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ORIGINAL PAPER

Carbon sequestration potential of hydrothermal carbonization char (hydrochar) in two contrasting soils; results of a 1-year field study

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Abstract Soil amendment with hydrochar produced by hydrothermal carbonization of biomass is suggested as a simple, cheap, and effective method for increasing soil C. We traced C derived from corn silage hydrochar ($\delta^{13}C$ of −13‰) added to "coarse" and "fine" textured soils ($\delta^{13}C$ of −27‰ for native soil C (SOC)) over two cropping seasons. Respiration rates increased in both soils ($p<0.001$) following hydrochar addition, and most of this extra respiration was derived from hydrochar C. Dissolved losses accounted for ~5 % of added hydrochar C ($p<0.001$). After 1 year, 33±8 % of the added hydrochar C was lost from both soils. Decomposition rates for the roughly two thirds of hydrochar that remained were very low, with half-life for less estimated at 19 years. In addition, hydrochar-amended soils preserved 15±4 % more native SOC compared to controls (negative priming). Hydrochar negatively affected plant height ($p<0.01$) and biomass ($p<0.05$) in the first but not the second crop grown on both soils. Our results confirm previous laboratory studies showing that initially, hydrochar decomposes rapidly and limits plant growth. However, the negative priming effect and persistence of added hydrochar C after 1 year highlight its soil C sequestration potential, at least on decadal timescales.

Keywords Hydrochar · Plant growth · Soil respiration · Soil leachate · Carbon isotopes · Physical soil parameters

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Introduction

Conversion of biomass into biochar and its application to soil is an emerging mitigation technique that has received much recent interest. Several methods are known for biochar production and they differ in factors such as the type and pretreatment of biomass or feedstock used and the temperature, pressure, and other conditions during conversion. Thus, chars produced by different methods also vary significantly in chemical and physical characteristics and in their potential for C sequestration (Malghani et al. 2013). Biochar produced by dry pyrolysis (pyrochar) is the most documented material used for carbon sequestration. Pyrochar can persist in soil for decades or longer (Lehmann 2007) and also affects other soil properties (Sohi et al. 2009) including bulk density (Abel et al. 2013), soil aeration, water retention capacity (Abel et al. 2013), pH (Rillig et al. 2010), nutrient availability (Farrell et al. 2014; Prayogo et al. 2014), and microbial community composition (Khodadad et al. 2011; Song et al. 2014). It has been estimated that each ton of dry biomass pyrolysed and applied to soil could offset up to 800–900 kg of CO_2 emissions (Roberts et al. 2010).

Pyrolysis techniques are derived from methods of conventional charcoal production (Ogawa and Okimori 2010) and generally require dry biomass. The use of the moist biomass in these processes wastes a large portion of the added energy to evaporate water (Antal and Grønli 2003). Hydrothermal carbonization (HTC) has recently been suggested as a simple, cheap, and effective way of increasing the C content of biomass (Titirici et al. 2007). This method of carbonization is of particular interest for wet biomass that is produced in large quantities and is not suitable for other carbonization methods, such as sewage sludge, industrial bio wastes, and green household wastes (Ramke et al. 2009; Berge et al. 2011; Liu et al. 2013; Oliveira et al. 2013). HTC uses low temperatures that produce very low gas yields, with the majority of the biomass either converted into brown coal or dissolved in liquid (Ramke et al. 2009). The overall end product yield varies depending on the treatment time, feedstock type, and other parameters like process temperature, pressure, and the presence of catalysts (Hu et al. 2010; Cao et al. 2011).

HTC is a well-documented process in terms of production conditions and the end-product characteristics (Hoekman et al. 2011) but very few studies exist for evaluating its proposed use as a tool for C sequestration in soils. The final product is a "slurry-like" material that consists of solid products (suspended brown coal) of different sizes, shapes, and surface functional groups (Libra et al. 2011). It has been suggested that this material may have low potential for C sequestration because a large fraction of the C remains in dissolved form and is subject to rapid decomposition (Libra et al. 2011; Malghani et al. 2013). Compared to pyrochar produced at high temperatures, hydrochar has higher H/C and O/C ratios making it more susceptible to microbial degradation (Schimmelpfennig and Glaser 2012) and it may undergo microbial transformation before it can act as long-term storage for the C content.

Because sequestration timescales may depend on interactions between dissolved or microbially transformed C with soil mineral surfaces, soil properties, particularly texture, may play an important role in the fate of hydrochar C amendments. In this context, a previous laboratory incubation study found no impact of soil type on hydrochar mineralization when incubated at 1 % mass HTC/mass soil ratios (Malghani et al. 2013). To date, studies on the potential of hydrochar for C sequestration and the role of soil type are limited to either lab-based soil incubations or greenhouse-based mesocosms. The objective of this study was to estimate the C sequestration potential of hydrochar and its impact on plant growth in arable field settings. Hydrochar C derived from C4 plants (here corn silage) was added to lysimeter soils with soil organic matter produced only from C3 plants. Hence, its fate could be monitored using C-stable isotope-measured CO_2, dissolved organic C (DOC) in soil leachate, and bulk soil C (SOC).

Materials and methods

Hydrochar characteristics

Hydrochar produced from corn silage was obtained commercially from Carbon Solutions Ltd., Kleinmachnow, Germany. It was produced in two stages, one at 230 °C and the second at 180 °C (Naisse et al. 2014). Hydrochar was applied as it was delivered, in a slurry containing ~10 % dry matter, with a considerable fraction of the total C in dissolved form (2.85±0.06 g C/L). The slurry was acidic with a pH of 4.15, measured directly in the slurry after thorough shaking. The dry matter of hydrochar had 51 % C, 1.9 % N, 5.7 % H, and 19 % O. The O/C ratio of 0.28 suggests the suitability of this hydrochar for potential C sequestration (Schimmelpfennig and Glaser 2012). Details of hydrochar characteristics have been described elsewhere by Malghani et al. (2013). Our choice of corn silage as a feedstock was dictated by the need to obtain hydrochar with C4 isotopic signals to allow us for tracking hydrochar C.

Soil characteristics and experimental setup

The experiment used a field lysimeter experimental site maintained at the Max Planck Institute for Biogeochemistry, Jena, Germany. In 2002, two soils with contrasting texture, coarse, and fine, were removed from the field and placed in separate 48-m^2 plots. Over the subsequent decade, these plots experienced free succession of local C3 plants. Initial $\delta^{13}C$ values of −27.8 and −26.7‰ (V-PDB), respectively (Table 1), indicated no prior influence of C4-C. While these soils are not strictly field agricultural soils, they allowed continuous monitoring and installation of lysimeters for tracking dissolved C losses. The average annual temperature at the site was 9.87 °C and mean precipitation was 580 mm during the experimental period in year 2011–2012.

Each large plot was sub-divided into six smaller plots (3.45 m^2), and two rings (D=30 cm, H=15 cm) were installed within each small plot, for a total of 24 rings. To collect soil leachate, suction plates (D=9 cm) were installed in the center of each ring at a depth of 15 cm. In addition, sensors were also installed at 10-cm depth in each ring for continuous measurement of soil moisture (% *v*/*v*, ML3x probes, DeltaT, Campbell scientific) and temperature (NTC resistance thermometer, Campbell scientific). For soil respiration measurement, two small collars (D=7 cm, H=9 cm) were inserted permanently into the soil inside each large ring (the total of 48), the bottom of one of two respiration collars was sealed with mesh (25 μm) to prevent root ingrowth. Respiration rates from this root exclusion collar were assumed to include predominantly heterotrophic respiration while the paired collar with no mesh was assumed to measure both autotrophic and heterotrophic component (Moyano et al. 2008).

Table 1 General characteristics of two agricultural soils

Soil	SOC	TN	SIC	DOC	Microbial biomass	$\delta^{13}C$ (SOC)	pH	Soil texture (%)		
	%	%	%	(μg C g^{-1} soil)	(μg C g^{-1}soil)	‰VPDB		Clay	Silt	Sand
Coarse	4.30	0.27	0.03	26.8	65.6	−27.8	6.09	6	44	50
Fine	2.06	0.22	0.74	30.4	106.3	−26.7	7.89	16	75	9

Mean (n=6). All characters were analyzed in samples taken before starting the experiment

SOC soil organic C, *TN* total N, *SIC* soil inorganic C

For the hydrochar treatment, soil within each large ring (12 rings in total) was excavated up to the depth of the suction plate (15 cm) and mixed thoroughly with hydrochar. The amount of hydrochar added to the soil was calculated corresponding to a C addition of approximately 20±2 and 30±2 % of the initial SOC content of coarse and fine soils, respectively. After thorough mixing, soil samples were filled back into respective places. For the control treatment, soil was excavated from the remaining 12 large rings and mixed with water but no HTC was added. There were six replicates of each treatment in each soil type.

Plant growth and plant biomass characteristics

Three replicates of each treatment were planted either with wheat (*Triticum aestivum*) or colza (*Brassica rapa*) according to typical German cropping practices. Identical seed numbers, determined according to local agricultural practice, were used on each plot, including in the large rings. Seeds were sown relatively late in the first season, with the result that the 2011 growing seasons was shorter than the 2012 season. In 2011, crops were sown 1 week after hydrochar application and the first harvest took place in the first week of October. In the next cropping season, crops were rotated as they would be in agricultural practice, i.e., treatments planted with wheat in first season were sown with colza and vice versa. The harvest of the winter crops occurred in the first week of July 2012. During each harvest, we measured plant height and total biomass after drying at 70 °C for each treatment ring.

Soil analysis

Soil samples were analyzed three times, at the start of the experiment (June 2011, right after the establishment of treatments), after harvesting the first crop (October 2011), and at the end of the experiment (July 2012). Each soil sample was homogenized and divided into two aliquots. The first was used to determine extractable DOC and microbial biomass, while the second was air-dried at 40 °C and used for further soil analysis. Total soil C content was analyzed on ball-milled subsamples (time 4 min) by an elemental analyzer at 1150 °C (vario Max CN, Elementar Analysensysteme GmbH, Hanau, Germany). Organic C concentration was determined by calculating the difference between elemental analyses of the total C concentration and soil inorganic C concentration (Steinbeiss et al. 2008). Extractable dissolved organic C (DOC) and soil microbial biomass was determined by extraction using 0.05 M K_2SO_4 without and with chloroform fumigation (Brookers et al. 2007; Karsten et al. 2007) and analyzed with a "high TOC" analyzer (Elementar Analysensysteme GmbH, Hanau, Germany).

The ^{13}C content of SOC was measured by coupling an elemental analyzer (EA 1100, CE Instruments, Milano, Italy) to an isotope ratio mass spectrometer (Delta^{Plus}XL, Thermo Finnigan MAT Bremen, Germany). Values were reported as $\delta^{13}C$ in per mill (‰) calibrated relative to the VPDB reference standard using NBS19 (Werner and Brand 2001) and represent repeated measurements with a standard deviation of less than 0.3‰. To avoid inorganic C impact on $\delta^{13}C$ values, samples were pre-treated with week acid, 6 % H_2SO_3 (Bisutti et al. 2004; Steinbeiss et al. 2009). This was required particular for the fine soil samples, which were derived from soils with a limestone parent material and contained small amounts of calcium carbonate as a result.

Soil leachate collection and analysis

Soil leachate was collected using borosilicate glass suction plates (thickness 9 mm, diameter 90 mm, pore size 1 μm; UMS, Germany) at 15-cm depth in all treatments. A starting vacuum of 200 mbar was applied to suck soil solution into 2-L glass flasks. Sampling was carried out biweekly throughout the experimental period June 2011 to July 2012; however, during dry periods soil moisture was too low for collecting soil leachate.

After volume measurement, the leachate samples were divided into two aliquots. One aliquot was used to measure DOC and dissolved inorganic C (DIC) and the other was freeze dried, after acid treatment to remove DIC, and subsequently combusted for $\delta^{13}C$ measurement (Delta^{Plus}XL, Thermo Finnigan MAT Bremen, Germany). When only a small volume of soil leachate was collected, only C concentrations were measured.

Gas sampling and analysis

Soil respiration was measured using a closed chamber technique (LiCOR 6400–09, Li-COR, Nebraska, USA), and all measurements took place during the day, between 9 and 12 am, except in the winter season, when measurements took all day due to very low respiration rates. To collect gas samples for determining $\delta^{13}C$ of respired CO_2, a closed chamber equipped with a fan to mix air was placed on the small collars installed within each treatment. Three minutes after placing the chamber, 50 mL of headspace air was removed and used to flush and fill a 12-mL glass vial that was previously flushed with N_2 to remove any CO_2. Background air samples were taken at 2-m height above the soil. Carbon dioxide concentrations and $\delta^{13}C$ values of air in the vials were determined on a Gasbench II (Finnigan MAT, Bremen, Germany), equipped with a CTC PAL-80 auto sampler (CTC Analytics AG, Zwingen, Switzerland) that was connected to a continuous-flow isotope ratio mass spectrometer (IRMS, Finnigan MAT DeltaPlusXL, Bremen, Germany). This method was highly precise with a standard variation of 0.05‰ (Knohl et al. 2004).

Fluxes and the $\delta^{13}C$ values of respired CO_2 were measured once per week initially and later fortnightly except for the three winter months (Dec 2011, Jan, and Feb 2012) when fluxes were measured monthly. In winter, chambers were also allowed to accumulate CO_2 prior to sampling in order to achieve a minimum difference of 20 μmol mol^{-1} (CO_2) between chamber air and background. Normally, the difference between chamber air and background was at least 70 μmol mol^{-1}, to minimize errors with variability in the background for calculating the isotopic signature of soil respiration-derived CO_2.

In the fine-textured soil, the presence of small amounts of calcium carbonate (from parent material limestone) limited our ability to interpret ^{13}C of respired CO_2; therefore, data from only the coarse textured soil are presented.

Calculations and statistics

To calculate $\delta\ ^{13}CO_2$ value of respired C from each treatment, the equation from Miller and Tans (2003) was applied as follows:

$$(\delta_{obs} * C_{obs}) - (\delta_{bg} * C_{bg}) = \delta_t (C_{obs} - C_{bg}) \quad (1)$$

Where, C and δ refers to CO_2 and $\delta^{13}C$, respectively, and subscripts obs, bg, and *t* refer to observed, background, and treatment values.

To determine the contribution of hydrochar to respired C (coarse-textured soil only), a two-component mixing model was used (Balesdent and Mariotti 1996; Gleixner et al. 2002). In this experiment, SOC has a $\delta^{13}C$ signature reflecting C3 plants, while hydrochar has a signature reflecting the C4 origin of corn used in production.

$$\delta^{13}\ C_{(mxiture)} = (f_{char} \times \delta^{13}C_{char}) + (f_{soc} \times \delta^{13}C_{soc}) \quad (2)$$
$$\text{since}: f_{soc} + f_{char} = 1$$

The fraction of hydrochar in respired C (f_{char}) was calculated as:

$$f_{char} = (\delta^{13}CO_{2\,treatment} - \delta^{13}CO_{2\,control}) / (\delta^{13}CO_{2\,char} - \delta^{13}CO_{2\,control}) \quad (3)$$

where,$\delta^{13}CO_{2\ control}$=unamended and $\delta^{13}CO_{2\ treatment}$=amended hydrochar.

To derive the $\delta^{13}CO_{2char}$ value, hydrochar was incubated at room temperature and the $\delta^{13}C$ value of evolved CO_2 was measured. This $\delta^{13}C$ value equaled that of the initial char to ±1‰ (Malghani et al. 2013). We implicitly assume that any fractionation associated with mineralization of SOC was the same with and without hydrochar amendment (Steinbeiss et al. 2009).

We used a two-pool decomposition model to simulate the loss of hydrochar C in soil respiration and the amount of hydrochar C remaining in soil (Johnson et al. 2007),

$$C_t = C_a(e^{-k_a t}) + C_b(e^{-k_b t}) \quad (4)$$

where C_t is mass of hydrochar remaining in soil at any given time (*t*), C_a and C_b represent the mass of C in fast and slow pool, respectively, and k_a and k_b represent the (first order) decomposition rates (day^{-1}) of fast and slow C fractions. The half-life for loss of hydrochar in fast and slow pools is thus:

$$t_{1/2} = \frac{ln(2)}{k_i} \quad (5)$$

To determine the relative amount of C derived from hydrochar in soil leachate and bulk soil C, we used a two-pool mixing model:

$$(f_{char}) = \frac{\delta^{13}C_{DOC\,treatment} - \delta^{13}C_{DOC\,control}}{\delta^{13}C_{char} - \delta^{13}C_{DOC\,control}} \quad (6)$$

The fraction of hydrochar C in soil leachate determined at different intervals was multiplied by the mass of DOC in leachate for the respective sampling date, then summed to obtain the cumulative amount of hydrochar C loss via leaching through time. For missing data points where the collected volume was too low to measure $\delta^{13}C$ values of DOC, values were estimated by interpolating linearly between sampling events.

The contribution of hydrochar to bulk soil C was measured twice, once after the first harvest (October 2011) and again at

the end of the experiment (July 2012). Comparing these two time points allowed us to calculate the total hydrochar C mineralized during the experiment:

$$f\text{char}_{\text{min}} = f\text{char}_{\text{start(June2011)}} - f\text{char}_{\text{end(Oct 2011 or July 2012)}} \quad (7)$$

The impact of hydrochar addition on native soil C (priming effect; PE) was also determined by comparing the SOC contribution to overall respiration in the treatment compared to the control. The PE was calculated only in coarse soil (see above) using the following equation:

$$\text{PE} = f_{\text{soc}} * \text{CO}_{2(\text{amended})} - \text{CO}_{2(\text{control})} \quad (8)$$

All data were expressed as means of the six replicates±the standard error. Significance of differences among/between treatments was determined using one-way analysis of variance (ANOVA). This was followed by a post hoc test (Tukey, α=0.05). All statistical analyses were carried out using SPSS (PASW statistics-18) and graphs were prepared in SigmaPlot (Version 12.5) or MS-Excel 2010.

Results

Respiration and leaching losses of hydrochar C

Rates of soil respiration in control treatments were slightly lower in fine soils, averaging 1.72 g C m^{-2} day^{-1} compared to 2.26 g C m^{-2} day^{-1} in coarse soils (Fig. 1). Soil respiration rates increased immediately after HTC amendment and remained significantly (p<0.05) higher for the next 12 weeks in the coarse soil (p<0.05; Fig. 1), though less consistently in the fine soil (Fig. 1a). After these initial 12 weeks, HTC-amended and control soils emitted CO_2 at the same rate.

The CO_2 respired from hydrochar-amended coarse soil remained significantly (p<0.01) enriched in ^{13}C from the start to end of the experiment (June 2011 to July 2012) except during the month of May 2012 (Fig. 2). The $\delta^{13}CO_2$ values of respired C in the hydrochar treatment reached close to those of the hydrochar C during the first month of experiment and then gradually decreased, although remaining significantly higher than coarse control treatment.

In the coarse soil, the main pathway for hydrochar C loss was soil respiration as the proportion of hydrochar C calculated in cumulative CO_2 emissions was equal to 37±2 % of the initial hydrochar- C concentrations (Fig. 3a). A relatively small proportion (~5 %) of hydrochar C was lost in soil leachate (Fig. 3b). As noted previously, the presence of small amounts of calcium carbonate meant we could not use the isotopes for respiration partitioning, but we were able to estimate the amount leached from the soil in DOC (~3.5 %) (Fig. 3b).

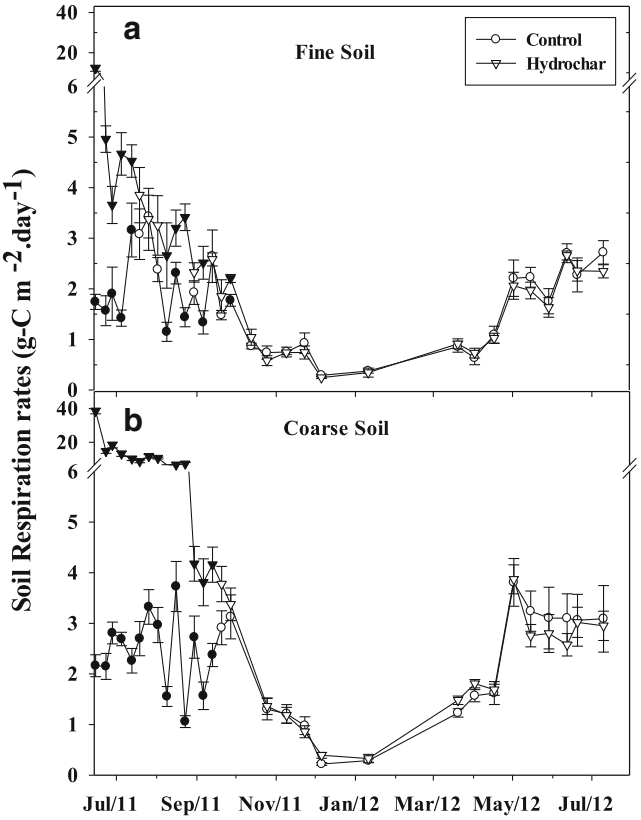

Fig. 1 Heterotrophic soil respiration rates measured using the closed chamber technique during 1 year of field experiment. **a** Fine soil. **b** Coarse soil. *Points* are the means and *vertical bars* represent standard error (n=6). *Filled symbols* indicate statistical significance (Tukey, α=0.05)

The double exponential decay for hydrochar CO_2 loss in the coarse textured soil (Eq. 4) suggested that almost 31 % of hydrochar C belonged to an easily degradable pool. The half-lives of fast and passive C pools were estimated to be 0.08 and 19 years, respectively (Fig. 4).

Priming effects of hydrochar on native soil C

The two phases of hydrochar decomposition also had differing effects on the rates of native soil C mineralization. In the coarse soil, hydrochar C was responsible for nearly 100 % of the respired CO_2 immediately following hydrochar amendment. During the subsequent 3–4 months, when respiration in amended soils was much greater than in controls and declined rapidly over time, we observed positive priming, i.e., higher CO_2 fluxes derived from native soil C in the amended soil compared to the control. During the second phase of hydrochar mineralization, when respiration in control and amended soils was not significantly different (Fig. 1), the CO_2 emitted from the coarse soil more native soil C than the hydrochar treatment (negative priming) (Fig. 2b).

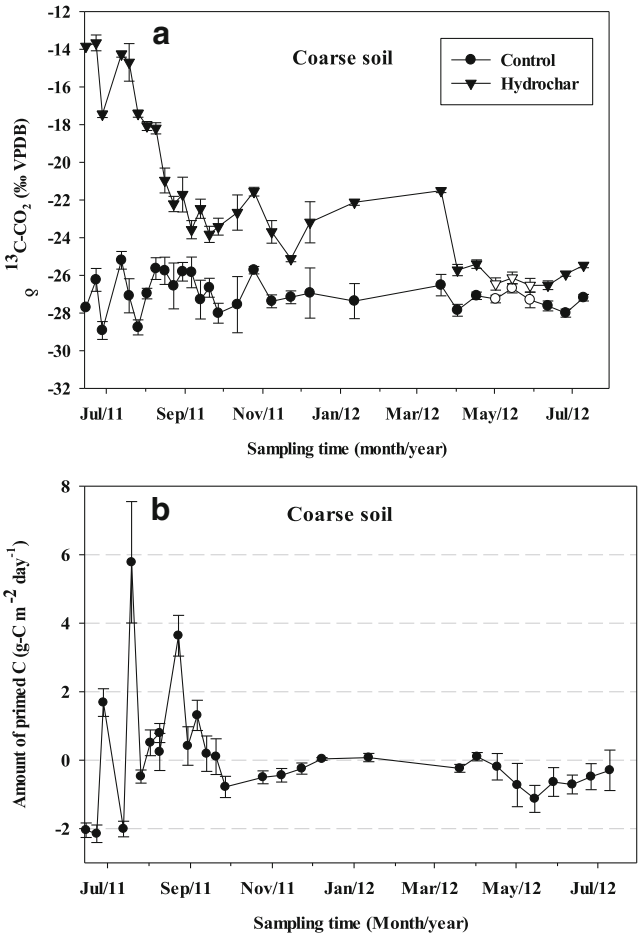

Fig. 2 **a** Stable isotope signature ($\delta^{13}CO_2$) of respired C from the coarse soil calculated based on the Miller and Tans (2003) model. *Unfilled symbols* represent statistical insignificance (Tukey, α=.05). **b** Amount of native SOC emitted or preserved due to positive or negative priming of hydrochar in coarse soil. *Vertical bars* represent standard error (n=6)

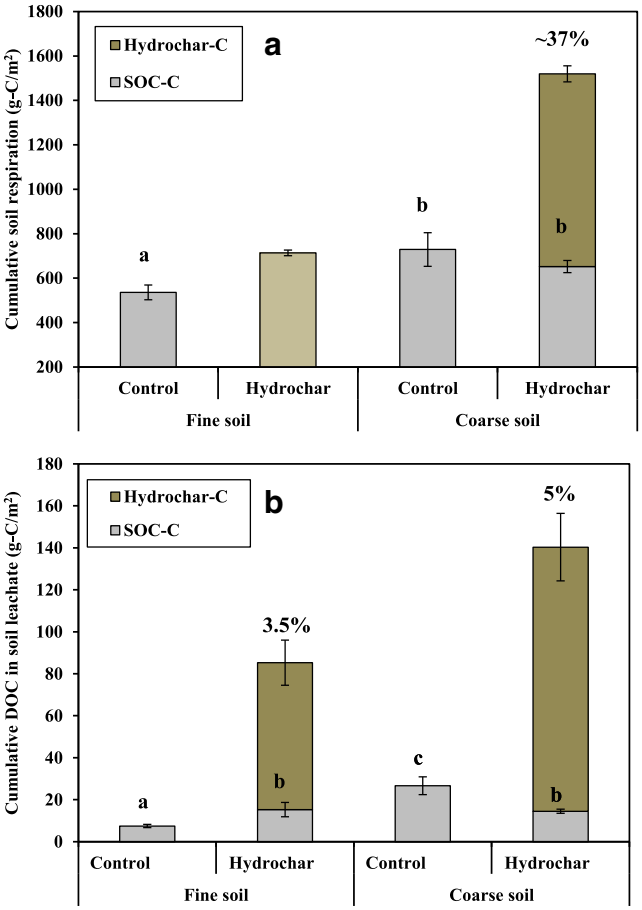

Fig. 3 Cumulative amount of C loss via **a** soil respiration and **b** DOC in soil leachate. A moving average of ($\delta^{13}C$) for two bracketing measurement dates was used to fill in for missing values for DOC. To fill in between measurement dates, for cumulative soil respiration rates, we extrapolated values linearly between bracketing measurement dates. The relative contributions of hydrochar and native soil **c** were calculated using a two-pool C model. *Different letters* represent statistical significance in the amount of soil derived **c** among treatments (Tukey α=0.05)

The net effect of hydrochar amendment on native soil C was calculated using the isotopic mass balance approach for bulk soil C, which showed overall that less native soil C was lost in hydrochar-amended soils than in controls. The SOC (native) content of hydrochar treatments was considerably higher than control treatments in both soil types (Table 2) but this impact was statistically significant only in fine soil (Table 2).

Hydrochar mass balance based on SOM in coarse and fine soils

We calculated the hydrochar C remaining in the soil using the isotopic mass balance of bulk soil at different time points in the experiment (Fig. 4). Hydrochar C decreased rapidly during the first 60 days of the experiment, then at a much slower rate over the following 340 days (Fig. 4). Initially, hydrochar C was lost rapidly, with 21±8 % lost in coarse and 14±3 % in fine soils between 15 June 2011 and 4 Oct. 2011 (Fig. 5). Subsequent loss rates slowed in both soils (Fig. 5). Variability among replicates was large in both types of soils, with no significant difference in overall loss between fine- and coarse-textured soils. A range of 48–77 % of the originally added hydrochar C remained in individual collars after 1 year of the field experiment.

Impact of hydrochar on soil characteristics

Hydrochar addition resulted in considerable changes in the physical, chemical, and biological properties for both amended soils. Soil moisture was the main soil physical property that differed significantly among treatments, mostly due to the fact that the hydrochar is known to be hydrophilic. As a result, the hydrochar-amended rings had significantly

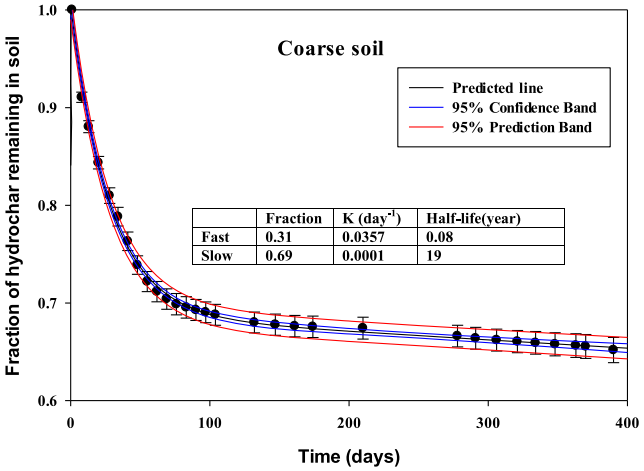

Fig. 4 The fraction of hydrochar C remaining in soil, based on estimated losses of hydrochar in cumulative CO_2 emissions compared to the initial hydrochar C input. Losses via soil leachate were small so not included. *Vertical bars* are SE, n=6. Model decomposition parameters for the two-pool model used to estimate respiration losses are presented in a *table* within the figure; The model is a double exponential equation: $C_t=C_a \exp^{(-kat)}+(C_b) \exp^{(-kbt)}$, where k_a is the decomposition rate for C_a, which represents the rapidly decomposing or fast pool, k_b is the decomposition rate of C_b, which represents the slowly decomposing hydrochar C, and C_a, and C_b are the fractions of fast and slow pools of hydrochar remaining in the soil

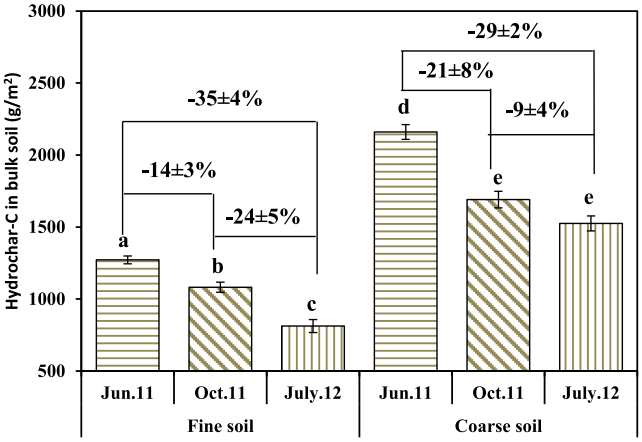

Fig. 5 Amount of hydrochar C present in bulk soil at different time intervals: the initial concentration at start of experiment and the amounts remaining after 3–4 months and after 1 year of experiment. The amount of remaining hydrochar C was calculated by using bulk SOC amount and $\delta^{13}C$. *Different letters* represent statistical significance among treatments (Tukey α=0.05)

($p<0.01$) higher moisture, persisting for more than 40 weeks in the fine soil (Fig. 6a), but with more variable effects in the coarse soil (Fig. 6b).

Microbial biomass, DOC and total N were significantly higher ($p<0.05$) in hydrochar treatments of both soils compared to their respective controls (Table 2) even after 1 year of hydrochar application. The impact of hydrochar on soil pH varied with soil type, with significantly higher pH ($p<0.05$) in the more acidic coarse soil compared to its control at the end of experiment. In contrast, the carbonate-containing fine soil amended with hydrochar had lower pH relative to its control but this difference was not significant ($p>0.05$). Microbial biomass and total N content were considerably higher ($p<0.05$) in the fine soil than in the coarse soil though DOC concentration in K_2SO_4 extracts was similar in both soils (Table 2). The differences between amended soils and controls were larger than the differences between the two soil types or two different cropping schemes.

Impact of hydrochar treatment on plant performance

A negative impact of hydrochar amendment on plants growth was recorded during the first cropping season on both colza and wheat (Fig. 7a). This impact was highly significant ($p<0.01$) for the colza crop, while the wheat crop had less biomass only in the coarse soil ($p<0.05$). In the second season, sown in winter 2011–2012, no differences in crop height or biomass were recorded in the amended plots (Fig. 7b). In control plots, the initial crops had less biomass in the first season due to the late sowing of the seed and relatively shorter growth period (105 days), compared to the second crop growth season (~250 days).

Table 2 Differences in general characteristics of two contrasting soils with or without hydrochar, analyzed after 1 year of field trial (July 2012)

Soil	Treatment	SOC (%)	TN (%)	TIC (%)	Microbial biomass (μg C g^{-1} soil)	DOC (μg C g^{-1} soil)	pH	$\delta^{13}C$ (bulk soil) ‰VPDB
Coarse	Control	4.40	0.27	0.03	316.8±17	24.6±1.8	6.09	−27.7±0.04
	Hydrochar	4.76[a]	0.32***	0.03	440.4±32**	57.1±2.1***	6.37*	−26.1±0.07***
Fine	Control	2.01	0.22	0.82	601.7±41	20.1±2.2	7.88	−26.7±0.04
	Hydrochar	2.32***[a]	0.26***	0.95***	804.6±56*	38.9±5.01**	7.82	−24.8±0.12***

Mean±standard error (n=6)

SOC soil organic C, *TN* total N, *TIC* total inorganic carbon, *DOC* dissolved organic C

Tukey *α=0.05; **α=0.01; ***α=0.001

[a] Represents proportion of native soil C

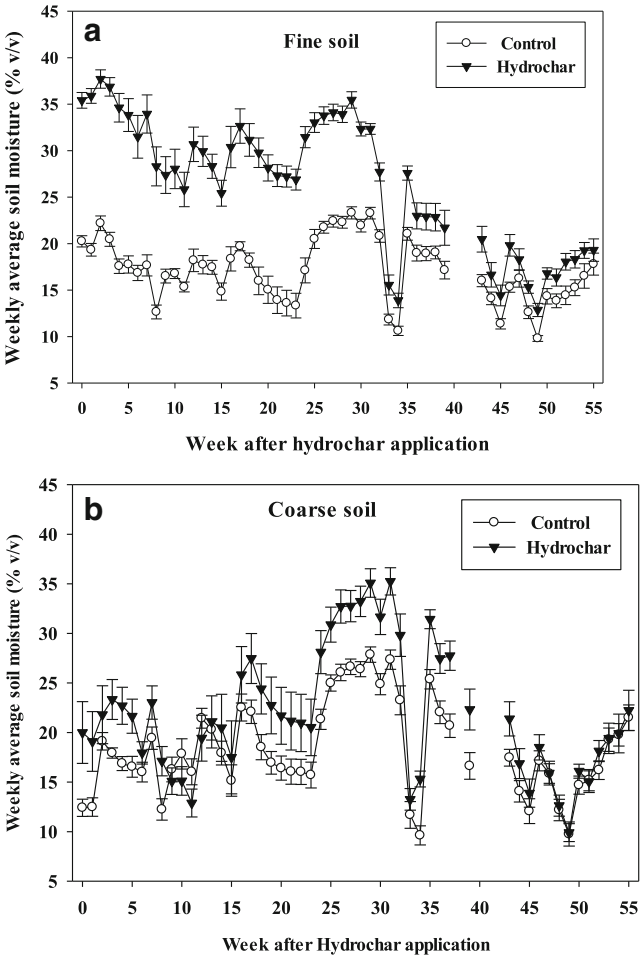

Fig. 6 Weekly mean±S.E (n=6) soil moisture contents observed at 10-cm depth during the complete 1 year of field trial for **a** fine soil and **b** coarse soil. Data for missing dates was lost due to the malfunctioning of the data logger

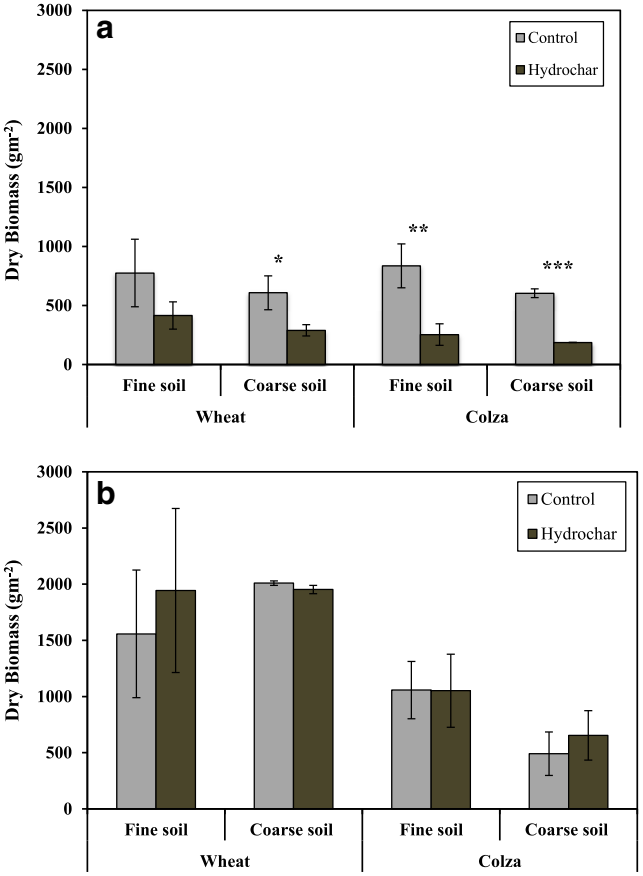

Fig. 7 Dry biomass (g m^{-2}) of wheat and colza crops after drying at 70 °C measured after **a** first cropping season and **b** second cropping season. *Symbols* on top of the column represent statistical significance for differences between control and hydrochar treatments for each soil type. Mean±S.E (n=3)

Discussion

Dynamics of hydrochar decomposition in experimental soils

While the lysimeter soils used in our study are not actual agricultural soils, they have been cropped for a decade since they were filled, and they share characteristics of recent disturbance from plowing with regional agricultural soils. Further, the two-stage decomposition of hydrochar observed in our field trials were very similar to those obtained previously in laboratory incubations using a range of soils collected in the field (Malghani et al. 2013), including rapid mineralization of hydrochar C in the initial months followed by subsequent low rates of loss and including neutral (for forest soils) to negative priming in an agricultural soil. Hence, we are confident that our study provides a representative picture of the behavior of hydrochar amendments, though the details for any given soil or hydrochar will of course vary with the chemistry of the added char, the soil characteristics, and the local factors influencing rates of decomposition (abiotic and biotic).

The two methods of estimating the dynamics of hydrochar C loss in the coarse-textured soil showed similar results. Both indicated that most hydrochar C loss occurred in the initial months, followed by slower losses. In the coarse-textured soil, by summing hydrochar losses in CO_2 emissions (37 %) leached in DOC (~5 %), we estimate that about 42 % of the added hydrochar was lost by the end of the experiment, i.e., 58 % should remain in the soil. This agrees in general with the estimates of 62–77 % remaining (for individual collars, coarse soil only) based on the mass balance of C in soil organic matter. The similarity of these two measures indicates that the similar estimates for a long-term portion of hydrochar C remaining in the fine-textured soil are robust.

Carbon sequestration potential of hydrochar

Estimating the C sequestration potential for hydrochar once it is added to the soil requires that we consider the net effect of all direct and indirect of the amendment on soil properties and C cycling processes. In this study, we focused on two main points: first, on the stability of hydrochar C itself and, second,

on the impact of hydrochar on the stability of native soil C. Hydrochar has a number of properties that make it very reactive in soils, such as the presence of large amounts of oxygen-containing groups (Fuertes et al. 2010; Sevilla et al. 2011). Moreover, 15–30 % of the biomass-derived C in hydrochar is in dissolved form (Ramke et al. 2009) and this liquid phase of hydrochar is rich in organic acids, especially formic, lactic acid, and sugars like glucose/xylose and arabinose (Hoekman et al. 2011). These properties or characteristics indicate high degradability of a large portion of the hydrochar C (O'Toole et al. 2013; Malghani et al. 2013), and generally, hydrochar is not recommended as amendments for soil C sequestration (Schimmelpfennig and Glaser 2012).

Thermo-gravimetric analysis of the hydrochar used in this study indicated that ~50 % of the C was stable at low temperature, with the other half was comprised of aliphatic or thermally stable compounds (Malghani et al. 2013). The presence of a large labile C pool in hydrochar could be the source of C lost rapidly as increased respiration and DOC losses (Figs. 1 and 3). Within 3 months after application, approximately17±5 and 24±4 % of the applied hydrochar C was lost in fine and coarse soils, respectively (Fig. 5). Initially (i.e., in the first 3 months), the rate of hydrochar mineralization was lower in fine soil, possibly due to higher water content (Fig. 6) and improved aggregation ability due to promotion of AM fungi growth (Rillig et al. 2010; George et al. 2012). However, 1 year after its application, there was no difference in the amount of hydrochar C loss between the two soil types (Fig. 5), suggesting that composition of the added C source may exert a stronger influence on its fate than soil type as seen in similarly short-term incubation studies (Bai et al. 2013; Malghani et al. 2013; Naisse et al. 2014). Further studies with a larger variety of soil types are needed to finally conclude on the effect of soil type on biochar decomposition. Approximately two thirds of the added hydrochar C remained in both coarse and fine soils even 1 year after its application (Fig. 5), although the stable isotopic signatures of respired CO_2 and DOC in soil leachate still showed significant contributions from hydrochar C (Fig. 2 and 2s) in the coarse soil that were otherwise not detectable as differences in bulk C fluxes (Fig. 1).

All parameters regarding decomposition of hydrochar C showed two phases, initially fast losses followed by slower losses. Decomposition kinetics of hydrochar C was determined from nonlinear regression of the fraction of hydrochar C remaining in coarse soil with time (Fig. 4). The inferred half-life (~19 years) of the passive component of hydrochar C determined in our study was similar to that determined by incubation studies (Qayyum et al. 2012), highlighting similar behavior of hydrochar materials in contrasting experimental setups. However, the expected decadal time stability of passive pool of hydrochar is much lower than expected for pyrochar that could persist for centuries (Kuzyakov et al. 2014).

A critical issue for the effect of soil amendments is the effect of added char or biomass on the decomposition of native soil C (Keith et al. 2011). Priming is known as the short-term acceleration or decline of native C decomposition associated with the addition of a readily decomposable substrate (Fontaine et al. 2003; Kuzyakov 2010). As discussed above, hydrochar generally contain a large fraction of labile or easily decomposable compounds, and we observed both positive and negative priming effects in the amended coarse soil (Fig. 2b). Positive priming was observed in the first 3 months, when the majority of the hydrochar C was respired; this positive priming is often associated with the availability of easily decomposable substrate (Figs. 1 and 4). In the second phase of experiment when hydrochar decomposition rates were slow, an opposite effect on native SOC was observed (Fig. 2). A protective impact of hydrochar C on the decomposition of native soil C was demonstrated by the isotopic mass balance. The amount of remaining native soil C was considerably higher in hydrochar treated plots. Fine and coarse soils had 13.8±1.4 % (n=4, two outliers were not included in calculations) and 8.8±3.4 % (n=5) more native soil C than their respective controls (Table 2). These results indicate that a positive priming effect of hydrochar, as observed in short-term incubation studies (Steinbeiss et al. 2009; Kammann et al. 2012) and the first months of our experiment, may not persist over the long term. This positive role of hydrochar could be related with enhanced aggregation in hydrochar-treated soils, due to promotion of fungal growth by hydrochar material (Rillig et al. 2010; George et al. 2012) or by the formation of "protected" microbial biomass (Gleixner et al. 2002).

Potential changes in soil properties caused by hydrochar

Hydrochar is unique in its physical and chemical characteristics, which in turn depend on feedstock type and process conditions, and its addition can have considerable impact on soil properties. Hydrochar can increase soil water by enhancing soil porosity (Abel et al. 2013) and aggregate formation (Rillig et al. 2010) and by changing soil tortuosity; large particles of char can block pores. Moreover, hydrochar particles are known for having more porosity due to their spherical shape and deformability and can retain water (Abel et al. 2013). We recorded significantly higher moisture contents in hydrochar-amended treatments but these differences were time- and soil-dependent (Fig. 6). In this study, amended and control soils of both coarse and fine soils did not differ in bulk density (data not presented). Therefore, the observed increase in water content could be associated with hydrochar particle characteristics and changes in soil tortuosity/hydraulic conductivity in the fine soil. After 10 months, diminished effects of amendment on soil water content may have been related to the loss of the labile pool of hydrochar C or changes in the

surface chemistry of hydrochar particles, though this requires further exploration.

Another unique property of hydrochar is their "liming" effect on soils in spite of their acidic nature (Rillig et al. 2010). The hydrochar production processes are sensitive to pH, and generally, an acidic pH (<7) is a pre-requisite for the hydrothermal carbonization method (Meyer et al. 2011). Lower pH is achieved with addition of low-strength acids (e.g., citric acid) (Hu et al. 2010; Cao et al. 2011), and usually, hydrochar has a pH similar to the liquid added to biomass prior to carbonization (Liang et al. 2011). The hydrochar used in this study had a pH of 4.75 but a significant increase in soil pH was recorded 1 year after its application. The pH of soil leachate of hydrochar and control treatments, collected after 1 week of hydrochar experiment were 8.03±.2 and 7.4±.2, respectively. This suggests that enhanced microbial reduction reactions may be the reason for the liming effect of hydrochar (Rillig et al. 2010); however, it is still unknown which reactions are responsible.

Initial negative impact of hydrochar on plant growth

Our observation of reduced plant height and dry biomass yield in the first crop after hydrochar amendment has also been reported in other studies (Busch et al. 2012, 2013; Gajic and Koch 2012). These studies proposed two explanations. The first involved the production of phytotoxic and/or volatile compounds from easily degradable portions of hydrochar that have a negative impact on seed germination rate (Busch et al. 2012). Jandl et al. (2013) proposed that the phytotoxic compound could also be ethylene produced by degradation of long C-chain aliphatic compounds. In addition, hydrochar's surface adhered volatile organic acids such as lactic acid, formic acid, and laevulic acid that may present in large amount in crude or fresh hydrochar (Hoekman et al. 2011) could also be responsible for low plant growth as later are known for their growth retardant functions. The second explanation is related to nutrients available to seeds that do successfully germinate (Bargmann et al. 2014). Hydrochar application may inhibit N-availability due to N-immobilization and ultimately could negatively impact plants (Gajic and Koch 2012; Bargmann et al. 2014). We did not measure changes in inorganic N (NO_3^-, NH_4^+) in this study but we observed significantly ($p<0.05$) higher TN content in hydrochar-treated soils (Table 2). We observed no differences in N content of plant biomass harvested in the first cropping interval, so we assume that N-related impacts were limited to the initial stages of plant growth. Moreover, the negative impact of hydrochar on plant growth was not observed during the second cropping season, though we also did not observe fertilization effects of hydrochar that have been reported by some studies (Busch et al. 2012; Bargmann et al. 2014). Consequently, agricultural use of hydrochar must be carried out carefully and application management like the use of nitrogen fertilizer (Gajic and Koch 2012) or composting of hydrochar (Busch et al. 2013) should be performed.

Conclusions

The addition of hydrochar C in amounts initially sufficient to raise overall soil C content by 20–30 % showed considerable effects on soil properties as well as on plant growth. Total organic C, TN, DOC, water content, and microbial biomass were among the measures that increased as a result of hydrochar amendment, even 1 year following its application. Although hydrochar C was initially lost very rapidly through decomposition and leaching, roughly two thirds of the added C remained in the soil after two cropping seasons. Interestingly, hydrochar protected native soil C from decomposition (negative priming). On the other hand, it initially had a negative impact on plant performance. We conclude that hydrothermal carbonization has a high potential for its proposed use of C sequestration for two reasons; first, this method is especially useful to produce carbonaceous products from unconventional sources like bio wastes or sewage sludge. Second, the passive fraction of hydrochar C may persist in soil over three decades or more. For future work, there is a need to better understand the relation between charring procedure, yielded char structure, and its reactivity in different soils.

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