

# Mid-Infrared Spectroscopic Properties of Humic Acid and Fulvic Acid-Soil Mixtures.

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## 1. Introduction

The detection of humic materials in soils is essential in order to determine organic matter (SOM) stability and C sequestration on agricultural land. Mid-Infrared (MidIR) spectroscopy has been used to characterize SOM quality [1], study extracted soil humic acids [2], develop calibrations for quantifying SOM [3], and to study decomposition of organic matter in soil [4]. However, infrared spectra from soils are the result of a multitude of combined absorbances from organic and mineral bands, and some of the spectral signatures of humic acids can be lost or confounded in soil matrices.

In this study, we added different amounts of authentic humic and fulvic acid standards to ashed soil in order to identify reliable spectral MidIR bands for marking the presence and amount of stable organic matter in soil.

## 2. Materials and Methods

In order to obtain soils free of organic matter background, we ashed Elliott Silt Loam Soil (International Humic Substances Society (IHSS), St Paul, MN) at 550 °C for 3 h. Besides the Elliott soil standard, we also ashed two soils from Akron Colorado, one was an eroded (high erosion) soil of low SOM, and the second was a prairie top soil of moderately high SOM (low erosion). We obtained the following standards from the IHSS to be mixed with the ashed soils: Suwannee River Humic Acid, Suwannee River Fulvic Acid, Elliott Soil Humic Acid, Pahokee Peat Humic Acid, and Pahokee Peat Fulvic Acid. The standards were mixed with the soils using a dilution series of 1/10, 1/100 and 1/1000 standard/soil ratios before scanning. The mixtures, as well as the neat soils and standards were scanned on a Digilab FTS7000 Fourier transform spectrometer (Varian, Inc., Palo Alto, CA) in line with a Pike AutoDIFF diffuse reflectance sampler (Pike Technologies, Madison, WI) in the MidIR range (4000 to 400 cm<sup>-1</sup>).

## 3. Results and Discussion

**Mid IR observations of the spectra from the pure humic acids, fulvic acids, soils, and ashed soils.** The humic acids absorbed prominently at the broad band around  $3400\text{ cm}^{-1}$ , commonly assigned to OH (or NH) stretching in plant-derived materials, although it will be largely to OH in the humic acids [4]. This prominent wide band can be observed in the Suwannee River Humic Acid spectrum (Fig. 1). Whole soils and fulvic acids absorb moderately in this region. Ashed soils lost absorbance at  $3400\text{ cm}^{-1}$  because of the combustion and loss of organics. From  $2870\text{-}2950\text{ cm}^{-1}$  lies the aliphatic CH stretching band that marks the presence of methyl and methylene groups [1, 3, 4]. Humic acids absorb in this band (Fig. 1), with whole soils and fulvic acids having intermediate absorbance, and ashed soils having the least absorbance. At  $2600\text{ cm}^{-1}$  is the carboxylic acid OH stretching band, which forms a shoulder on humic acid spectra (Fig. 1). At  $1730\text{ cm}^{-1}$  is the C=O bond stretching band of carboxylic acid [3,4], and esters [1], which is one of the most marked spectral features in humic and fulvic acids. Cox et al., [5] state that this band is characteristic to soil humic compounds. Our results support this, as seen in the Suwannee River Humic Acid spectrum (Fig. 1). Bands at  $1640$  and  $1560\text{ cm}^{-1}$  mark the presence of amides in organic materials, but others have shown them to be present in humic acids, which can contain N due to free radical coupling of nitrogenous substances [2]. The Pahokee Peat and Elliott Soil humic acids were strong absorbers, and ashing soils diminished the absorbance in this spectral region (data not shown). The same pattern was found for absorbance at  $1610\text{-}1620$  and  $1517\text{ cm}^{-1}$ , both aromatic bands present in the stable fraction of soil organic matter. The Suwannee River fulvic acid, Pahokee Peat humic acid, and Elliott Soil humic acid absorb strongly in the region between  $1400$  and  $1350\text{ cm}^{-1}$  dominated by phenolic, or COO stretching vibrations of oxidized carbon and  $\text{CH}_3$  bending [3, 4]. At  $1335\text{ cm}^{-1}$  is a peak of possible mineral influence given the high absorbance of the ashed soil (Fig. 1). The fulvic and humic acids absorb in the region around  $1230\text{ cm}^{-1}$  for aromatic  $-\text{CH}$  (Fig. 1), and at  $1030\text{-}1160\text{ cm}^{-1}$ , a region assigned to  $-\text{COH}$  stretching. Note that bands at  $2200\text{-}2000$ ,  $1230$ ,  $1030\text{-}1160\text{ cm}^{-1}$  have been found by others to be important for soil organic C calibrations [3]. The  $1030\text{-}1160\text{ cm}^{-1}$  region lies in the quartz inversion band, which explains the low absorbance in the neat soil samples (data not shown). Note that absorbance between  $1030$  and  $400\text{ cm}^{-1}$  varies widely among the humic and fulvic acids. This region is difficult to interpret, with many bands of uncertain mineral or organic origin.

The MidIR spectra also provide useful information about the mineral composition of the soils. All the intact and ashed soils have the clay OH stretching peak at  $3600\text{ cm}^{-1}$  (Fig. 1) [6]. The

high erosion soils (ashed and intact) have a peak at and  $2517\text{ cm}^{-1}$  indicative of the presence of calcium carbonate (data not shown) [6]. This is due to the fact that erosion has removed the original soil surface to a level where the caliche layer is exposed on these soils. All the soil spectra show the peaks at 1970-2000, 1870, and  $1790\text{ cm}^{-1}$ , which are quartz overtone combination bands [6] indicative of sand content, and can be seen in the ashed Elliott soil (Fig. 1).

**Spectral subtraction of standard-soil mixture spectra from ashed soil spectra.** The spectral subtraction approach allows us to mathematically isolate spectral bands of humic and fulvic acid standards when they are in the presence of a mineral soil matrix. The subtracted spectrum in Figure 1 indicates that the addition of humic acid to soil increases absorbance in the region between  $3400\text{-}2800\text{ cm}^{-1}$ , due to the increased concentration of OH and CH groups. Perhaps the most marked effect on the spectra was an increase in the absorbance near  $1730\text{-}1630\text{ cm}^{-1}$ , possibly due to C=O bonds, amides, and/or aromatics. These effects were observed across most humic and fulvic acids, and in some cases could be found at up to 1/1000 dilution of standard in ashed soil (data not shown).

#### **4. Conclusions**

Several regions of the MidIR spectrum decrease in soils upon ashing, and at the same time are highly absorbed by humic and/or fulvic acids. These regions include  $3500\text{-}2000$ ,  $1830\text{-}1520$ , and  $1260\text{-}990\text{ cm}^{-1}$  and should thus be considered organic matter bands in soils. Other MidIR regions outside these bands are predominantly of mineral absorption or from a mixture of organic-mineral absorption. The  $2870\text{-}2950\text{ cm}^{-1}$  is one of the few regions of the MidIR soil spectrum where absorbance is almost exclusively from organics, with little absorbance due to mineral sources. Our spectral subtraction approach suggests that  $3400\text{-}2800$  and  $1730\text{-}1630\text{ cm}^{-1}$  are regions that can be attributed to stable organic compounds in soil spectra.

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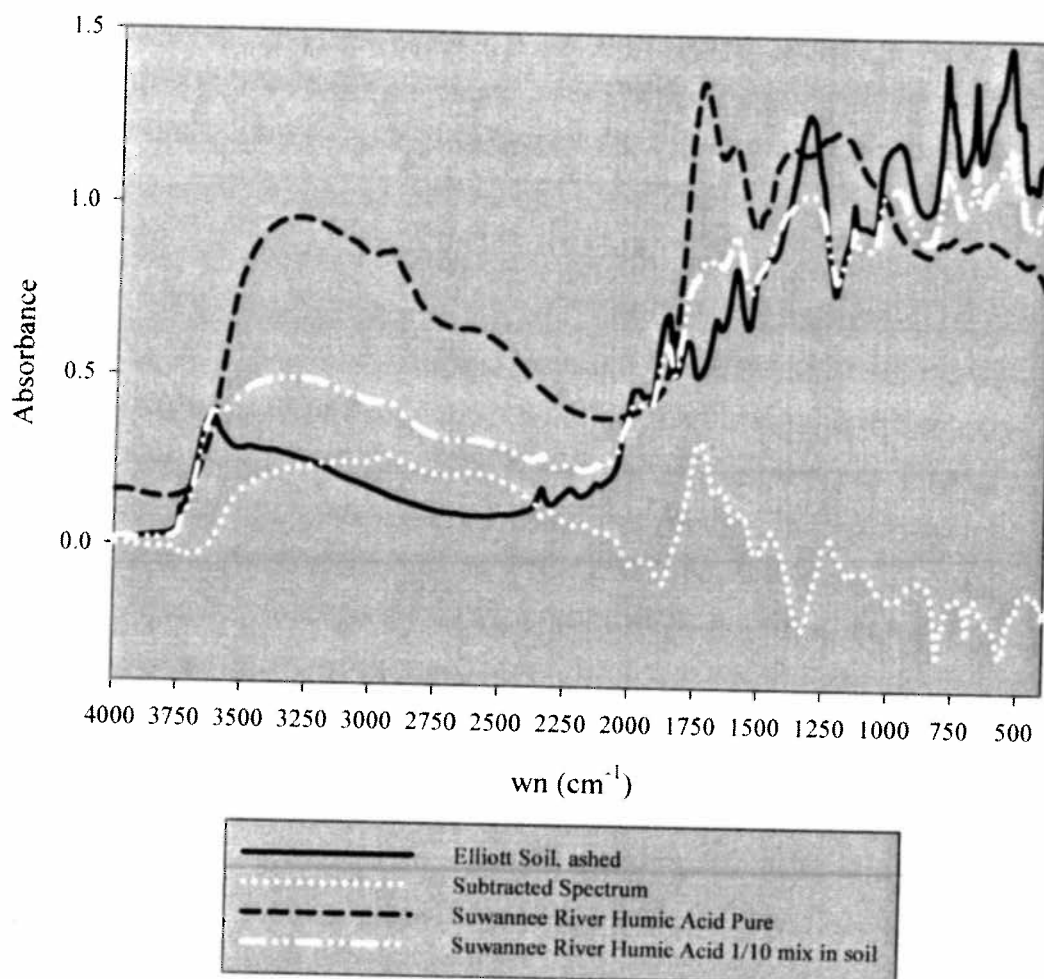


Figure 1. Mid Infrared spectra of the Elliott ashed soil, Suwannee River Humic Acid, the soil and humic acid mix. The subtracted spectrum is: (ashed soil and humic acid mixture) – (ashed soil).

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