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ERDC 6.1 Geospatial Research and Engineering (GRE) and
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Spectral Assessment of Soil Properties

Standoff Quantification of Soil Organic Matter Content in Surface Mineral Soils and Alaskan Peat

Stacey L. Jarvis, Thomas A. Douglas, Karen L. Foley, Robert M. Jones, John E. Anderson, Stephen D. Newman, and Robyn A. Barbato

August 2017

View overlooking the Alaska Peatland Experiment (APEX) bog site

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and Robyn A. Barbato

U.S. Army Engineer Research and Development Center (ERDC)
Cold Regions Research and Engineering Laboratory (CRREL)
72 Lyme Road
Hanover, NH 03755

Thomas A. Douglas

U.S. Army Engineer Research and Development Center (ERDC)
Cold Regions Research and Engineering Laboratory (CRREL)
Building 4070, Second Avenue
Fort Wainwright, AK 99703

John E. Anderson

U.S. Army Engineer Research and Development Center (ERDC)
Geospatial Research Laboratory (GRL)
Corbin Field Station c/o NOAA NOS
15319 Magnetic Lane
Woodford, VA 22580

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Abstract

Characterization of soil properties typically requires time-intensive, ground-based sampling. Therefore, technologies that allow for rapid assessment of particular attributes would be greatly beneficial. One example is Fourier transform infrared (FTIR) spectroscopy, which uses an infrared spectrum to qualitatively identify a variety of compounds in solid, liquid, or gaseous samples. This study investigated the infrared reflectance signatures of peat and mineral soil samples with varying amounts of organic matter and coupled FTIR spectroscopy with a thermogravimetric analyzer (TGA) to more accurately identify and quantify soil organic matter (SOM). Clear differences were observed between the soil and peat FTIR spectral profiles. When compared to traditional analysis by loss on ignition, the coupled TGA-FTIR method resulted in an underestimation of the percent SOM for peat samples and an overestimation of the percent SOM in mineral soil samples. These results may have been influenced by low sample mass and moisture present in the sample. In total, our project results show that FTIR measurements provide a rapid yet qualitative means of assessing sample organic matter versus mineral content, but the TGA-FTIR measurement capability needs more refinement before it can be used for qualitative SOM measurements.

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Preface

This study was conducted for the Assistant Secretary of the Army for Acquisition, Logistics, and Technology under the U.S. Army Engineer Research and Development Center (ERDC) 6.1 Geospatial Research and Engineering (GRE) Program's "Variations in Wetland Terrain Feature conditions: the Role of Permafrost and Impacts to Military Operations" and the ERDC 6.2 GRE Program's Army Terrestrial-Environmental Modeling and Intelligence System Science Technology Objective—Research (ARTEMIS STO-R), "Dynamic Representation of Terrestrial Soil Predictions of Organisms' Response to the Environment (DRTSPORE)." This work was funded by the ERDC Basic and Applied Research Program Office. The technical monitor was Dr. Robyn Barbato, CEERD-RRN.

The work was performed by the Biogeochemical Sciences Branch (CEERD-RRN) of the Research and Engineering Division (CEERD-RR), ERDC Cold Regions Research and Engineering Laboratory (CRREL). At the time of publication, Dr. Justin Berman was Chief, CEERD-RRN, and CDR J. D. Horne, USN (Ret), was Chief, CEERD-RR. The Deputy Director of ERDC-CRREL was Dr. Lance Hansen, and the Director was Dr. Joseph L. Corriveau.

COL Bryan S. Green was the Commander of ERDC, and Dr. David W. Pittman was the Director.

Acronyms and Abbreviations

APEX	Alaska Peatland Experiment
ARTEMIS	Army Terrestrial-Environmental Modeling and Intelligence System
ATR	Attenuated Total Reflectance
CEC	Cation Exchange Capacity
C-H	Carbon-Hydrogen
C=O	Carbonyl
CRREL	Cold Regions Research and Engineering Laboratory
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
DRTSPORE	Dynamic Representation of Terrestrial Soil Predictions of Organisms' Response to the Environment
ERDC	U.S. Army Engineer Research and Development Center
FTIR	Fourier Transform Infrared
GRE	Geospatial Research and Engineering
KBr	Potassium Bromide
L	Loam
N	Nitrogen
O-H	Hydroxyl Group
OM	Organic Matter
SL	Sandy Loam
SOM	Soil Organic Mater
STO-R	Science Technology Objective—Research
TGA	Thermogravimetric Analyzer

1 Introduction

1.1 Background

Organic matter is a critical component of all terrestrial soil systems. Varying levels of organic matter can result in direct and indirect effects on soil characteristics, such as biological activity, water retention, and soil strength (Kamnev 2008; Simkovic et al. 2008; Six et al. 2004). In total, these characteristics control how soils respond to environmental disturbance. Soil organic matter (SOM) abundance and quality effect many trophic levels, from microorganisms to higher-order plants (Bauer and Black 1994) and plays an integral role in soil aggregate formation and stabilization (Six et al. 2004). Quantification of SOM in soil could provide insight into biological processes such as carbon and nitrogen mineralization and organic nitrogen fixation (Bauer and Black 1994) as well as many physical processes controlled by local environmental conditions. For example, degradation of organic structures in soil by heating is associated with a decrease in soil water repellency (Simkovic et al. 2008). Current approaches to measuring organic matter rely on time-consuming laboratory analyses. The ability to rapidly assess SOM content across a large area would greatly benefit activities where soil composition and strength are important to mission success, such as revegetation of degraded lands, assured mobility across terrain, or predictions of soil state as influenced by local weather patterns (Sheoran et al. 2010; Barbato et al. 2016). Of particular utility would be a field-deployable rapid means of assessing SOM to reduce the costs of sample identification, collection, and analysis by constraining environmental sampling campaign efforts.

Fourier transform infrared (FTIR) spectroscopy is a non-destructive, rapid method of analysis. It can be used to qualitatively identify a variety of compounds in solid, liquid, or gaseous samples (King et al. 2004). Infrared spectra provide insight into the identity of functional groups present in a sample, particularly in organic compounds (Skoog 2004). FTIR spectroscopy has been used to characterize organic compounds in a variety of materials, including soils. For example, it has been used to determine the degree of decomposition occurring in peats by comparing the spectral signatures observed across different soil horizons (Artz et al. 2006). Statistical analysis can be used to compare the spectral signature of a sample to other chemical and biological data that have been collected (Chapman et al.

2001). FTIR analysis has also been successfully applied in assessing soil responses to environmental changes, such as thermal destruction; the effect of stressors such as heavy metal presence; and plant responses to nutritional stress (Kamnev 2008; Dlapa et al. 2013; Simkovic et al. 2008). Changes in soil biogeochemical attributes can be deduced from peak shifts and intensity fluctuations. In addition, statistical analysis can be used to relate the spectral signature of a sample to other chemical and biological data inherent to that sample to gain insight into soil processes (Chapman et al. 2001).

Because of the complexity of soils and the presence of matrix interferences, infrared spectral analysis of soils can be more difficult than for more chemically consistent or predictable samples such as pharmaceuticals (Margenot et al. 2016). To overcome many of these issues, there are several advantages to using FTIR instruments rather than dispersive infrared instruments. FTIR spectroscopy is a faster method because all wavelengths of the spectrum are detected and measured simultaneously. Dispersive instruments separate frequencies using gratings, so only one wavelength can be measured at a time. The source energy that interacts with the sample is limited by a slit in the instrument, which decreases the quality of the data. As energy reaching the sample is not limited in FTIR instruments, they have better sensitivity because the signal-to-noise ratio is much higher (Skoog 2004). FTIR instruments also have better precision and accuracy because the same laser is used for every sample (Skoog 2004). Dispersion instruments depend on external calibrations, which makes it more difficult to compare data.

Thermogravimetric analysis (TGA) is a technique traditionally used to determine the mineral components in a soil but can also be applied to broadly distinguish carbon compounds through controlled heating rates (Pallasser et al. 2013). TGA is based on the continuous measurement of mass loss of a sample during heating in a controlled atmosphere (Oudghiri et al. 2015). This methodology has proven to be successful when coupled with FTIR in obtaining a temporal resolution of sample components via acquisition of spectral signatures concurrent with mass loss measurements due to volatilization (Oudghiri et al. 2016). FTIR spectra, collected from the off-gas generated as samples are heated, can be used to identify the composition of volatile organic compounds evolved at a particular temperature.

1.2 Objectives

Recognizing that FTIR has been used in a variety of soil science applications, we sought to adapt and refine these protocols to provide a well-established, streamlined, in-house analytical procedure for analyzing complex mineral soil and organic rich peat samples using FTIR or FTIR coupled with TGA. We acquired and analyzed spectral signatures of soil and peat containing varying amounts of organic matter to determine if the organic matter content could be quantified using thermogravimetric analysis (TGA) coupled with Fourier transform infrared (FTIR) spectroscopy (TGA-FTIR). The coupled TGA-FTIR approach provides a spectral fingerprint of a soil and a measure of mass loss whereas traditional methods for quantifying percent organic matter address mass loss only. We evaluated FTIR spectroscopy as a potential standoff sensing application for the rapid assessment of SOM quality and content to save time and resources and to provide information on soil condition and mineralogy. This type of information may prove useful in making soil assessments that then inform specific applications, such as assured mobility, or in obtaining environmental intelligence. Our ultimate goal is to develop field-deployable rapid measurement tools to identify SOM in a variety of soil types.

1.3 Approach

We evaluated spectral signatures of soil and peat to determine if FTIR spectroscopy is a sufficient alternative method to characterize SOM. We analyzed FTIR and TGA-FTIR signatures to determine if spectral outputs compared favorably to soil composition and percent organic matter measured through traditional laboratory methods. We investigated how the FTIR signatures of peat samples differed from mineral soils and changes in TGA-FTIR-derived signatures of peat and mineral soils containing varying amounts of soil organic matter to better assess this technology as a useful measurement of SOM. Our peat samples were collected in central Alaska, near Fairbanks, at field sites where the soil, organic matter, and vegetation characteristics are well known from previous work. Mineral samples were collected from test plots in Hanover, New Hampshire.

1.4 Limitations and gaps

Interpretation of FTIR spectra of soil and other complex matrices has proven to be difficult because of the heterogeneous nature of the material

(Margenot et al. 2016), and spectroscopic resolution of SOM is often limited by this complexity and by the dominance of the mineral component of the soil (Margenot et al. 2016). The spectral subtraction technique has been used to isolate components of a spectrum; however, one must consider the limitations and validity of the resulting spectra (Margenot et al. 2016). Typically, a background is subtracted from the sample spectrum to yield a resulting spectrum with a targeted objective. For example, to increase the organic infrared spectral signal in a soil sample, the sample is initially analyzed, heated to 350°C to remove the organic component, and then reanalyzed. The resulting spectral subtraction, initial minus combusted, in theory would exhibit an enhanced SOM profile (Margenot et al. 2016). However, even following subtraction, band overlapping of different functional groups makes for particularly difficult interpretations. This has been somewhat overcome by using the first and second derivate of the spectrum. These derivations enhance differences in peak intensity and can be used to determine significant differences between samples through statistical analysis.

At the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), we are currently quantifying SOM by using the traditional loss on ignition method. Loss on ignition involves a sample being heated to a particular temperature, typically between 200°C and 430°C, to burn off organic compounds. The change in mass is then reported as a percent organic matter. However, the resulting compounds that were volatilized are not known. Using TGA-FTIR, we can determine the change in mass as a sample is heated, monitor this change over time, and obtain spectra of compounds as they are volatilized. In theory, using all data points, SOM can be quantified and identified, providing a more thorough understanding of the SOM present in a sample.

There is limited research and methodology pertaining to handheld FTIR instruments being used to determine SOM content in situ (Robertson et al. 2015). Ambient atmosphere conditions make it difficult to take FTIR analysis into the field due to strong water absorptions in the mid-infrared when using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) (Reeves et al. 2010). However, spectral signatures are a potential way to characterize soils by using standoff sensing and would eliminate the need to rely on field collections and destructive laboratory analyses to obtain accurate chemical and biological measurements. To develop standoff sensing as a means of characterizing soils over a large area, a more thorough understanding of the reflectance properties of soils is needed so that the technology can move from a qualitative to a quantitative application.

2 Part One: Mineral Soils vs. Peat—SOM Characterization

2.1 Experimental methods

Phase one of the initial investigation began with establishing a protocol for analyzing soils by using a Nicolet 6700 diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) module (ThermoFisher Scientific, Waltham, MA). DRIFTS, as a method, may be more appropriate for analyzing soil than attenuated total reflectance (ATR) due to the roughness of soil. ATR measures internal reflectance and involves the interaction between the sample and a crystal, and therefore good contact between the two is necessary. This intimate contact could be hindered by soil particles, resulting in limitations in using ATR for soil assessment. DRIFTS analyzes the bulk of the sample through diffuse reflection. Specular reflection occurs when the laser source hits the surface of the sample and reflects back at one angle to the detector. Alternatively, diffuse reflectance occurs when the laser penetrates the sample and the incident ray is reflected at many different angles, moving through the matrix before reaching the detector. DRIFTS has proven useful when analyzing samples with a rough surface, such as soil, since it accounts for diffuse scattering between particles (Khoshhesab 2012).

This study analyzed four soils with diverse soil properties. The soils included a loam soil with a low organic matter content (L−OM), a sandy loam soil with organic matter (SL+OM), a sandy loam soil with low organic matter content (SL−OM), and a sandy loam soil (SL). These samples were collected from test plots at the Soil Microbiology Field Site located at the Cold Regions Research and Engineering Laboratory in Hanover, New Hampshire, as described in Barbato et al. (2016) (Table 1). Samples Peat 1 and Peat 2 were collected from two biologically discrete Alaskan bogs, the Farmers Loop bog (64.8751° N, 147.6831° W), an ERDC-CRREL National Geotechnical Engineering site, and the Alaska Peatland Experiment (APEX) bog site (64.6922° N, 148.3278° W), respectively. Site access to the APEX bog was provided by Dr. Merritt Turetsky at the University of Guelph as part of the Bonanza Creek Long Term Ecological Research program funded by the National Science Foundation.

For this study, dry mineral soils were sieved using a 250 μm sieve and stored in a desiccator until time of analysis. Peat samples required a slightly different preparation protocol. In brief, peat samples were ground using the A11 basic analytical mill (IKA Works, Inc., Wilmington, NC) and then sieved using a 250 µm sieve. Before each sample analysis, we collected background spectra for both peat and mineral soils by using a gold disk. The software automatically subtracted the background from the sample spectrum. Sample spectra were collected using the instrument's default setting of 32 scans at a resolution of 8 cm^{-1}.

Samples were also combined with potassium bromide (KBr) and analyzed separately to attempt to increase resolution. KBr does not absorb in the near infrared. Therefore, diluting samples with KBr allows the laser to penetrate deeper into the sample, which increases scattering and minimizes the specular reflection at the surface. Specular reflection can lead to changes in band shape and an increase in relative intensity. After being sieved, the soil samples and the peat samples and were combined with finely ground KBr in a 1:100 ratio. For these samples, a KBr background was used rather than the gold disk. For our purposes, we decided to report the neat samples that were not diluted with KBr as peaks were more easily distinguishable.

2.2 Results and discussion

We measured the spectral signatures of soil and peat samples and determined that the signatures were different through spectra observations. While this result was expected, the results can be used to develop a reference library from which to discern SOM. Because peat is composed of nearly 90% organic matter, it can serve as a reference fingerprint for assessing SOM. For example, the aliphatic and aromatic carbons present in the peat materials provide a signature for SOM that can be used to assess the abundance of SOM in other soils, such as the mineral soils examined in this study.

We found the spectral signatures of the mineral soils to be consistent with those previously reported for soils collected from Pantelleria, Italy (Saiano et al. 2013). Figure 1 illustrates the four mineral soil spectra along with peak assignments. Organic and inorganic compounds were observed in all spectra. Absorbance peaks from 3100 to 3600 cm^{-1} were assigned to hydroxyl group (O-H) vibrations of clay and iron oxides. Absorbance peaks from 800 to 600 cm^{-1} were assigned to other mineral vibrations (Saiano et al. 2013). Peaks in this area were particularly hard to decipher. Further resolution in this area may be possible through spectral subtraction techniques, such as ashing or chemical oxidation, to obtain a mineral background or through the use of a mineral standard as the background (Margenot et al. 2016). Peaks assigned to aliphatic and aromatic carbons were absorbed from 2980 to 2850 cm^{-1} and 1620 to 1600 cm^{-1}, respectively. The spectral signature of SL+OM had more intense aliphatic and aromatic peaks when compared to the other mineral soils. SL+OM had the highest percent organic matter of all of the four soils (Table 1).

Figure 1. Average spectral signature for each mineral soil, *n* = 3. (Peak assignments referenced from Saiano et al. 2013.)

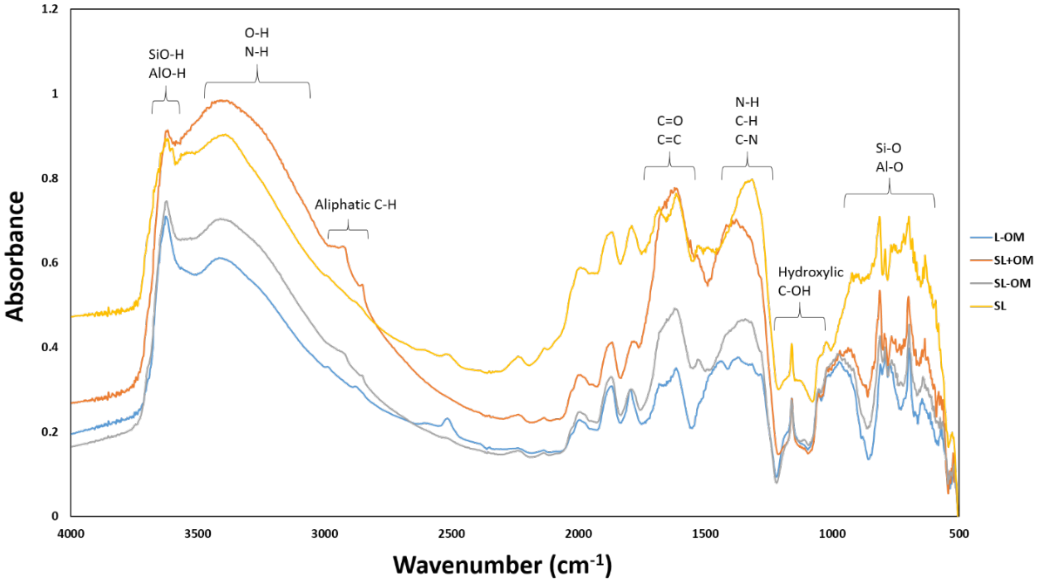
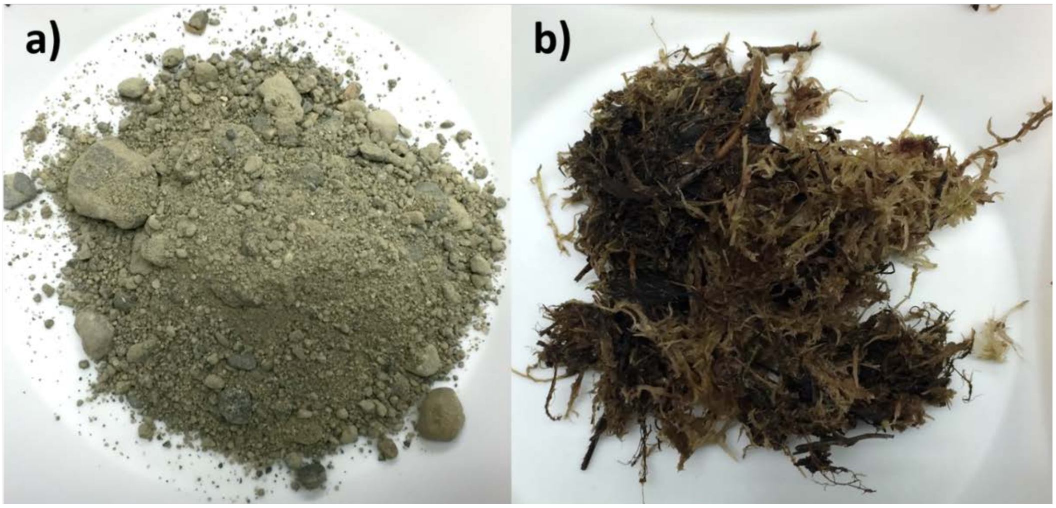


Table 1. Soil properties of the soils tested, including particle size distribution, pH, cation exchange capacity (CEC), organic matter content (OM), and nitrogen (N) content. Values are reported as means (standard error in parentheses) (*n* = 3). (Table from Barbato et al. 2016.)

Soil	Sand (%)	Silt (%)	Clay (%)	pH	CEC (meq/100g)	OM (%)	N (%)
SL+OM	67.2 (0.6)	26.3 (0.4)	6.5 (0.2)	7.0 (0.1)	10.9 (0.1)	3.3 (0.1)	0.20 (0.01)
SL	66.4 (0.2)	25.9 (0.6)	8.4 (1.0)	6.6 (0.0)	8.6 (0.1)	2.6 (0.0)	0.17 (0.00)
L−OM	47.6 (0.9)	40.8 (0.8)	11.5 (0.5)	8.1 (0.1)	14.0 (0.5)	ND	0.02 (0.00)
SL−OM	65.6 (0.8)	24.1 (0.6)	10.2 (0.2)	7.7 (0.0)	11.6 (0.2)	0.9 (0.1)	0.09 (0.00)

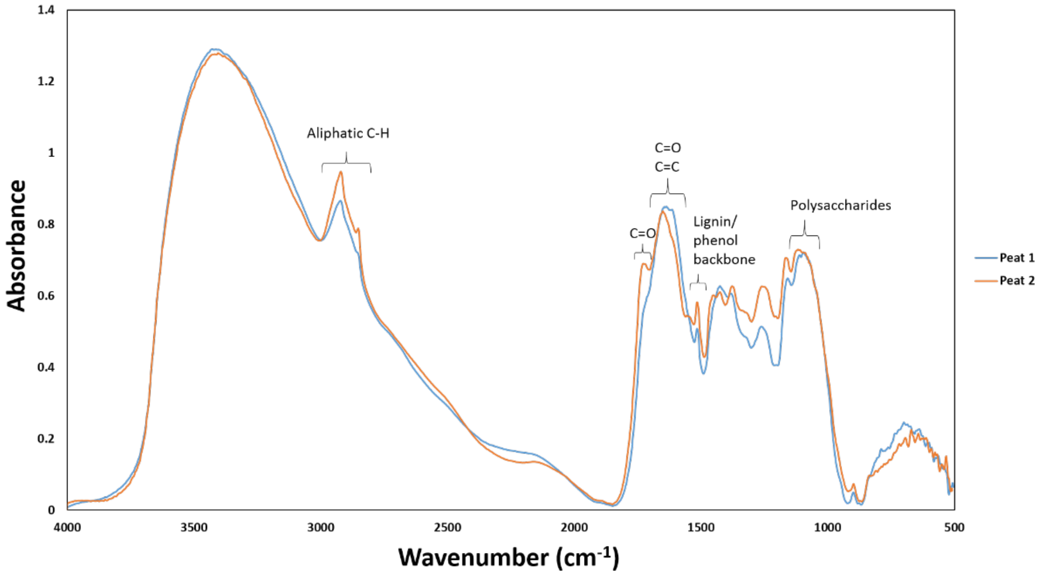
We analyzed two peat samples from Alaskan bogs to determine if there were obvious spectral differences between peat and soil. The term *peat* refers to saturated soil-like ground consisting of partially decomposed plant material. The spectral signatures of the two peat samples were very similar. The only obvious difference occurred at around 1720 cm^{-1}. This peak is indicative of carboxylic acids and aromatic esters (Hodgkins et al. 2014).

Figure 2. Comparison of (*a*) loam without organic matter (L–OM) and (*b*) peat from Farmers Loop, AK (Peat 1), prior to drying and sieving.



Visually, the peat samples were very different from the mineral soils (Figure 2) and this was reflected in the acquired infrared spectra (Figures 1 and 3). The peaks associated with mineral vibrations disappeared in the peat samples. This was expected as peat is mostly composed of decomposed plant material. An increase in aliphatic carbon intensity was seen in both peat samples when compared to the mineral soils. Lipids, fats, and waxes are examples of aliphatic carbon chains (Hodgkins et al. 2014), all of which would be expected in peat. The peak from 1600 to 1650 cm^{-1} had a greater intensity than the soil spectra. This peak has been attributed to lignin and other aromatics or aromatic or aliphatic carboxylates (Hodgkins et al. 2014). Lignin is a specific type of organic polymer found in the structural parts of plants, specifically cell walls. In the peat spectra, there was a pronounced peak from 1030 to 1080 cm^{-1}, showing the presence of polysaccharides. This peak was not noticeable in the mineral soil spectra because of the superimposed mineral absorptions.

Figure 3. Average spectral signature for each peat sample, $n = 3$. (Peak assignments referenced from Hodgkins et al. 2014.)



Because of the complexity of soil, chemical information is not easily accessible by visually looking at the spectral signatures. Statistical analysis is required to further decipher the signatures and quantitate the acquired data. In future work, we will perform statistical analyses such as least-squared analysis and ordination techniques (i.e., principle components analysis) on the data set generated in this study to determine whether we could identify significant differences in spectral signatures between the mineral soils, particularly with respect to abundance of SOM. These methods are useful for application to complex data sets in that they reduce the redundancy in the data to manageable levels and allow for the investigation of subtle changes in spectral shapes through analysis of derivatives (Plante et al. 2009). Spectral subtraction would also be a potential way to reduce the overlapping bands and to enhance identification of the peaks of interest. The identification of unique spectral signatures (for example, related to SOM), could also be related with other chemical and biological attributes of the same soil. If correlations are strong, then chemical and biological attributes could potentially be inferred from the infrared spectral measurements alone.

3 Part Two: TGA-FTIR

3.1 Experimental methods

Phase two of the initial investigation began with establishing a method for analyzing two of the mineral soils (L−OM and SL+OM) and both peat samples on the coupled TGA-FTIR system (TGA Q50, TA Instruments, New Castle, DE). Dried mineral soil and peat samples were sieved to remove particles greater than 250 µm. Approximately 10 mg of each sample was transferred to an aluminum low-mass, tared pan. The transfer line and gas cell were heated to 280°C for 1 hour prior to analysis. The purge gas through the TGA was nitrogen at flow rate of 20 mL/min with a balance purge of 40 mL/min. The furnace temperature was increased from 20°C to 600°C at a rate of 20°C/min. Spectra were collected from 4000 to 600 cm^{-1} every 12 s at 8 cm^{-1} resolution. The system was left to cool back to room temperature before the next run began.

Output from the TGA-FTIR includes a Gram-Schmidt thermogram, linked spectral signatures, mass-loss plot, and three-dimensional representations of the time-resolved spectra obtained during heating. The Gram-Schmidt thermogram uses algorithms to transform the independent data outputs from the instrument into one spectrum and depicts the total absorption of evolved components throughout the run. Prominent peaks on the thermogram, with linked spectra, indicate volatilized compounds for quantitative (area under the peak) and qualitative (spectral profile) assessments. The mass plot generated by the TGA is used in conjunction with the Gram-Schmidt thermogram when trying to determine when compounds are volatilized. Changes in slope of the mass-loss plot indicate mass loss, and the derivative of the mass plot is used to help determine at what time or temperature significant mass loss occurred.

3.2 Results and discussion

As expected, the output spectra from the peat samples and the soil samples were quite different from one another, particularly at 2370 cm^{-1}, which represents evolved CO_2 in the off-gas and was used as a proxy for SOM. This was expected because the peat has more plant material and organic matter as compared to the mineral soils.

3.2.1 Mineral soils

We chose L−OM and SL+OM mineral soils to encompass a range of organic matter content. Soil L−OM had the lowest percent organic matter, and SL+OM had the highest of the four mineral soils analyzed (Table 1). Results indicated no obvious absorptions on the Gram-Schmidt plots for either mineral soil (Figure 4). Neither soil showed a definable peak to indicate that a compound had been volatilized. The mass plot and derivative mass plot of L−OM did not show much mass loss; however, the SL+OM mass plot and derivative mass plot did (Figure 5). Mass loss from the SL+OM sample was calculated to be 5.6%, and mass loss from L-OM was calculated to be 1.1%. The loss in mass from both samples was slightly higher than the organic matter previously cited by Barbato et al. (2016) (Table 1); however, some of the mass loss could be attributed to moisture as these samples were only air dried prior to analysis. Linked spectra could not be resolved from the Gram-Schmidt plot for either soil, but the three-dimensional representation of SL+OM (Figure 6c and d) showed a slight increase in absorbance at 2370 cm^{-1}, which was also observed in the peat samples (Figure 9). This suggested that similar compounds were being volatilized, just in much smaller quantities, which is expected as peat has high organic matter content and the SL+OM soil has a small amount of organic matter (Table 1). No peaks could be resolved at this wavenumber in the three-dimensional representation of L−OM (Figure 6a and b), which may be due to untraceable amounts of organic matter in this soil.

Figure 4. Gram-Schmidt thermograms of (*a*) L−OM and (*b*) SL+OM.

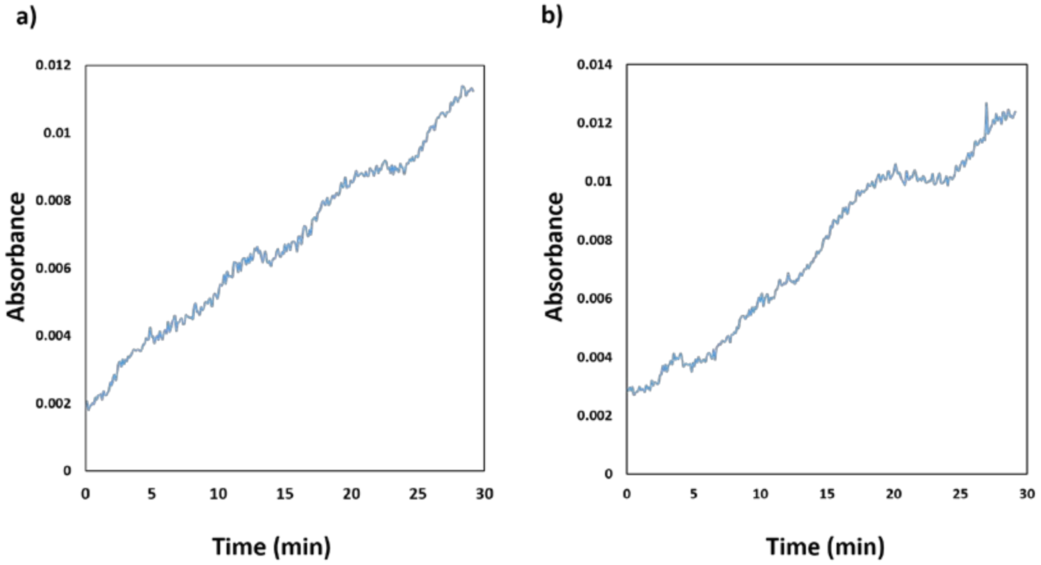


Figure 5. Mass and mass derivative plots of (*a*) L−OM and (*b*) SL+OM.

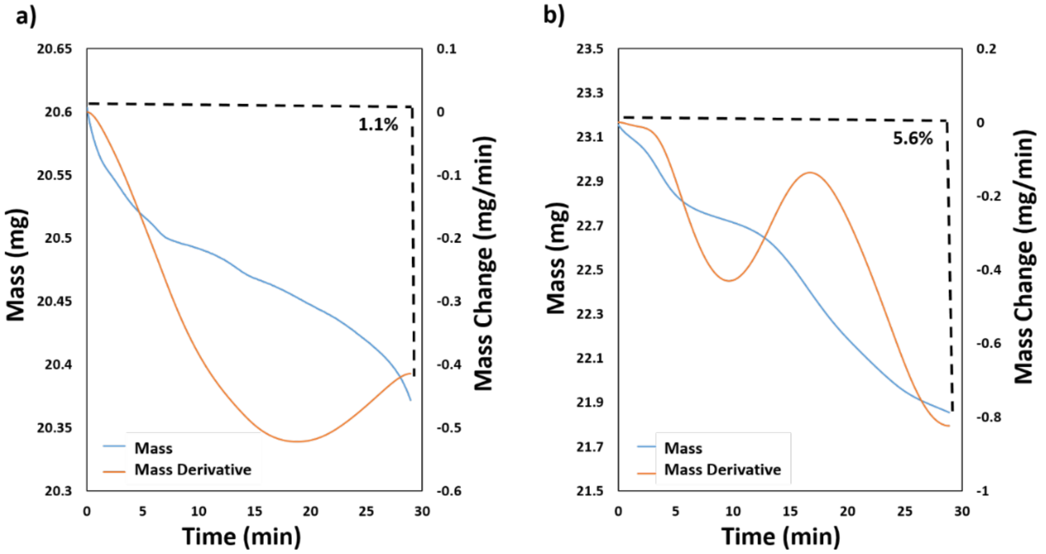
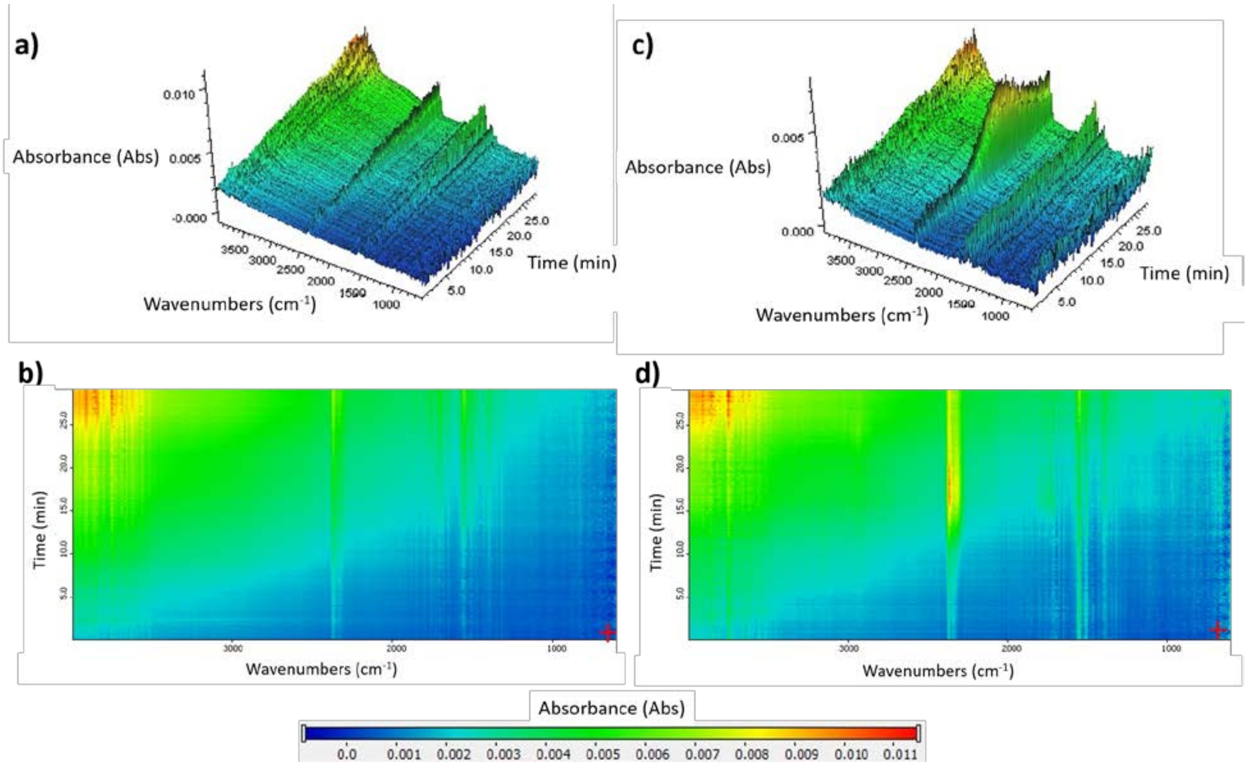


Figure 6. Three-dimensional plots of the time-resolved spectra of (*a*) L−OM and (*c*) SL+OM, and aerial views of the three-dimensional plots of (*b*) L−OM and (*d*) SL+OM.



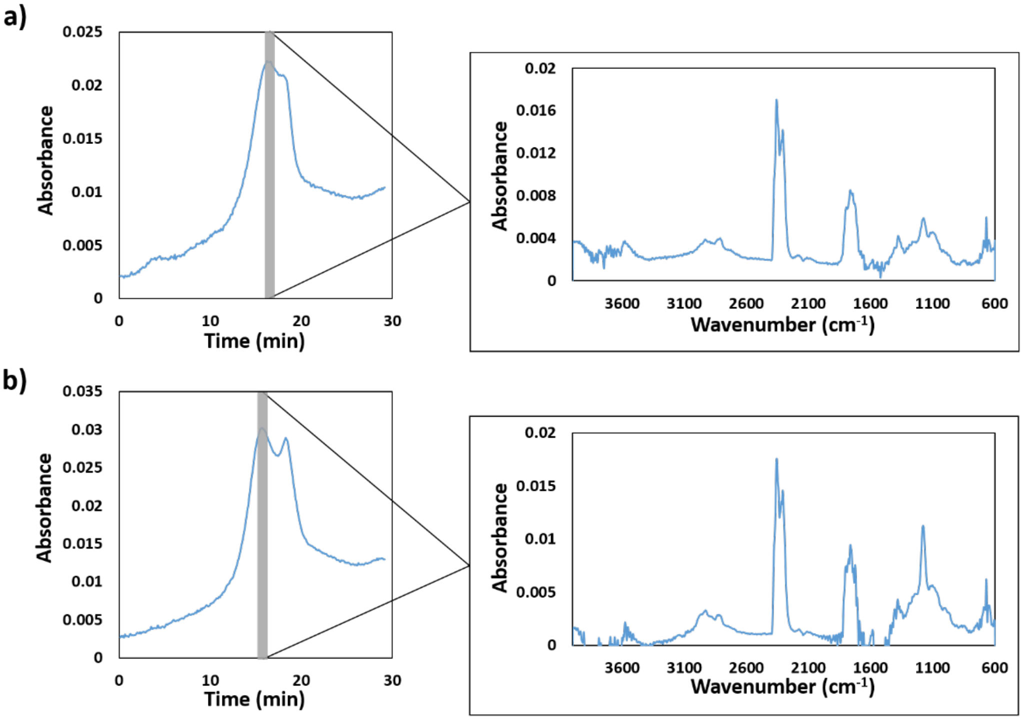
3.2.2 Peat samples

Peatlands are saturated environments consisting of organic matter at varying stages of decomposition. Typically, the rate of biomass production is greater than the rate of decomposition, which leads to the formation of a peat layer. Peat is a difficult material to study due to the dynamic biochemistry from degradation of the plant material and its heterogeneous make up.

We selected two bog areas that have different plant compositions and physical properties. Peat 1 was collected from the Farmers Loop bog in central Alaska, and Peat 2 was collected from the APEX bog in central Alaska. The Farmers Loop bog had greater plant diversity and microbial activity and a higher pH compared to the APEX bog (R. Barbato, unpublished data). Both Peats, 1 and 2, contained similar percent organic matter contents as determined by loss on ignition (i.e., 82% and 87% respectively).

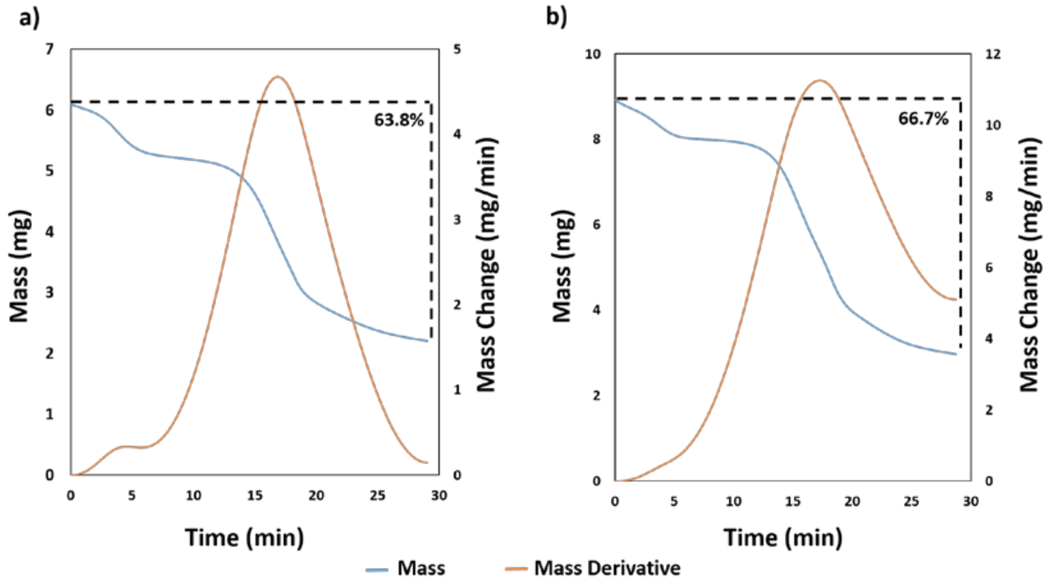
For both peat samples, Gram-Schmidt thermograms showed a strong absorbance from 15 to 20 min (Figure 7), corresponding to a temperature range of 280°C to 380°C, which indicated the off-gas of a volatilized compound.

Figure 7. Gram-Schmidt thermograms with corresponding linked spectra of (*a*) Peat 1 and (*b*) Peat 2. Linked spectra shown occurred as samples were heated to approximately 300°C, at 16.4 min and 15.7 min respectively.



The mass plots provided as Figure 8 also illustrated a sharp change in slope during this time. Taking the first derivative of the mass plots highlighted the change in mass. This mass loss may be associated with the direct oxidation of organic matter and volatilization of low molecular weight hydrocarbons (Oudghiri et al. 2015).

Figure 8. Mass and mass derivative plots of (*a*) Peat 1 and (*b*) Peat 2.



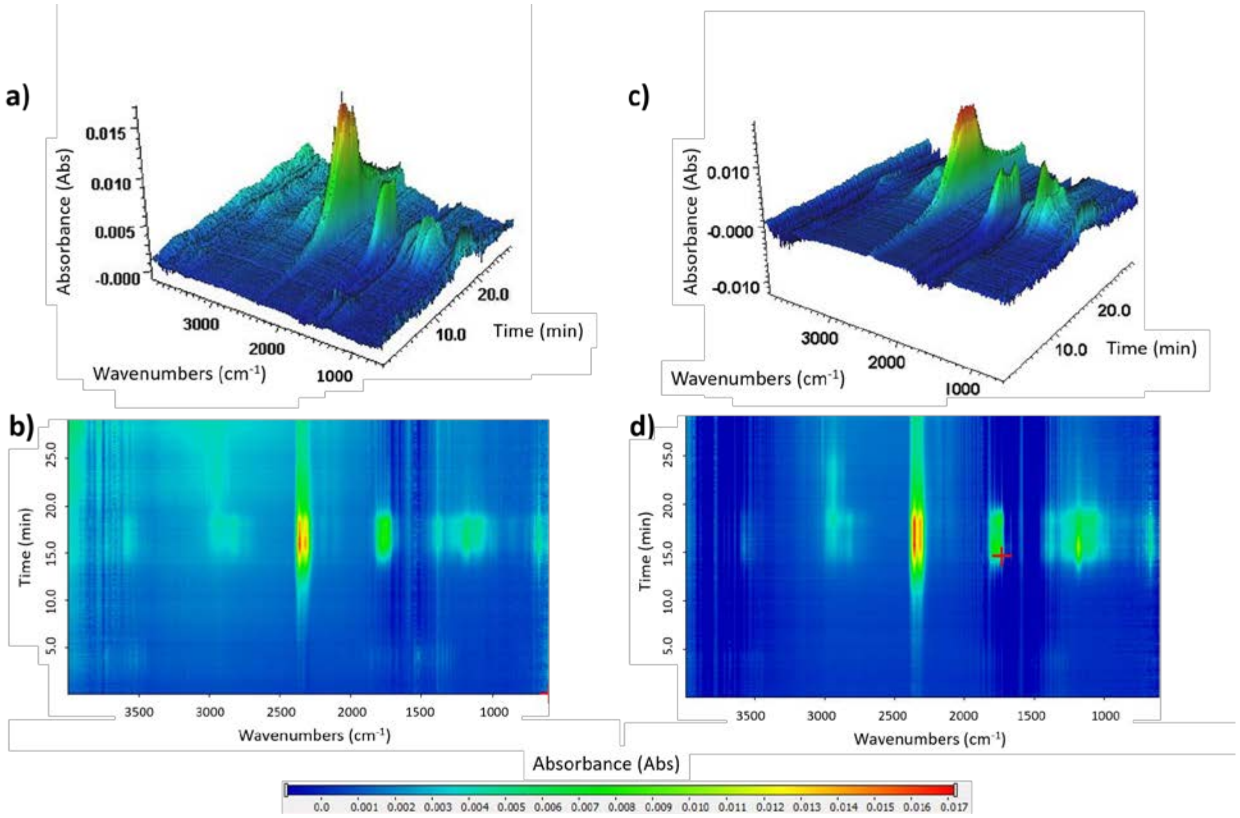
The linked spectra of the Gram-Schmidt peaks (Figure 7) were very similar for both peat samples. The most intense peak occurs at around 2370 cm^{-1}, which is indicative of carbon dioxide (Oudghiri et al. 2015). The second most intense peak at 1770 cm^{-1} corresponds to carbonyl (C=O) stretching, which is a bond present in carbon dioxide. There was also a slight aliphatic absorption observed from 3000 to 2790 cm^{-1}, which corresponds to the carbon-hydrogen (C-H) stretching, possibly due to the combustion of organic carbon in the samples (Oudghiri et al. 2015). The broad absorption observed at 1150 cm^{-1} could reflect polysaccharide absorption or the presence of water vapor (Oudghiri et al. 2015).

Carbon dioxide has been studied as a proxy for SOM in TGA studies (Pallasser et al. 2013; Oudghiri et al. 2015). In the study by Pallasser et al. (2013), oxygen was used as a purge gas; and as the sample was heated and volatized, carbon released from SOM was converted to carbon dioxide. Oudghiri et al. (2015) used synthetic air (20% oxygen and 80% nitrogen) as a purge gas, which compares more to our study where nitrogen was used as the purge gas.

To quantify carbon dioxide as a proxy for organic matter, we plotted the derivate of the mass (Figure 8), determined the beginning and end of the derivative peak, and calculated the percent mass loss over that period. Using this method, Peat 1 had a calculated mass loss of 50.9%, and Peat 2 had a calculated mass loss of 56.7%. These results were lower than the percent organic matter determined by loss on ignition, which was determined to be 82% in Peat 1 and 87% in Peat 2. Because there was such a large difference between SOM determined by thermogravimetrics compared to loss on ignition, the percent mass loss was recalculated over the entire run time rather than just over the derivative peak, which attributed any mass loss as SOM. This approach resulted in a mass loss of 63.8% for Peat 1 and 66.7% for Peat 2.

Figure 9 illustrates the three-dimensional representation of the time-resolved spectra. These spectra are useful for qualitatively identifying differences in evolved compounds between samples. Figures 9a and 9c show similar peaks were evolved from heating Peat 1 and Peat 2, the most prominent peak being 2370 cm^{-1}, which represents evolved CO_2 in the off-gas and was used as a proxy for SOM.

Figure 9. Three-dimensional plots of the time-resolved spectra of (*a*) Peat 1 and (*c*) Peat 2, and aerial views of the three-dimensional plots of (b) Peat 1 and (d) Peat 2.



TGA is an alternative method to traditional loss on ignition methods for determining percent organic matter in soil. In this study, the TGA actually underestimated percent organic matter by a factor of 1.3. This could potentially be resolved by using oxygen rather than nitrogen as the purge gas. The studies conducted by Pallasser et al. (2013) and Oudghiri et al. (2015) explored carbon dioxide as a proxy for SOM. Oudghiri et al. (2015) heated samples to 900°C and observed the degradation of more recalcitrant hydrocarbons. They also observed carbonate-associated inorganic compounds degrade at elevated temperature. Because of limitations in sample processing, we are currently unable to analyze samples at this temperature; however, it would be interesting to analyze the peat samples for more recalcitrant hydrocarbon degradation and for mineral soil samples to see if there is inorganic degradation. FTIR profiles obtained from the mineral soil samples in Part One of the study indicated a strong mineral component absorption that could be tracked with heating. The linked spectra in connection with the Gram-Schmidt plots collected in Part Two of the study could be used to determine the identity of the SOM, to a limited extent. The TGA data was less informative for soils containing a low organic matter content, where volatilization was minimal, at least at the temperatures used in this study.

4 Summary

Organic matter is a complex material embedded in a heterogeneous soil matrix. It both directly and indirectly affects soil characteristics and can provide critical information regarding the current soil state or a response to environmental changes. In this study, we assessed whether FTIR could be used to quantify SOM in soils containing varying levels of organic matter. We identified qualitative differences in spectral signatures between mineral soils and peat, the latter providing a surrogate spectral signature for SOM. We then used this information to quantitate percent organic matter in mineral soils and the peat samples by using a coupled TGA-FTIR approach. Our results showed peat samples contained more aliphatic and aromatic carbons, likely due to increased amounts of plant material, and found that the mineral soils showed a strong presence of mineral compounds such as silica and aluminum oxides. TGA-FTIR proved to be a useful technique for quantifying percent organic matter in peat but was an underestimation when compared to loss on ignition methods. The TGA-FTIR methodology for SOM quantification will likely improve with the incorporation of higher temperatures to investigate the mineral content of soil. Furthermore, FTIR can be used not only to measure spectral fingerprints of soil or peat but also to determine changes in their composition after exposure to treatment or environmental stressors. Future efforts will explore the use of FTIR as a standoff system for quantifying SOM over large areas and in difficult-to-access sites, such as peatlands.

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Stacey L. Jarvis, Thomas A. Douglas, Karen L. Foley, Robert M. Jones, John E. Anderson, Stephen D. Newman, and Robyn A. Barbato

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14. ABSTRACT
Characterization of soil properties typically requires time-intensive, ground-based sampling. Therefore, technologies that allow for rapid assessment of particular attributes would be greatly beneficial. One example is Fourier transform infrared (FTIR) spectroscopy, which uses an infrared spectrum to qualitatively identify a variety of compounds in solid, liquid, or gaseous samples. This study investigated the infrared reflectance signatures of peat and mineral soil samples with varying amounts of organic matter and coupled FTIR spectroscopy with a thermogravimetric analyzer (TGA) to more accurately identify and quantify soil organic matter (SOM). Clear differences were observed between the soil and peat FTIR spectral profiles. When compared to traditional analysis by loss on ignition, the coupled TGA-FTIR method resulted in an underestimation of the percent SOM for peat samples and an overestimation of the percent SOM in mineral soil samples. These results may have been influenced by low sample mass and moisture present in the sample. In total, our project results show that FTIR measurements provide a rapid yet qualitative means of assessing sample organic matter versus mineral content, but the TGA-FTIR measurement capability needs more refinement before it can be used for qualitative SOM measurements.

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