

Biochars influence differential distribution and chemical composition of soil organic matter

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ABSTRACT

In the present study, three soils (Ferralsol, Luvisol topsoil, and Luvisol subsoil) were amended with biochars (charcoal, hydrothermal carbonization coal (HTC) of bark, and low-temperature conversion coal of sewage sludge), wheat straw and a control (no amendment) and incubated over a period of 365 days. Each amendment was applied at a rate of 11.29 g C/kg soil. After incubation, the soils were analyzed to retrieve three density fractions (free fraction (FF), intra-aggregate fraction (IAF), and heavy fraction) which were analyzed for total carbon (TC) contents and scanned by fourier transform infrared spectroscopy (FTIR). The biochars and straw significantly increased the TC contents of soils as compared to control. Among soil organic matter (SOM) density fractions, higher TC contents were documented in the FF and IAF from biochar treatments as compared to the straw. The FTIR spectra of the FF from the charcoal and HTC treatments showed the presence of aluminosilicate minerals on surfaces of SOM. There were slight changes in the FF of straw and HTC treatments as compared to spectra of original amendments. The study suggests that the stability of charcoal and HTC in soils is due to the recalcitrant nature of biochar followed by occlusion into soil micro-aggregates.

Keywords: carbon stabilization; C sequestration; fourier transform infrared spectroscopy; density fractionation

Soil organic matter (SOM) is a key element affecting soil physical, chemical and biological properties. Therefore practices for stabilization of SOM in soils are given significance. The stability of SOM depends on its distribution in various density fractions which are differently protected against decomposition through distinct mechanisms (Bouajila and Gallali 2008). The least stable SOM fraction is the free fraction (FF) that may be plant-like and has high carbon contents (Swanston et al. 2002) and is considered to control microbial activity. The second fraction comprises carbon protected in the soil stable aggregates and is called intra-aggregate fraction (IAF). The most stable carbon fraction in soils is the heavy fraction (HF) which is protected by the soil minerals.

Biochar (BC) is a combustion product of waste-biomass, used as a soil amendment (Woolf et al.

2010). Biochar improves soil fertility, and mitigates greenhouse gases in the atmosphere (Kammann et al. 2012, Wu et al. 2013) and has high C sequestration potential in soils as compared to wheat straw and manures (Qayyum et al. 2012, Schulz et al. 2013). Reports describe the mean residence time of biochar's C in a range of thirty to thousands of years. However, the detailed mechanisms are in focus of research. Whalen et al. (2000) investigated the role of density fractions in black carbon stabilization in the Terra Preta compared to the adjacent soils and found greater carbon values in the light fraction (LF) followed by the medium and HF (organo-mineral interactions).

As summarized, reports are available regarding stabilization of various density fractions in soils. However, no information is available about the contribution of various biochars to SOM density

fractions and changes occurring on biochar surfaces in various soils. The objectives of our study were: (i) to investigate the effects of various biochars on carbon distribution in the density fractions and (ii) to study the changes occurring on biochar surfaces in the SOM density fractions retrieved from three soils after 365 days of incubation.

MATERIAL AND METHODS

Soils and treatments. In the present study, three soils were selected, (i) a Ferralsol (a relic tertiary soil that is a mixture of various soil horizons) sampled from an area of Lich near Giessen, Germany (ii) loess derived topsoil and subsoil which were collected from 0–25 cm and 80–120 cm depths at arable land in Huenfeld, and Kleinlinden Germany, respectively. The detailed physicochemical properties of the soils are already published in Qayyum et al. (2012).

Wheat straw was obtained from a harvested wheat crop at farmer's field near Giessen, Germany. Charcoal was purchased from Sommer-hit® Co. Germany, where it was produced by burning wood under limited oxygen environment at 550°C. Hydrothermal carbonization coal (HTC) was a product of low temperature (200°C) hydrothermal-carbonization of bark. The low-temperature conversion coal (LTC) was obtained from Loteco TEC® Co. Germany, where it was produced by anaerobic thermo-catalytic conversion of sewage sludge at 400°C. The general term 'organic amendments' will be used throughout this manuscript when discussing wheat straw and biochars. The physicochemical properties of the organic amendments are already published (Qayyum et al. 2012).

Soil incubation. For the incubation experiment, the three selected soils were amended with straw, charcoal, HTC, LTC including a control (non-amended soil). The application of C from the various organic amendments was equivalent to 11.29 g C/kg soil (50 t charcoal/ha). As the C concentrations in the straw and biochars were different, the following amounts of the amendments were mixed with the soils (straw = 26.66, charcoal = 12.82, HTC = 22.15, and LTC = 42.57 g/kg soil). Nitrogen (N), phosphorus (P), potassium (K) and magnesium (Mg) were maintained (g/kg soil) at: N as $\text{NH}_4\text{NO}_3 = 1.49$; P as $\text{Ca}(\text{H}_2\text{PO}_4)_2 = 1.63$; K as $\text{KCl} = 0.37$; Mg as $\text{MgSO}_4 = 0.42$, by considering their content in applied organic amendments.

The calculated amounts of amendments were mixed with 900 g soil (air-dried ≤ 4 mm) and the mixtures were filled into plastic pots. Each treatment was replicated three times. In each pot, soil moisture content was maintained at 60% of water-holding capacity. The pots were incubated over a period of 365 days. A release of CO_2 during incubation and kinetics of C mineralization were published previously (Qayyum et al. 2012). In the present study, soil samples taken after 365 days were fractionated for SOM density fractions and analyzed for TC contents and chemical surface properties.

Laboratory analyses

SOM density fractionation. The soil samples taken after 365 days of incubation were analyzed for the SOM density fractions according to Sohi et al. (2001) with slight modifications. With this methodology, three fractions (free fraction, intra-aggregate fraction and heavy fraction) were retrieved, oven-dried at 40°C, weighed, finely ground using pestle and mortar, and kept for analyses.

Elemental analyses and fourier transform infrared spectroscopy (FTIR) of the soil density fractions. The total carbon (TC) concentrations in the bulk soil samples and the SOM density fractions were determined with an elemental analyzer (Vario EL-III, Hanau, Germany). The amounts of TC increased in the SOM density fractions relative to control were regarded as stabilized carbon. The proportion of stabilized carbon among various fractions was calculated as:

$$\begin{aligned} \text{\% of total C stabilized in a SOM density fraction} &= \\ &= \frac{(\text{fraction TC}_{(\text{C compound})} - \text{fraction TC}_{(\text{control})})}{(\text{bulk soil TC}_{(\text{C compound})} - \text{bulk soil TC}_{(\text{control})})} \times 100 \end{aligned}$$

The amendments before incubation, SOM density fractions, and bulk soil samples after incubation were scanned using FTIR spectroscopy with a Bruker IFS 48 spectrometer (Bruker Optik GmbH, Ettlingen, Germany) in the range from 4000 to 400/cm with 32 scans per spectrum. All spectra were recorded using KBr pellets (1 mg sample + 200 mg KBr). The infrared peaks assignments were made according to Madejová and Komadel (2001) and Steinbeiss et al. (2009).

Statistical analyses. To statistically distinguish the treatments, analysis of variance and the Tukey's-HSD test were performed using PASW

Statistics 18, Release Version 18.0.0 (SPSS, Inc., 2009, Chicago, USA).

RESULTS

Total carbon content in soil density fractions.

The TC contents in three soils were significantly ($P \leq 0.05$) different (Table 1). In the Ferralsol, charcoal, HTC, and LTC resulted in the highest values of TC content. In the Luvisol topsoil and Luvisol subsoil, the LTC and charcoal treatments showed a maximum increase of TC over the control treatment.

In the Ferralsol and Luvisol topsoil, the highest TC contents of the FF and IAF fraction were found in the charcoal treatment (Table 1). Straw treatment resulted in smaller values of TC in the FF and IAF compared to biochars. In the Luvisol subsoil, all biochars revealed significantly ($P \leq 0.05$) higher values of TC in the FF and IAF compared to the control. The straw application did not show a significant difference with the control in the FF. The LTC showed the highest relative increase of

TC content in the HF of all soils in comparison to the control.

Carbon distribution in soil density fractions.

In all soils, biochars showed relatively higher proportions of stabilized TC in the FF (in the range of 22% to 85%) than control soils (Table 2). The straw treatment resulted in higher proportions of stabilized TC in the IAF and FF (in Ferralsol) and in the FF (in other two soils). In the Ferralsol and Luvisol topsoil, after stabilization in the FF, higher proportions of TC were found in the IAF of all treatments except LTC, in which higher proportions were found in the HF.

Fourier transform infrared spectroscopy. The FTIR spectra of control treatments and their descriptions are provided in Figure 1. In the Ferralsol, major infrared peaks were observed due to OH stretching associated with kaolinite clay minerals (3694, 3620, and 3526/cm), characteristic for OH stretching vibrations of water (3444/cm), deformation vibrations of water (1631/cm), N-O stretching of nitrate (1384/cm), Si-O stretching (1031/cm), and Al-Al-OH deformation (913/cm).

Table 1. Effect of straw, charcoal, hydrothermal carbonization coal (HTC), and low-temperature conversion coal (LTC) on the total carbon content in the bulk soils and soil density fractions after 365 days of incubation

Soil	Treatment	Bulk soil	Free fraction	Intra-aggregate fraction	Heavy fraction
		(C g/kg soil)			
Ferralsol	control	3.3 ± 0.1 ^c	0.0 ± 0.0 ^c	0.0 ± 0.0 ^c	3.2 ± 0.1 ^c
	straw	8.5 ± 0.1 ^b	0.4 ± 0.1 ^c	1.1 ± 0.2 ^{bc}	4.3 ± 0.3 ^b
	charcoal	14.3 ± 1.3 ^a	6.2 ± 1.1 ^a	3.7 ± 0.3 ^a	4.0 ± 0.4 ^{bc}
	HTC	11.3 ± 0.7 ^{ab}	4.6 ± 0.4 ^{ab}	2.0 ± 0.0 ^b	3.9 ± 0.3 ^{bc}
	LTC	11.9 ± 2.6 ^{ab}	3.5 ± 0.8 ^b	1.7 ± 1.0 ^b	6.5 ± 0.4 ^a
Luvisol topsoil	control	14.1 ± 0.1 ^d	0.5 ± 0.1 ^c	0.6 ± 0.0 ^d	12.2 ± 0.4 ^d
	straw	19.9 ± 0.4 ^c	2.9 ± 0.3 ^b	1.3 ± 0.2 ^{cd}	13.6 ± 0.3 ^{bc}
	charcoal	26.3 ± 2.5 ^{ab}	6.0 ± 0.3 ^a	5.1 ± 0.6 ^a	14.3 ± 0.7 ^b
	HTC	21.8 ± 2.7 ^{bc}	5.4 ± 0.8 ^a	2.6 ± 0.1 ^b	12.8 ± 0.5 ^{cd}
	LTC	28.4 ± 1.6 ^a	3.7 ± 0.3 ^b	1.8 ± 0.1 ^{bc}	19.7 ± 0.1 ^a
Luvisol subsoil	control	2.2 ± 0.1 ^d	0.0 ± 0.0 ^b	0.0 ± 0.0 ^b	1.8 ± 0.2 ^b
	straw	6.4 ± 0.3 ^c	1.9 ± 0.1 ^b	1.2 ± 0.2 ^a	2.2 ± 0.1 ^b
	charcoal	13.6 ± 1.9 ^a	8.3 ± 1.8 ^a	2.0 ± 0.4 ^a	1.5 ± 0.3 ^b
	HTC	9.5 ± 0.4 ^b	6.2 ± 0.3 ^a	1.5 ± 0.2 ^a	1.8 ± 0.1 ^b
	LTC	11.6 ± 0.4 ^{ab}	5.5 ± 1.1 ^a	1.7 ± 0.4 ^a	5.2 ± 1.6 ^a

The values are means of three replicates ± standard error. For each soil, values followed by different letters in columns are statistically different at $P \leq 0.05$

Table 2. Effect of straw, charcoal, hydrothermal carbonization coal (HTC), and low-temperature conversion coal (LTC) on the distribution of stabilized total carbon content in the soil density fractions after 365 days of incubation

Soil	Treatment	Fraction		
		free	intra-aggregate	heavy
		(%) ^a		
Ferralsol	straw	7.7	21.2	21.2
	charcoal	56.4	33.6	7.3
	HTC	57.7	25.0	8.8
	LTC	40.7	19.8	38.4
Luvisol topsoil	straw	41.4	12.1	24.1
	charcoal	45.1	36.9	17.2
	HTC	63.6	26.0	7.8
	LTC	22.4	8.4	52.4
Luvisol subsoil	straw	45.2	28.6	9.5
	charcoal	72.8	17.5	-2.6
	HTC	84.9	20.5	0.0
	LTC	58.5	18.1	36.2

^apercentage of increased total carbon content relative to control treatment

The FTIR of straw-FF derived from all soils show a decrease in OH stretching vibrations (3410–3440/cm in combination with 1642/cm) when compared with straw without incubation (Figure 2). The spectra show loss of polysaccharides in straw treatment (a decrease in intensity of infrared absorption at 1050–1000/cm) in the three soils. There were some new peaks in the straw-FF at wavelength 2361, 778, 693, and 468/cm in Luvisol topsoil and at 532, and 469/cm in Luvisol subsoil.

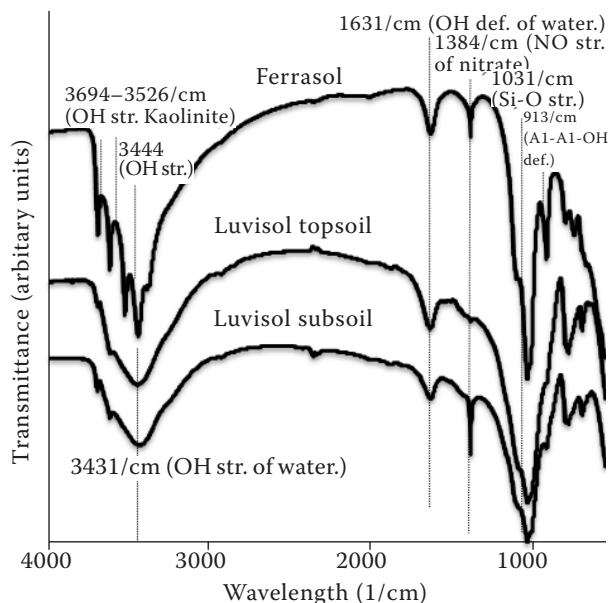
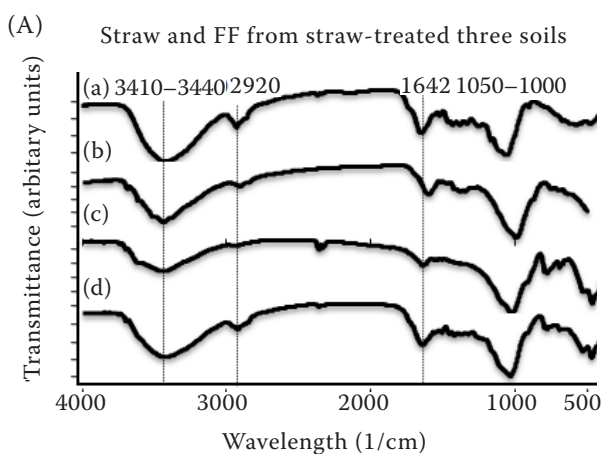


Figure 1. Fourier transform infrared spectra of the control treatments of Ferralsol, Luvisol topsoil, and Luvisol subsoil after 365 days of incubation

The FTIR spectra of charcoal without incubation showed highly condensed carbon with no characteristic band (Figure 3). The infrared absorption was increased in the fingerprint region (1400–500/cm) of FF retrieved from charcoal-treated soils. This was due to additions of inorganic components of soils on charcoal surfaces. The FTIR spectrum of HTC without incubation show infrared peaks at 3392/cm (OH stretching of water), 2920/cm (CH stretching), 1614/cm (deformations of water), 1058/cm (polysaccharides), and 559/cm (inorganic substances) (Figure 4). There were additional absorbance bands at 1032/cm (smectite or Si-O) and 3527–3620/cm

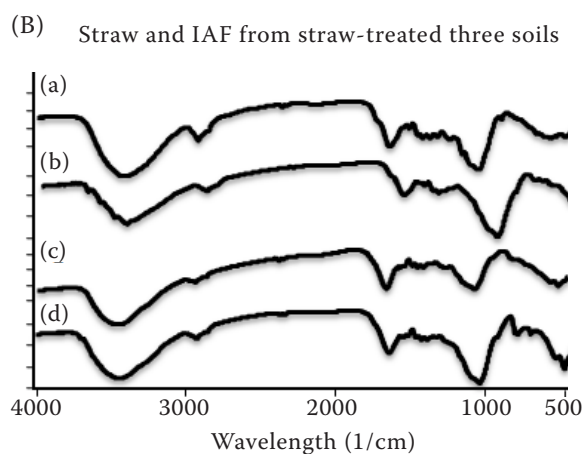


Figure 2. Fourier transform infrared spectra of straw without incubation (a), free fractions (FF) (A), and intra-aggregate fractions (IAF) (B) retrieved from Ferralsol (b), Luvisol topsoil (c), and Luvisol subsoil (d) after 365 days of incubation with straw

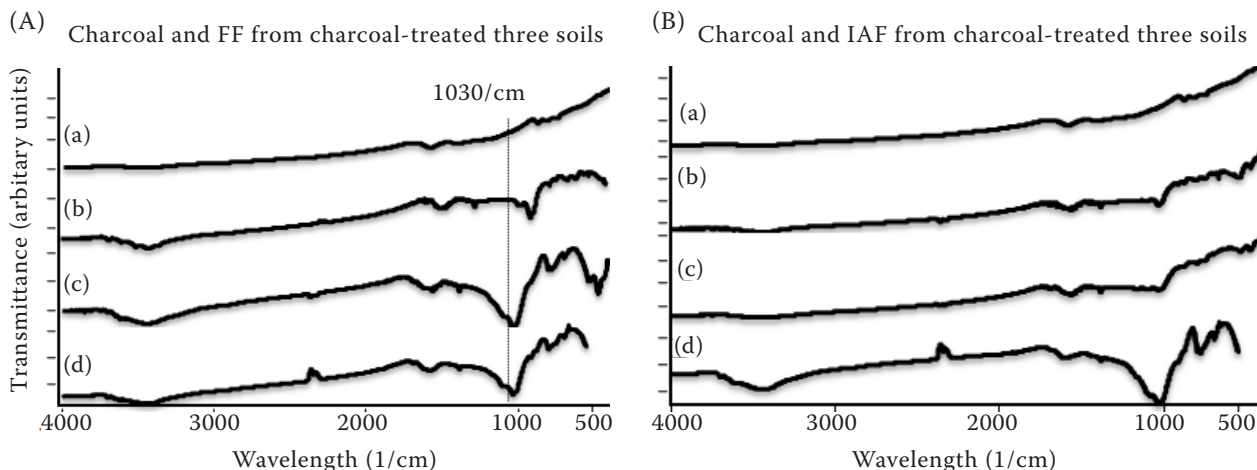


Figure 3. Fourier transform infrared spectra of the charcoal without incubation (a), free fractions (FF) (A), and intra-aggregate fractions (IAF) (B) retrieved from Ferralsol (b), Luvisol topsoil (c), and Luvisol subsoil (d) after 365 days of incubation with charcoal

(Si-O-H) in FF of the HTC treatments as compared to spectra of HTC. The intensity of changes was higher in the Ferralsol followed by the Luvisol subsoil and Luvisol topsoil. In the straw, charcoal and HTC treatments, no important differences were observed between compounds and IAF.

The comparison of the LTC and its density fractions from the three soils showed only absence of absorbance band at wavelength 1435/cm (carbonate) in the Luvisol topsoil (Figure 5). The FTIR spectra of the heavy fraction from the three soils show no differences between the treatments within soil (not shown). These results suggest no change in the HF of soils with the application of organic amendments.

DISCUSSION

Our results indicate that in the biochars (BCs), higher proportions of stabilized C were found in the FFs which suggest its chemical recalcitrance. The charcoal used in our experiment had the highest C concentration (Qayyum et al. 2012) but that was recalcitrant black C with no significant bands of FTIR (Figure 3). Previously, in the Terra Preta soils, higher stability of C was found due to chemical inertness (Glaser et al. 2002). Our results of the FTIR spectra show indications of charcoal surface depositions of the aluminosilicates. These surface interactions may have increased the stability of charcoal-C in the FF in addition to inert-

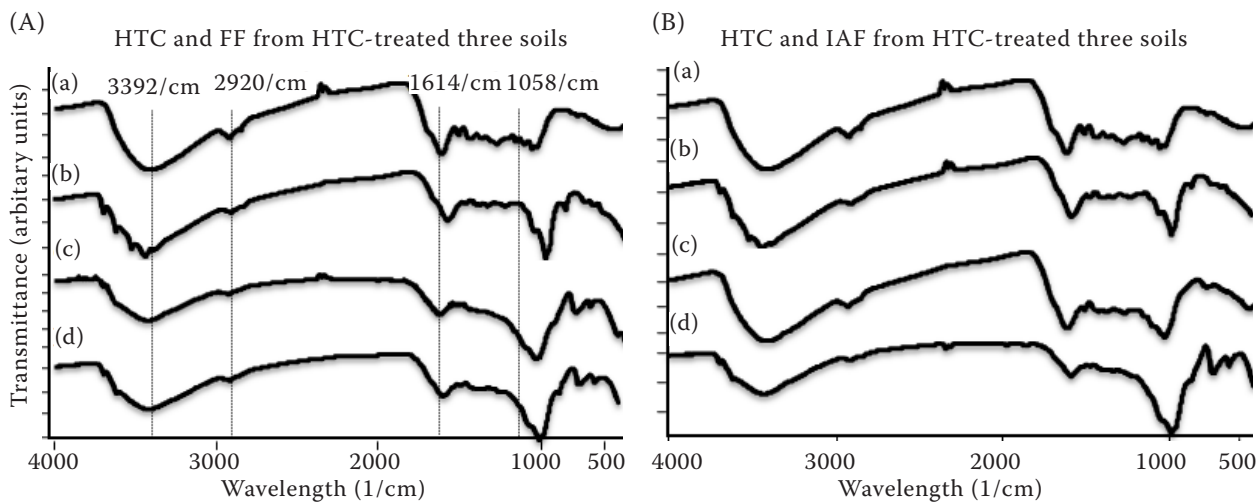


Figure 4. Fourier transform infrared spectra of the hydrothermal carbonization coal (HTC) without incubation (a), free fractions (FF) (A), and intra-aggregate fractions (IAF) (B) retrieved from Ferralsol (b), Luvisol topsoil (c), and Luvisol subsoil (d) after 365 days of incubation with HTC

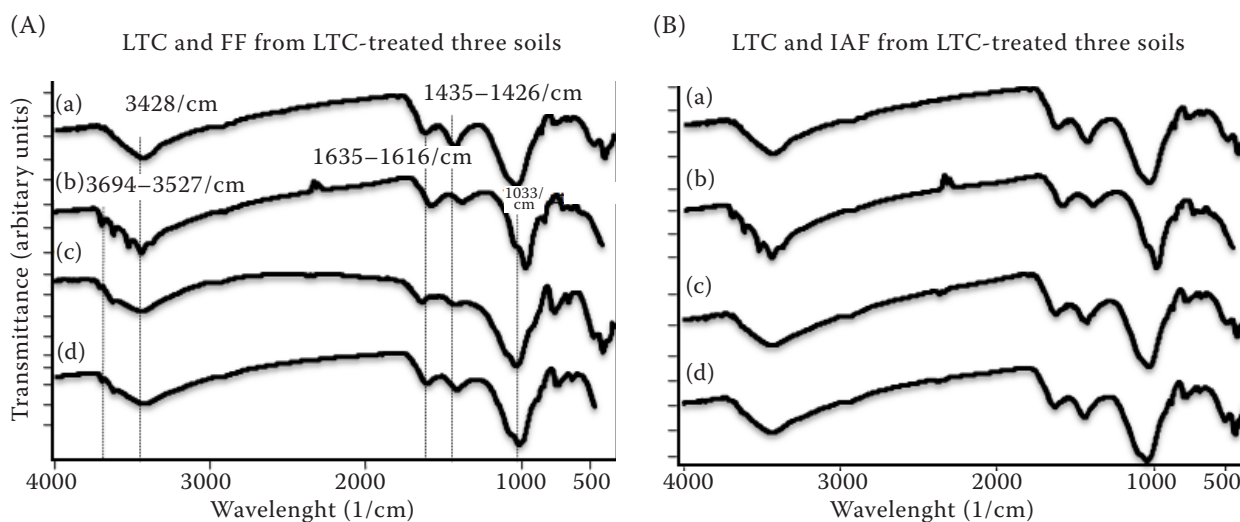


Figure 5. Fourier transform infrared spectra of the low-temperature conversion coal (LTC) without incubation (a), free fractions (FF) (A), and intra-aggregate fractions (IAF) (B) retrieved from Ferralsol (b), Luvisol topsoil (c), and Luvisol subsoil (d) after 365 days of incubation with LTC

ness. Similarly, Joseph et al. (2010) reported that charcoal surface-depositions of Al, Ca, and Si may enhance the inertness of carbon in the soils. In our study, the FTIR spectra of the FF of the HTC treatment indicate some surface-depositions of clay minerals (Figure 4). This suggests that despite higher mineralization (Qayyum et al. 2012), a part of carbon in the HTC is also stable in soils in the form of recalcitrant black carbon.

The FTIR spectra of IAF from all treatments in the Ferralsol and Luvisol topsoil were not different from those of the carbon compounds (Figures 2–5). This suggests a lack of surface reactions of the straw and biochars when present in micro-aggregates. Similar findings were reported by Mutuo et al. (2006), who incubated two soils and SOM fractions separately and found higher carbon concentrations in micro-aggregates as compared to macro-aggregates. The other mechanism of SOM stabilization is due to interaction of carbon compounds with clay minerals (Golchin et al. 1994).

In the LTC-treated soils and straw treatment in the Ferralsol and Luvisol topsoil TC in the HF significantly ($P \leq 0.05$) increased (Table 2). This indicates a possibility of carbon stabilization in the LTC-treated soils due to organo-mineral interactions (Hammes and Schmidt 2009). The other possible reason may be that the LTC biochar produced from sewage sludge might contain carbon compounds with higher density, which were not retrieved in the free and intra-aggregate fractions. From the FTIR spectra of LTC-treated soils and SOM fractions in this treatment no information

could be drawn to support any mechanism of stabilization. The exact mechanisms for carbon stabilization in this treatment need further investigation.

It is concluded that the recalcitrant nature of the applied carbon and the occlusion into soil micro-aggregates are responsible for stabilization of charcoal and HTC in the soils. Moreover, the FTIR of the SOM density-fractions exposed aluminosilicate mineral associations on the surfaces of charcoal and HTC. These surface interactions may enhance the stabilization potential of these biochars. However, for the LTC produced from sewage sludge, major mechanism of C stabilization was binding in the heavy fraction of SOM. Complete description of C stabilization in LTC thus needs further investigations.

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