Spectral effects of biochar on NIR and mid-IR spectra of soil/char mixtures

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Abstract
The objective was to investigate the effect of adding biochar to soil on the spectra of mixed biochar and soil in the near- (NIR, 10,000 to 1000 cm^{-1}) and mid- infrared (mid-IR, 4000 to 400 cm^{-1}). Biochar produced from the Ingá (*Ingá edulis* Mart.) tree at 3 temperatures (400, 500 and 600^{o}C) was added to soil by mixing or grinding together and at 0 to 6% by wt. Results indicated that the addition of biochar to soil results in spectral distortions which tend to distort/mask, the signature of the original soil. These effects are very evident when applying spectral subtraction to the resulting spectra, e.g., the spectra of biochar and soil are not additive, i.e., (A + B) <> (A+B). Significant distortions in the NIR were seen between 5000 and 4000 cm^{-1} where significant information on soil C is found and could have profound effects on attempts to determine total soil C (TSC) by NIR in biochar amended soils. Similar distortions were found in the mid-IR, but primarily in the silica spectral region, and while making spectral interpretation more difficult, may have less effect on the ability to develop calibrations for TSC in biochar amended soils, but further research will be needed in both spectral regions to answer this question.

Key Words
Biochar, Mid-Infrared, Mid-IR, Near-Infrared, NIR, soil

Introduction
Biochar is the C rich product produced when biomass is heated in the absence of oxygen (pyrolysis). The liquids produced, often called bio-oils and along with the gaseous products can be burned or used as feedstock for bio-based fuels or chemicals (Biochar, 2009). Much of the interest in biochar has come from research on the *terra preta* or dark earths found in the Amazon Basin (Lehmann and Joseph, 2009). The production and use of biochar is being highly touted as a way to sequester C in soils and to improve soil quality and productivity (Laird, 2008; Bracmort, 2009), but as discussed at the recent N. Amer. Biochar Conf. (http://cees.colorado.edu/northamericanbiochar.html, August 2009), there are still questions to be resolved. An investigation into the effect of biochar on C mineralization in soil, using near-infrared (NIR) and mid-infrared (mid-IR) spectroscopy showed spectra to exhibit some very unexpected properties. The objective of this investigation was to investigate the spectral properties of mixtures of biochar and soils.

Methods
Biochar production Biochar was made from the Inga tree species (*Ingá edulis* Mart.) at two temperatures (400 and 500 ^{0}C). Ingá biomass from a 7-yr old tree was collected from secondary forest growth at the National Institute of Amazonian Res. (INPA) Tropical Fruit Culture Expe. Station. Woody material was chosen so that similar diameter samples (other biochars not discussed) were placed in the pyrolysis chamber, in place of selecting material from similar locations on the trees. In the case of Ingá, the branches were used and biochar made from fresh material in the pyrolysis furnace at the Cellulose and Charcoal Lab., Forest Prod. Div., INPA, Manaus, BR. Slow pyrolysis was accomplished in a furnace of refractory brick with a 20L capacity, with samples brought to temperature over 2h. After reaching temperature the furnace was turned off and allowed to cool. After combustion, samples were ground to pass a 2mm sieve. The biochar yield, as well as yield of associated products that characterize the feedstock and biochar is provided in Table 1.
Spectroscopy Spectra were obtained in the near- (NIR, 10,000 to 4000 cm^{-1}, quartz beamsplitter, lq. N_2 cooled InSb detector, sulfur background) and mid-infrared (mid-IR, 4000 to 400 cm^{-1}, KBr beamsplitter, Peltier cooled DTGS detector, KBr background) ranges using diffuse reflectance on non-KBr diluted samples (Digilab FTS7000 Fourier transform spectrometer, Varian, Inc., Lake Forest, CA, equipped with a Pike Autodiff autosampler, Pike Technologies, Watertown, WI). Samples consisted of biochar mixed with soil (Millhopper sand, pH 5.2 or pure sand) by gentle swirling or by grinding the previously mixed materials together in a mortar and pestle. Some samples were also stored in a desiccator over water for various periods. Spectra were processed using GRAMS AI Ver. 8 (Thermo Fisher Scientific, Waltham, MA) and Panorama Ver. 1.2 LabCognition Gmdh & Comp., Cologne, Germany) software. Spectra of multiple sub-samples were

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often taken and averaged, but no differences were found between replicate spectra indicating homogenous samples.

Results

Table 1. Yield of biochar, wood tar and vinegar and C-mineralization results for Inga biochar.

	Sub-products of Pyrolysis					C-Mineralization Results		
	Wood, Dry	Biochar	Biochar	Wood	Wood	Net C Released mg/g		
Temp.	Wt (Kg)	(kg)	(%)	Tar (ml)	Vinegar (L)	Max.	Day	Day 162
400	13.3	3.4	25.6	0.1	9.3	4.93	35	-47.41
500	13.6	3.4	25	0.1	9.3	1.83	21	-55.68

As shown in Table 1, the yield of char and other products can vary significantly with temperature. Significant differences between different biomass sources also existed, but are not part of this discussion. Results from experiments examining the amount of C mineralized as CO_2 over a period of 162 days also indicate that compositional changes vary with temperature and not necessarily in a linear fashion.
In Figure 1, the NIR spectra of Inga 500 ^{0}C biochar, soil, and a mixture of 6% biochar by wt. in soil are shown. As can be seen, the addition of biochar appears to mask the spectral signature of the soil even when only mixed by swirling. As shown in Figure 2, spectral subtraction of the biochar from the biochar-soil mixture does not produce the spectrum of that of the original soil as would be expected. As all materials were dry powders, the effects must be physical such as coating of the soil particles by biochar. This was still not expected as the biochar is present at only 6% of the concentration of the soil and NIR radiation can penetrate at least a mm deep in such samples. Initial thoughts that the biochar might also be causing dehydration effects were shown not to be so as demonstrated for samples stored over water for up to 11 days which showed only a modest change in the water bands (Figure 3). As shown in Figure 4, grinding the char and soil together after mixing only intensifies the effect supporting the concept of a physical coating of soil particles by biochar which NIR radiation does not seem to penetrate well.

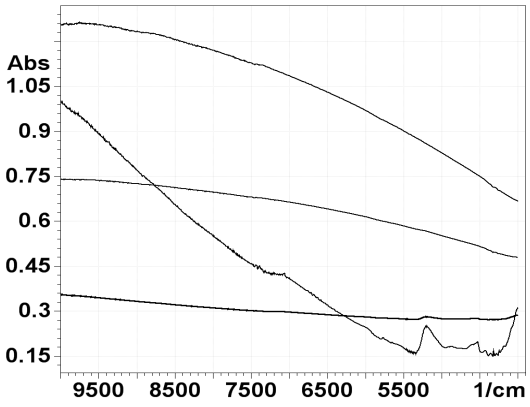

Figure 1. Near-infrared spectra of (Top to bottom) Inga 500 C biochar (IG500), soil + 6% IG500, soil, and normalized soil spectrum.

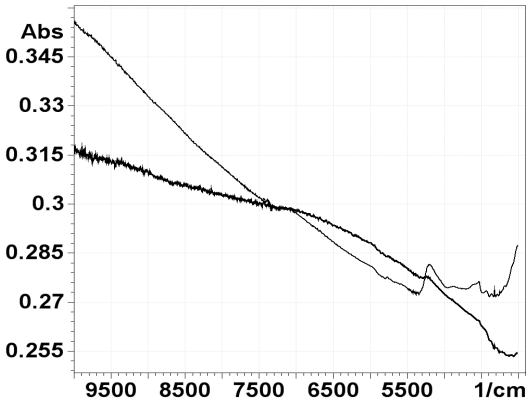

Figure 2. Near-infrared spectrum of soil (Top) and spectrum resulting from subtraction of spectrum of Inga 500 C biochar (IG500) from spectrum of 6% IG500 in soil (Bottom).

As demonstrated in Figures. 6-8, similar spectral distortions were found in the mid-IR spectral region but primarily in the 2300 to 1700 spectral region where silica strongly absorbs (Figures. 5 and 6). Interestingly, the same results were not as apparently in work using sand and biochar (Results not presented). Again the distortions are readily apparent if spectral subtraction is attempted (Figure 7), but grinding does not seem to have any additional significant effects over just simply mixing (Figure 8). This is the opposite of what was seen in the NIR where grinding the mixed materials together intensified the effects. Thus overall, the effects in the mid-IR of adding biochar to soils appears to be less than in the NIR despite the fact that NIR radiation penetrates much deeper than mid-IR radiation and thus any particle coating effects should be much greater in the mid-IR. As silica does not absorb in the NIR, the effects seen in the mid-IR are not expected in the NIR, but the effects on the C-H and N-H regions seen in the NIR between 5000 and 4000 cm^{-1} might well have been expected in the mid-IR. These results overall seem to support a physical spectral effect, which nevertheless could have significant effects on calibration development especially for remote sensing using visible (Not examined here) or NIR spectra.

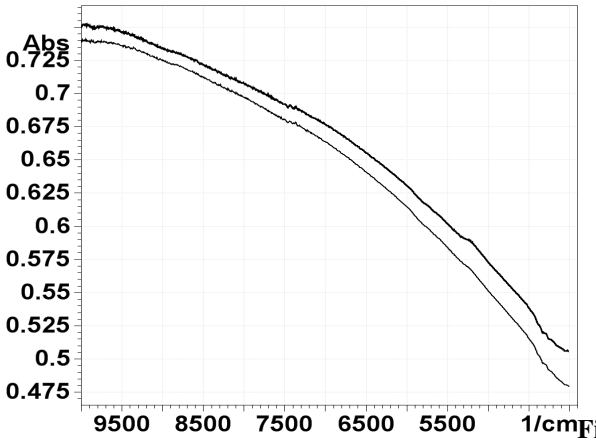

Figure 3. Spectra of 6% Inga 500 biochar in soil (Bottom) and after storage for 11 days over water (Top).

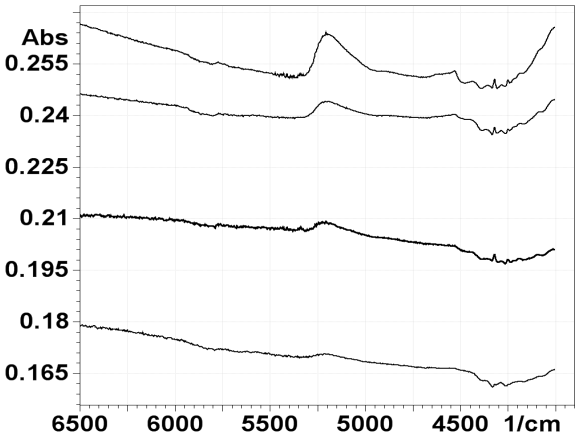

Figure 4. Spectra of (Top to bottom): a. non-ground, and b, ground soil, c. from spectral sub. of Inga 400 C biochar spec. from spec. of 6% IG400 mixed with soil, and d. ground with soil.

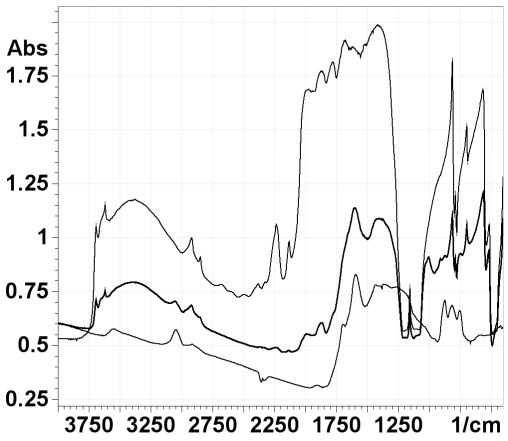

Figure 5. Mid-infrared spectra of soil, soil + 6% Inga 500 biochar (IG500) and IG500 (Top to bottom).

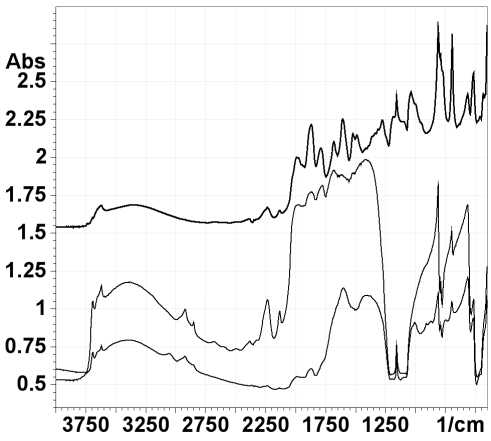

Figure 6. Mid-infrared spectra of (Top to bottom): 50% silica in KBr (Shifted + 1.5 A), of soil, soil + 6% Inga 500 biochar (IG500).

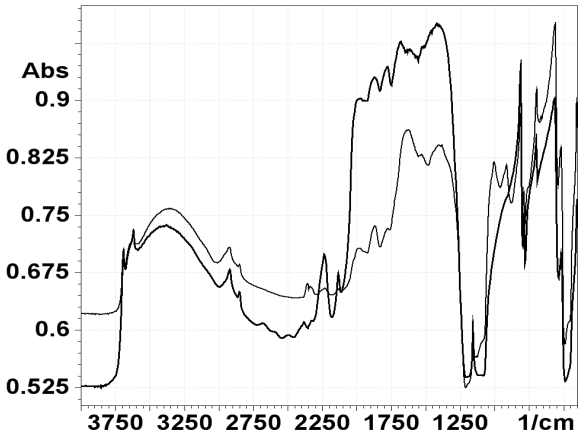

Figure 7. Normalized mid-infrared spectra of soil and from spectral sub. of Inga 400 C biochar spec. from spec. of 6% IG500 mixed with soil.

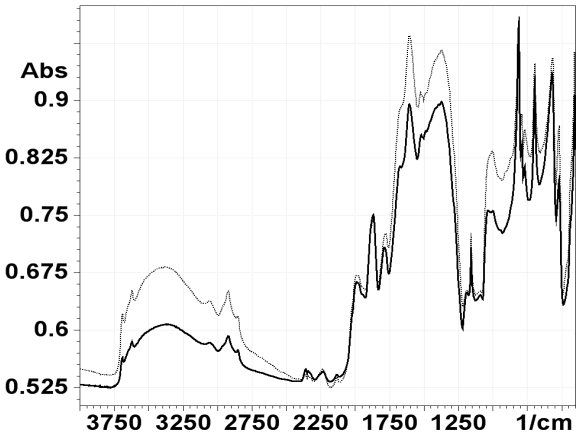

Figure 8. Spectra of 6% IG400 mixed with soil (Dotted line) and ground with soil (Solid line).

Conclusions

Results on biochar amended soils showed that the addition of biochar to soil results in spectral distortions which tend to mask, and or distort, the spectral signature of the original soil carbon. These effects are particularly evident when applying spectral subtraction to the resulting spectra in that the combined spectra of biochar and soil are not additive, e.g. spectrum of (mixed char + soil) – spectrum of char <> spectrum of

soil, as should be the case if there were no physical or chemical interactions. These effects are particular evident in the NIR region between 5000 and 4000 cm^{-1} where significant information on soil carbon is found and could have profound effects on attempts to determine total soil carbon by NIR in biochar amended soils. Similar distortions were found in the mid-IR, but primarily in the region dominated by silica, and while making spectral interpretation potentially more difficult, may have less effect on the ability to develop calibrations for soil carbon in biochar amended soils, but further research will be needed in both spectral regions to answer this question. Interestingly, results using sand in place of soil with mid-IR spectra did not show the same effects. The difference between the NIR and mid-IR results are curious as one would expect less rather than greater effects in the NIR due to the greater ability of NIR radiation to penetrate deeper into the samples. As silica does not absorb in the NIR, the effects seen in the mid-IR are not expected in the NIR, but the effects on the C-H and N-H regions seen in the NIR between 5000 and 4000 cm^{-1} might well have been expected in the mid-IR. These results overall seem to support a physical spectral effect, which nevertheless could have significant effects on calibration development especially for remote sensing using visible (Not examined here) or NIR spectra.

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