal any considerable differences between the control and the biochar-amended composts. Interestingly, FTIR also did not show the presence of high concentrations of aromatic moieties, which would have been expected when residual biochar particles remained in the analyzed composts. In contrast, NMR revealed up to 30% aryl C among the total ^{13}C signal. Considerable contributions of aryl C to total ^{13}C NMR signal of mature composts was described before (Adani and Spagnol, 2008; Jindo et al., 2012) and result from the relative enrichment of recalcitrant organic matter due to the preferential degradation of labile, non-aromatic organic matter (Lehmann and Kleber, 2015). The differences in aryl C content between the composts correlated with the carbon content of the respective biochars. It is also possible that the fraction of small biochar particles that could not be manually removed increases over time due to physical disintegration of biochar. In the presence of water/moisture, biochar can physically disintegrate into smaller particles in the μm to nm range, potentially without major changes to its carbon speciation, i.e. its aromatic moieties are maintained (Spokas et al., 2014). This process is likely to also happen during composting (water content ~40%, Kammann et al., 2016).

The FTIR absorbance ratio $2925\text{ cm}^{-1}/1034\text{ cm}^{-1}$ (Smidt et al., 2002) suggested a lower degree of decomposition of the compost organic matter for all biochar-amended composts compared to the control compost. However, FTIR has to be considered as a rather qualitative method and ^{13}C NMR could not confirm any differences in the *O*-alkyl/alkyl C ratio, which has been suggested as an indicator for organic matter degradation (Jindo et al., 2012). Thus, the differences in the FTIR absorbance ratio $2925\text{ cm}^{-1}/1034\text{ cm}^{-1}$ should be interpreted with care. In summary, both FTIR and NMR did not reveal any considerable biochar-induced differences in the quality of the OM or changes in ^{13}C -speciation.

Previous studies concluded that biochar amendment to compost feedstock could enhance the degradation of organic matter and, with that led to a more stable final product. However, these studies often produced composts in windrows that were aerated less frequently, e.g. weekly (Sanchez-Garcia et al., 2015) or twice a month (Jindo et al., 2012). Thus, these composts were not produced under conditions that promote aerobic carbon degradation. Under anoxic conditions, biochar might have supported organic matter degradation by serving as alternative electron acceptor for heterotrophic microorganisms (Kluepfel et al., 2014a). Under conditions in which composts were frequently aerated

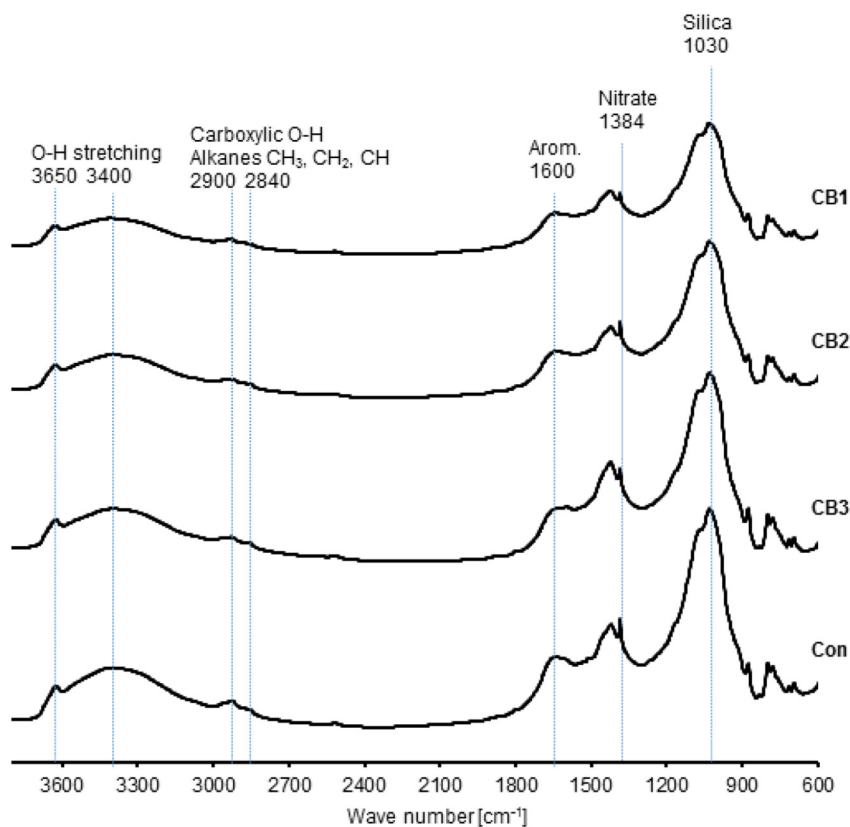


Fig. 2. Fourier-transformed infra-red (FTIR) absorption spectra of compost (Con) and three different biochar-amended composts (CB1, CB2, CB3) after manual removal of biochar particles visible to the naked eye. All composts were produced from the same composting feedstock (mixed manures and green plant material). Spectra represent the average of measurements on triplicate pellets of each sample. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

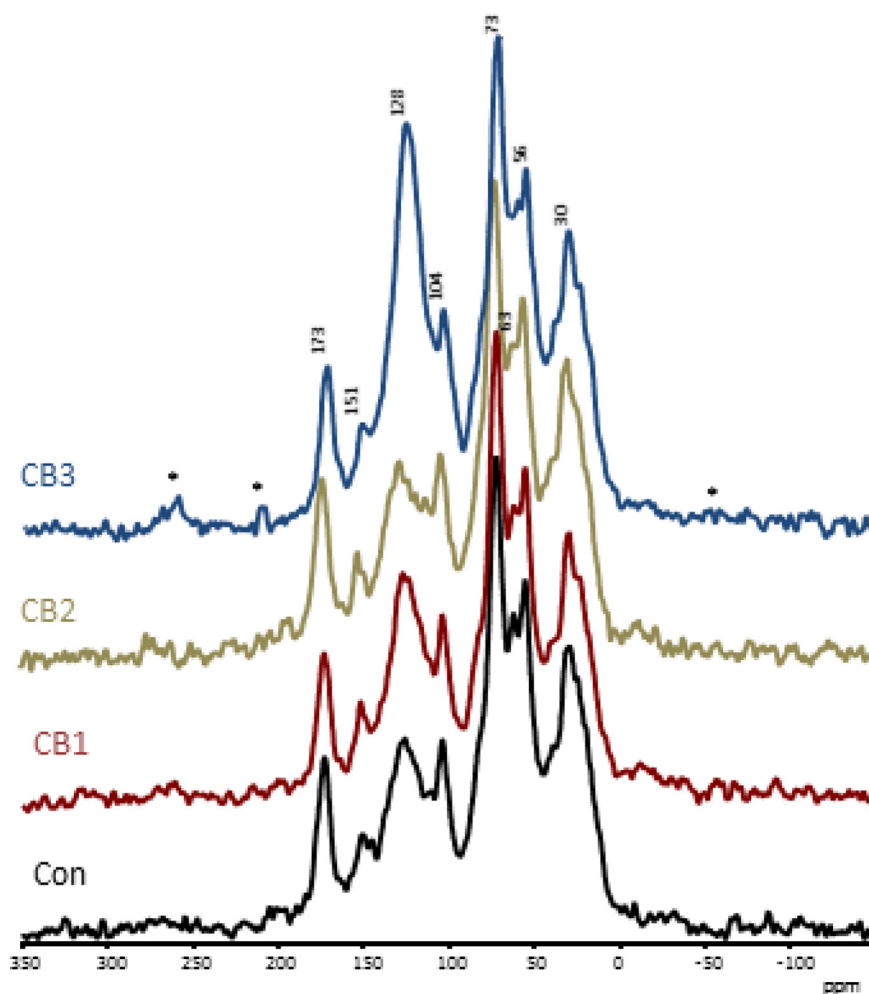


Fig. 3. Solid-state ^{13}C NMR spectra of compost (Con) and three different biochar-amended composts (CB1, CB2, CB3) after manual removal of biochar particles visible to the naked eye.

during the composting process to achieve a high quality product (Kammann et al., 2016), such as in this study, the effect of biochar as an alternative terminal electron acceptor that promotes microbial organic matter degradation might not be that pronounced.

Although biochar addition to composts did not appear to affect the quality of the organic matter in the compost, it increased the total organic carbon content of the compost. This effect can be mostly explained by high carbon content of the biochars applied, as the calculated “expected TOC” matched with the measured values. Only CB3 showed a higher TOC than expected, which might indicate an additional preservation of C during composting. However, this had to be interpreted with care. In order to verify this observation, a holistic mass balance of initial compost feedstock and resulting mature compost would have been required. However, this was not possible in this large scale composting experiment.

4.3. Analysis of DOM as the labile fraction of OM

Overall, the DOC contents of the composts quantified in this study were within the range of previously reported DOC values for composts published by Khan et al. (2016) (3 h extraction with deionized water), but were about 5 times lower when compared to DOC values reported by Jindo et al. (2012). However, Jindo et al. performed an alkali extraction that is likely to extract more DOC than 0.1 M KCl. CB2 had a lower absolute DOC content than the control, while CB1 and CB3 did not impact DOC concentrations. In contrast, Khan et al. (2016) found reduced DOC contents in composts amended with different biochars produced from macadamia nutshell, hardwood shavings, and chicken litter.

Overall, biochar addition reduced the relative contribution of DOC to total compost TOC in CB2 and CB3, but no differences to Con were observed for CB1. Thus, in comparison of the four different compost

Table 7

^{13}C intensity distribution according to NMR on compost (Con) and biochar-amended composts (CB1, CB2, CB3) after manual removal of biochar particles visible to the naked eye.

	Chemical shift (ppm)						Sum	Intensity ratios Alkyl C/O-alkyl
	245–185	185–160	160–110	110–60	60–45	45–0		
	Carboxyl-C	C=O	Aryl-C	O-alkyl	N-alkyl/methoxyl C	Alkyl-C		
Con	2%	7%	23%	34%	12%	23%	100%	0.66
CB1	1%	5%	31%	32%	11%	20%	100%	0.62
CB2	2%	7%	22%	35%	12%	23%	100%	0.65
CB3	1%	6%	26%	34%	12%	22%	100%	0.63

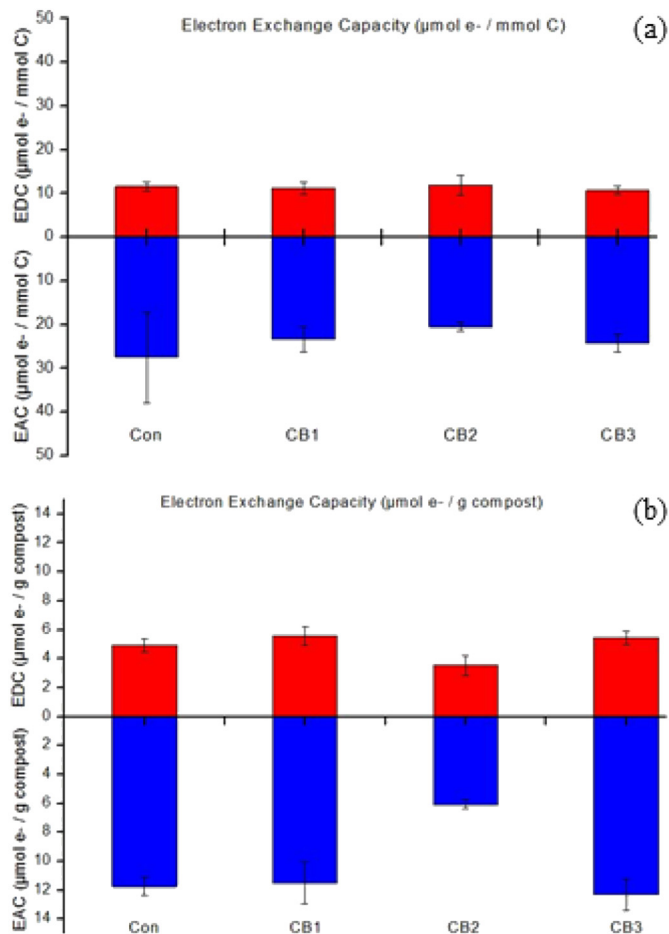


Fig. 4. Electron exchange capacity (EEC) as electron accepting (blue) and donating (red) capacity (EAC/EDC) of 0.1 M KCl extracts of biochar-amended composts CB1, CB2, CB3 and a non-amended control compost Con. (a) EECs were normalized to the dissolved carbon content (DOC) of the samples. (b) EECs were normalized to the mass of the original compost. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

samples analyzed in this study, less OM was lost through DOC leaching in CB2 and CB3 compared the non-amended control.

DOM of biochar-amended composts exhibited a relatively low $SUVA_{254}$ value, indicative of a lower contribution of aromatic moieties to DOM. This effect has been reported before (Zhang et al., 2016). However, biochar addition to compost barely affected the $SUVA_{254}$ value of compost DOM in the study of Zhang et al. (2014). Lower aromaticity in DOM could be indicative of a lower recalcitrance of this OM fraction, however, it could also mean that aromatic moieties were retained in the non-DOM fraction, e.g. through sorption onto biochar surfaces.

4.4. Future research

The present study highlighted the need for more research focusing on the molecular scale mechanisms of biochar organic matter interactions. For example:

The interplay of biochar addition and frequency of compost aeration should be investigated in a two factorial experiment. This should include a frequent aeration scheme as applied in the present study as well as a weekly or bi-weekly scheme, both with and without biochar addition. Similar information could be obtained in a composting study that applies forced aeration with different air flow rates. In contrast to mechanical aeration, forced aeration does not break up aggregates and does not homogenize moisture.

Despite some first studies on agronomic, chemical and spectromicroscopic evaluation of co-composted biochar (e.g. Kammann et al., 2015b; Khan et al., 2016; Wiedner et al., 2015), the effect of co-composting on biochar microstructure, carbon speciation and reactivity is widely unknown and should be researched in more detail e.g. as performed for soil-aged biochar (Joseph et al., 2010). If biochar-amended compost is to be used as an organic fertilizer in soil, the compost OM will degrade within several years, while the co-composted biochar might remain in the soil for centuries (Kuzyakov et al., 2014).

Although these questions specifically address issues of composting, they are also relevant for a more holistic understanding of the role and functioning of biochar and the ubiquitous natural pyrogenic carbon found in soil (Reisser et al., 2016), with respect to organic matter degradation in soil and the environmental relevance of biochar redox activity.

5. Conclusion

This study assessed the effect of biochar on the quality and quantity of compost OM after co-composting of biochar with manure. In contrast to previous studies, we could not identify major differences in C speciation in compost organic matter. We explained this by our intensive compost management strategy that included frequent (up to daily) aeration to create and maintain oxic conditions in order to achieve fully aerobic decomposition of labile organic matter and to obtain a high quality compost that can be applied as a beneficial fertilizer and soil amendment. Under these specific conditions biochar seemed to not further improve organic matter degradation, while the presence of biochar in less frequently aerated composts, as has been previously reported, can facilitate the oxidative degradation of organic matter. Nonetheless, biochar could be a valuable composting additive, even in intensively managed compost, with the potential to increase nutrient retention, water content, and total non-biochar organic carbon content in the mature compost making biochar-amended compost an attractive soil amendment.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2017.08.161>.

Acknowledgements

We thank Ellen Struve, Katharina Mayer and Patricia Riede for their support in the lab, Gerald Buck and Klaus Nickel for freeze-drying, Annette Flicker and Marcus Nowak for access to the FTIR and their support during the measurements, Sabine Flaiz and Peter Kühn for access to the microwave, for their support during aqua regia extractions and for ICP-OES measurements and Wolfgang Gerber for photographs. NH was financially supported by a BMBF PhD scholarship provided by the Rosa Luxemburg Foundation, Berlin, Germany. The composts were produced during a “Short Term Scientific Mission” (STSM) granted to NH by the EU COST Action TD1107 “Biochar as option for sustainable resource management”. We thank Kevin Friedrich and Pyreg GmbH, Dörth, Germany for providing biochar B2. JMR thanks The Spanish Ministry of Economy and Competitiveness (MINECO) for his “Ramón y Cajal” post-doctoral contract (RYC-2014-16338). MINECO is also thanked for the financial support of the projects CGL2015-64811-P and CGL2016-76498-R, which funded the NMR analyses. We thank Cindy Lockwood for valuable comments on the manuscript.

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