Preliminary Characterization of the Organic Composition of Icelandic Soil through Mid-infrared Spectroscopy

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ABSTRACT: The majority of Icelandic soil is volcanic and has either been reported or hypothesized to contain less than 25% of organic carbon content, garnering most of Iceland's soil to receive Andisol (Andosol) classification (Arnalds et al., n.d.).The Earlham College Field Science Department has performed research in Iceland, but little has been done on the characterization of Icelandic soil. To prepare for future research, preliminary characterization of Icelandic soil was achieved through mid-infrared spectroscopy. After standard curve creation, the organic composition of an Icelandic soil sample (taken from the Skálanes area) was measured to be 23 ± 2% (by weight), verifying Andisol classification. To validate the precision of such an answer, the uncertainties within these three components of the experimental set-up: sample preparation, instrumental analysis, and experimental robustness were calculated and determined to be 1%, 2%, and 1%, concerning % organic content, respectively.

1. Introduction

Soil composition has tremendous effects on plant growth, agricultural considerations, and environmental concerns. Over time, the organic composition of soil can be affected by human cultivation and pollution. Within the American Great Plains, much of the grasslands have lost what is reported to be up to nearly 38% of their organic composition due to cultivation of the soil with wheat-fallow (Calderón et al., 2011). The loss of organic carbon as CO_2 from soil is a legitimate concern. Carbon released in the form of CO_2 contributes to worldwide CO_2 emissions and, as a result, to the overall increase in global temperatures (Li et al., 2015). Since Andisols have less of an organic composition than other soil classifications, there is less of a concern about the loss of carbon as CO_2 from Andisols. However, the characterization of Andisols, and of soil in general, is still imperative in the determination of plant growth, crop rotation, and other environmental factors within a given area (Peng et al., 2014).

Near-infrared spectroscopy (NIRS) has been of more prominent use in the determination and prediction of soil composition (Ludwig et al., 2007). NIRS is both a quicker and less expensive analytical method than others. NIRS is also of more use when it comes to agricultural applications of diffuse reflectance spectroscopy because of the relative ease at which quantitative measurements can be procured (Madari et al., 2006). Mid-infrared spectroscopy (MIRS), however, also has its benefits in the determination of soil composition; it has been shown to reliably measure the total carbon content and other compositional characteristics (carbonates, proteins, et cetera) of soil (Calderón et al., 2011). While MIRS constitutes all spectral readings within the 4000-400cm^{-1} range, organic characterization of Icelandic soil was done through the analysis of the organic C-H peak around 2920 cm^{-1}. This peak was selected because it was an easily identifiable peak with little to no interference from either background noise or the presence of other soil constituents (such as silica and bentonite clay - found at 1100, 800, and 650 cm^{-1}), and fluctuations in its peak area, based on organic carbon composition, could be used in the creation of standard curves to help in the determination of the amount of organic carbon present in Icelandic soil.

2. Experimental Method

2.1. Soil Standards

Pre-dried soil standards, containing trace amounts of organic carbon, and the organic carbon standard (compost), were obtained from a bulk supply of AgroMAT soil (from SCP Science). Soil Ag-2 was a sandy standard while soils Stx-1b, KGa-1b, and Ag-1 were clay standards. All standards were prepped for and characterized by MIRS.

After initial characterization, four sets of compost/soil mixtures were created for each soil standard. Each set contained three mixtures of varying percentages (by weight) of compost and the standard soil. The mixtures created were 75% compost/25% X (where X = Ag-1, Ag-2, Kga-1b, or Stx-1b), 50% compost/50% X, and 25% compost/75% X. All mixtures were characterized by MIRS.

2.2. Standard Curve Creation

Two standard curves were created - one for clay soils and one for sandy soils.

Figure 1. Clay Standard Curve of Compost vs. Ag-1. Graphs area of organic carbon peak of interest (around 2900 cm^{-1}) versus compost (carbon) percentage present in mixture.

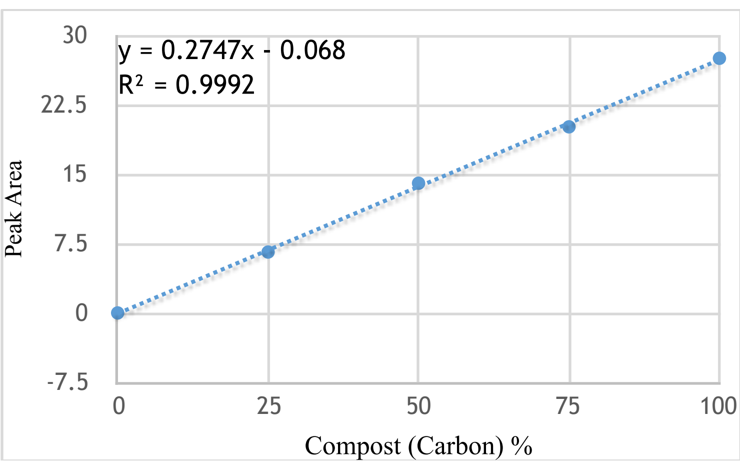
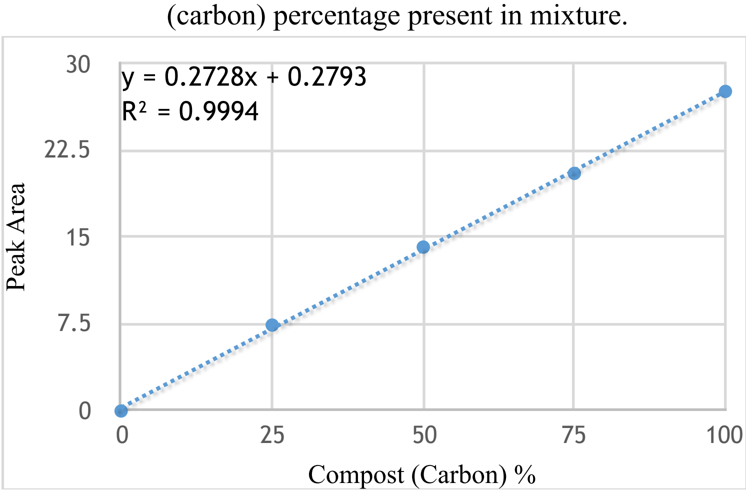


Figure 2. Sandy Standard Curve of Compost vs. Ag-2. Graphs area of organic carbon peak of interest (around 2900 cm^{-1}) versus compost (carbon) percentage present in mixture.



2.3. Uncertainty Calculations

In order to determine the majority uncertainty present within the experimental, three tests were performed:

1.) Test of Sample Preparation: A bulk mixture of 25% compost/75% Ag-1 was created. From that mixture, three samples (named Cup A, Cup B, and Cup C) were prepped for and characterized by MIRS. Their respective data for the peak of interest were compared to one another.

2.) Test of Instrument (MIR): Cup A was left under the MIR machine, and five data collection runs were performed.

3.) Test of Experimental Robustness: Cup A was run four times by the MIR machine. Between each run, Cup A was switched out for another standard soil sample.

Table 1. Compilation of each test's data and carbon content uncertainty (given as % RSD). Column 1 = Test Name; Column 2 = St. Dev. in Peak Area $(cm^{-1})^2$; Column 3 = Average Peak Area $(cm^{-1})^2$; Column 4 = (Column 2 / Figure 1. slope); Column 5 = RSD (%).

1	2	3	4	5
Sample Prep.	0.1	9.0	0.364033491	1%
Instrument (MIR)	0.2	8.9	0.728066982	2%
Exper. Robustness	0.1	8.8	0.364033491	1%

2.4. Characterization of Icelandic Soil

An Icelandic soil sample (from an archaeological dig at Skálanes) was obtained from the Biology Department's ancient DNA lab at Earlham College. In compliance with federal law, the sample was heated at 150ºC for a period of two days before undergoing characterization by MIRS. After characterization, the sample was properly discarded.

2.5. Measurement Calculations

MIRS spectra were obtained using Agilent Technologies and GRAMS/AI ™ Spectroscopy Software. Raw spectra were used for calculation purposes. The calibration curves were created by using the standard mixture data for the peak of interest, along with data from the 100% compost (carbon) standard and a blank (100% Ag-1 or Ag-2) standard, and applying blank corrections. For all calculations, all areas for the peak of interest were integrated by hand utilizing

GRAMS software.

2.6. The MIRS Instrument and Spectra

All soil samples and standards were run via MIRS. The instrument used was an Agilent Technologies 4100 ExoScan FTIR machine. The spectra received contained an approximate range of 5000 to 500 cm^{-1}.

3. Results and Discussion

During this research, all soil samples and standards were well dried and securely stored, so it is expected that there were no outside contaminates present. Based on the low uncertainty garnered from the Test of Sample Preparation (Table 1.) and the fact that, visually, standard mixtures were darker in color when they contained higher concentrations of compost (based on % weight), and standard mixtures with the same carbon content were of the approximate same color, it can be assured that all samples and standards were prepared accordingly.

The final uncertainty in the Icelandic soil carbon composition calculation was obtained from the propagation of all of the uncertainties within the experiment (as discussed in *2.3.* and seen in Table 1.). Surprisingly, the % RSD discovered for the MIR instrument was larger than that for both sample preparation and experimental robustness (Table 1.), even though the sample cup was left in the same spot and rerun over and over. As all of the area calculations were integrated by hand, this is probably a result of human error, and the fact that area integration could have been influenced by human biases. Future work should probably involve writing a software program which integrates the peak areas itself to produce more precise peak measurements. However, since none of the experimental uncertainties were high and were, in fact, very favorable, the potential errors produced by peak integrations done by hand were completely trivial.

Qualitatively, the raw spectrum of the Icelandic soil (Figure 3.) contained an organic peak of about the same transmittance level and area as those of the 25% compost/75% X (X = Ag-1 or Ag-2) mixtures (Figure 4. and Figure 5.), so it is no surprise, then, that the calculated carbon content was 23% (Table 2.). Although this calculated carbon percentage was a bit higher than what was expected, it is presumed that there were most likely increased agricultural activities in the area where the sample was collected, explaining the relatively high carbon content.
In the determination of the carbon composition of the Icelandic soil, the sandy Ag-2 calibration curve (Figure 2.) was utilized. The Ag-2 curve was chosen over the Ag-1 curve because most Icelandic soil is of a sandy, rough texture and not that of soft and clay-like. Therefore, on a purely qualitative basis, it was decided that the Ag-2 curve would provide the most accurate fit for Icelandic soil.

Table 2. Icelandic Soil % Carbon. Column 1 = Area of Carbon Peak $(cm^{-1})^2$; Column 2 = Calculated % Carbon; Column 3 = Unc. (%)

1	2	3
6.665153	23	2%

Figure 3. Raw Spectrum of Icelandic Soil.
Y-Axis Label: % Transmittance; X-Axis Label: cm^{-1}
Note that the peak of interest is located at approximately 2920 cm^{-1}.

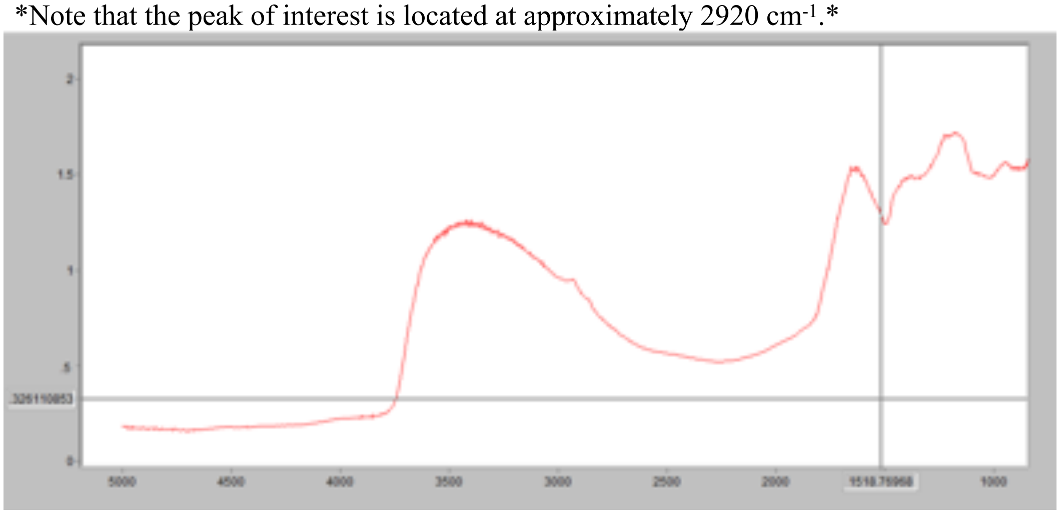


Figure 4. Raw Spectrum of Overlaid Sandy Standard Curve Data (Compost vs. Ag-1)
Data Key: Purple = 100% compost (Carbon); Green = 75% compost/25% Ag-1; Red = 50% compost/ 50% Ag-1; Cerulean = 25% compost/75% Ag-1; Navy Blue = Blank (100% Ag-1)
Y-Axis Label: % Transmittance; X-Axis Label: cm^{-1}
Note that the peak of interest is located at approximately 2920 cm^{-1}.

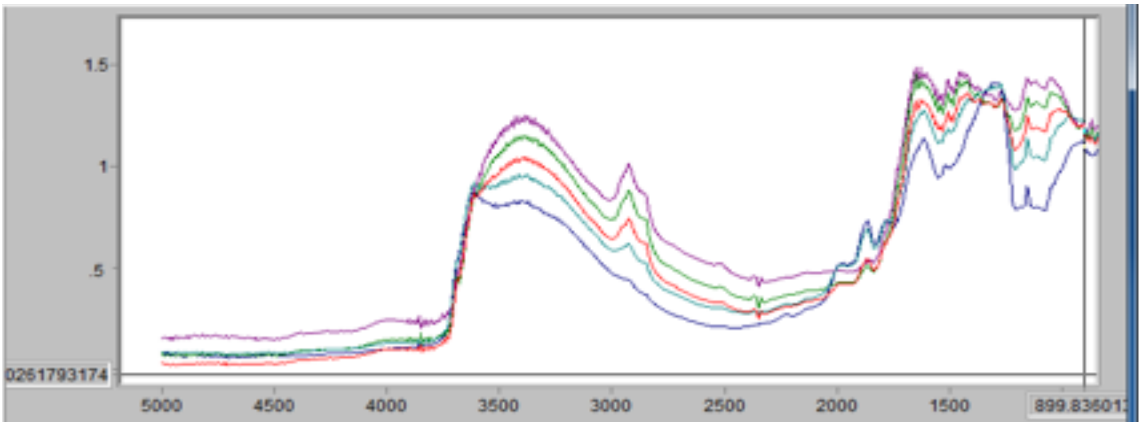
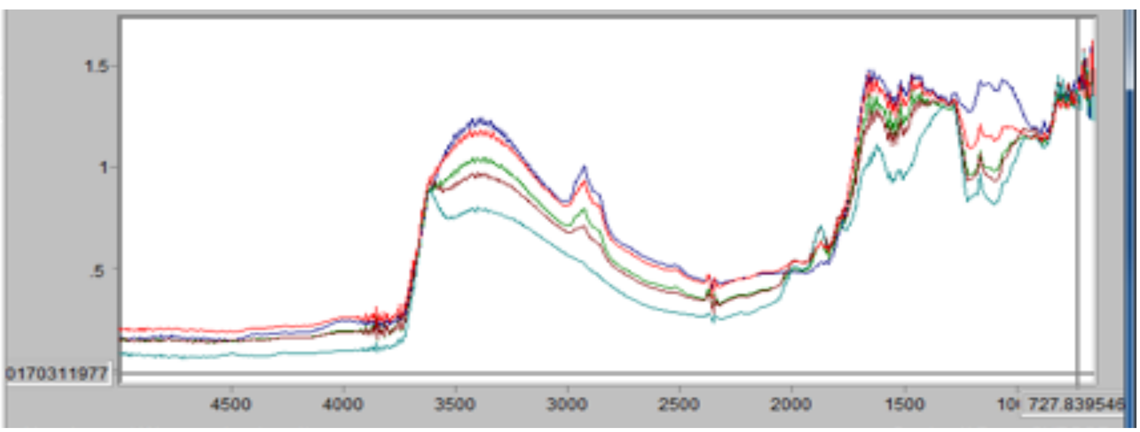


Figure 5. Raw Spectrum of Overlaid Sandy Standard Curve Data (Compost vs. Ag-2)
Data Key: Navy Blue = 100% compost (carbon); Red = 75% compost/25% Ag-2; Green = 50% compost/50% Ag-2; Brown = 25% compost/75% Ag-2; Cerulean = Blank (100% Ag-2)
Y-Axis Label: % Transmittance; X-Axis Label: cm^{-1}
Note that the peak of interest is located at approximately 2920 cm^{-1}.



4. Conclusions

As expected, the organic carbon content spectroscopically determined within the Icelandic soil reflected characteristic Andisol qualities. MIRS and standard curves were both utilized to characterize the soil. Based on the uncertainties obtained from the experimentation, the soil's organic carbon content determination is assumed to be a reliable and reasonable measurement. In the future, it would be advantageous to create a standard curve for Icelandic soil which would consist of smaller deviations in percentage changes of organic carbon content in soil mixtures and which would hone in more closely on the Andisol-Histosol soil classification range (25% organic carbon). It is acknowledged that a great additive to soil characterization research would be VIS Spectroscopy. As the composition of soil very much influences visible characteristics, the obtainment of quantitative visible data would help to further characterize soil types. Future work in this field should aim to integrate and compare MIRS data with that of NIRS. Although this project began NIRS characterization, little progress was made before the conclusion of the research. However, it is expected that, as Earlham College continues to travel to Iceland, more work will be done on the characterization of Icelandic soil.

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Supplementary Information

Table 3. Ag-1 Standard Curve Data (Before Blank Corrections)

% Carbon	Peak Area
0	3.16
25	9.75
50	17.2
75	23.3

Table 4. Ag-1 Standard Curve Data (After Blank Corrections)

% Carbon	Peak Area
0	0
25	6.59
50	14.04
75	20.14
100	27.56

Table 5. Ag-2 Standard Curve Data (Before Blank Corrections)

% Carbon	Peak Area
0	1.16877
25	8.578895
50	15.30526
75	21.659

Table 6. Ag-2 Standard Curve Data (After Blank Corrections)

% Carbon	Peak Area
0	0
25	7.410125
50	14.13649
75	20.49023
100	27.56