

Spectroscopic and Thermal Assessment of Organic Matter in Iowa Mollisols

IOWA STATE UNIVERSITY

Teresita Chua, Xiaowen Fang, Klaus Schmidt-Rohr, and Michael Thompson
Agronomy and Chemistry Departments, Iowa State University, Ames, IA



OVERVIEW

There are recent developments in analytical approaches in the characterization of soil organic matter which offer opportunities to investigate the fundamental processes that influence changes in soil carbon. Ideally, carbon models should have clearly defined set of soil C fractions to better describe turnover rates. To obtain distinction among soil C fractions, information on the nature or evolution of C functional groups as well as their amounts should be readily and cheaply available.

In this study we explore the use of diffuse reflectance infrared Fourier-transformed (DRIFT) spectroscopy as a quick and inexpensive tool that can allow us to explain changes in soil organic matter at landscape scales. We also utilize thermal gravimetric analysis to support findings obtained from infrared spectroscopy.

The general goal of this study is to provide means of accurate and precise predictions of key components particularly those that are recalcitrant on the cycling and storage of carbon.

SOIL ORGANIC MATTER FRACTIONATION

- 50 g ≤ 2 -mm surface soil dispersed in 250 mL H₂O by sonification @ 22 J mL⁻¹.
- Suspension passed through a 53- μ m sieve.
- Sieved residue treated with Na polytungstate (density = 1.8 g cm⁻³) to separate **particulate organic matter (POM)**.
- Clay + silt dispersed in H₂O (1:10) @ 450 J mL⁻¹ and < 2 μ m material separated by sedimentation of the silt
- Clay coagulated with MgCl₂, dialyzed against water, and then freeze-dried.
- **Whole/unfractionated** samples and clay fractions treated with 0.1 M HCl followed by four 10% HF treatments to dissolve minerals.
- The washed residue was freeze-dried and ground.

DRIFT SPECTROSCOPY

- Mixed and ground sample with IR-grade KBr @ 5 wt %
- Collected 200 scans @ 4 cm⁻¹ resolution using a Magna 550 IR spectrometer equipped with DTGS detector and KBr beam splitter.
- Resulting scans in Kubelka-Munk units were automatic baseline corrected and smoothed.
- Using the second derivative and Gaussian amplitude options in PeakFit™, peaks @ 3700-2200 and 1800-600 cm⁻¹ were deconvolved and areas were determined.

Table 1. Characteristics of surface soils used in the study.

Soil Map Unit	Classification	Drainage Class	Landscape Position	Texture	pH [†]
Black Hawk					
Dinsdale	Typic Argiudoll	Well	Side Slope, 5-9%	sicl	5.4
Maxfield	Typic Endoaquoll	Poor	Concave, 0-2%	sicl	6.2
Greene					
Clarion	Typic Hapludoll	Well	Summit, 2-9%	loam	4.8
Nicolett	Aquic Hapludoll	Somewhat poorly	Plane, 0-2%	clay loam	4.9
Webster	Typic Endoaquoll	Poor	Plane, 0-2%	loam-clay loam	5.5
Canisteo	Typic Endoaquoll	Poor/Very poorly	Plane, 0-2%	sicl	6.5

Table 2. Areas under the peaks obtained using Peakfit™ of the DRIFT spectra of samples diluted at 5% by weight in KBr.

Soil	Aromatic C-H	Aliphatic C-H	Carbonyl-C	Aromatic C=C	% Total Org C	Aromatic C-H Aliphatic C-H
	3200-3000	3000-2850	1735-1655	1600-1500		
POM						
Dinsdale (W)	34	25	14	17	32	1.4
Clarion (W)	24	10	5	6	24	2.4
Maxfield (P)	30	25	12	14	30	1.2
Webster (P)	20	12	12	13	24	1.7
Whole/Unfractionated						
Dinsdale (W)	7	2	4	1	4	3.4
Clarion (W)	10	5	4	1	2	1.8
Maxfield (P)	11	6	6	3	7	1.8
Webster (P)	14	9	9	5	5	1.5
Canisteo (P)	6	4	8	12	8	1.5
Nicollet (SP)	8	7	14	10	7	1.2
Clay Fraction						
Dinsdale (W)	22	14	13	7	16	1.6
Clarion (W)	24	20	19	9	23	1.2
Maxfield (P)	57	25	21	9	17	2.2
Webster (P)	32	19	26	16	32	1.7
Canisteo (P)	42	31	42	28	29	1.3
Nicollet (SP)	27	17	25	12	29	1.6

- In the POM fraction, the aromatic C-H and aliphatic C-H are higher in the loess- than the till-derived soils. The ratio of aromatic C-H to aliphatic C-H, however, is lower in the loess than till-derived soils.
- There is a considerable IR signal in the aromatic C-H region of clays, with the well-drained soils being less than the poorly drained soils.
- The generally low peak areas obtained for the unfractionated soils compared to the POM and clay fractions renders interpretation to be difficult. Thus, it is imperative to treat soil with HF to concentrate OM.
- There is potential for infrared spectroscopy in providing quick and economical means of quantifying organic C as demonstrated by strong correlations of carbonyl-C and aromatic-C IR peak areas with NMR spectroscopy.

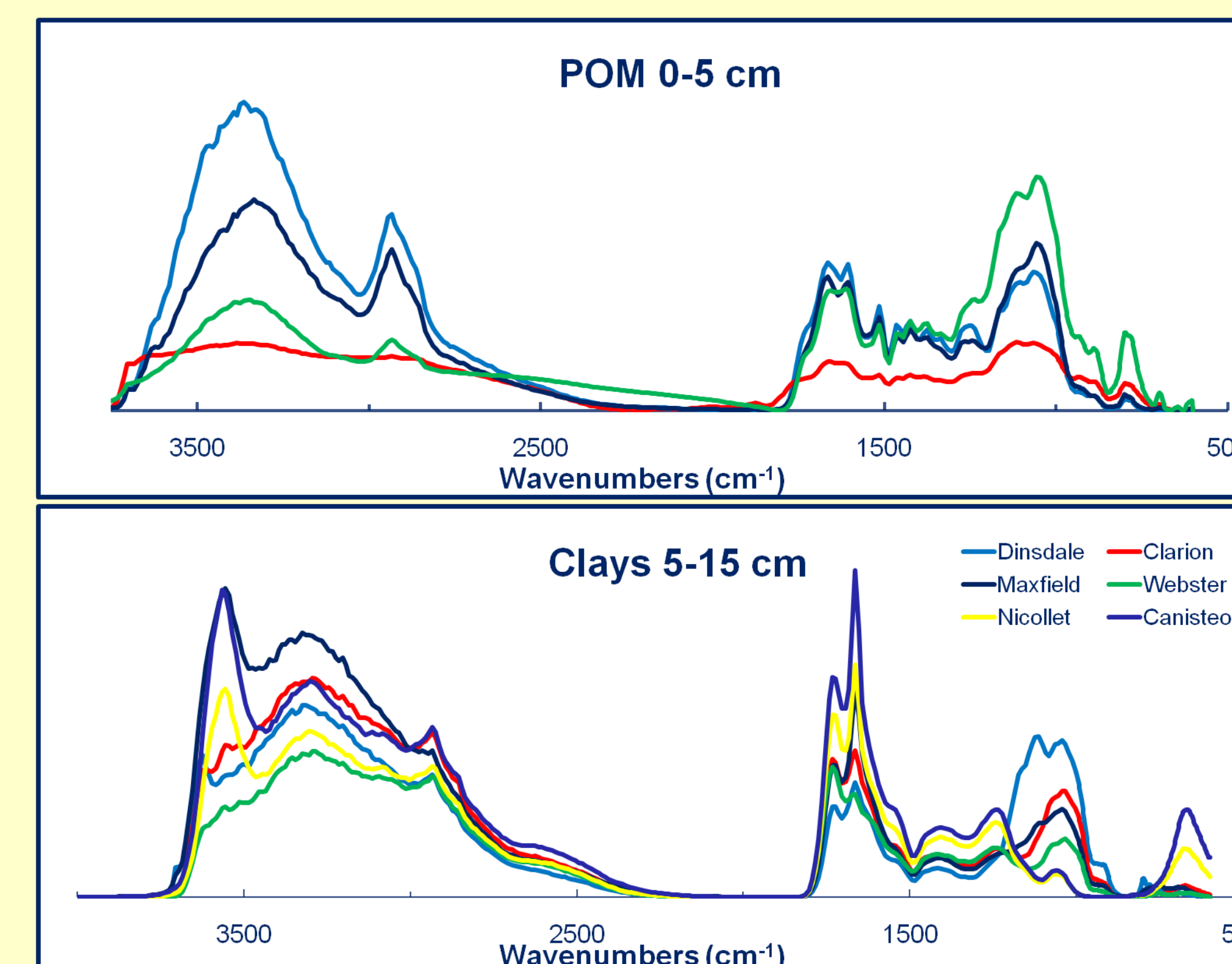


Fig 1. The DRIFT spectra of particulate organic matter and HF-treated clays revealed the presence of the COO- group centered @ 1730 cm⁻¹ and the carbonyl group of amides centered at 1650 cm⁻¹.

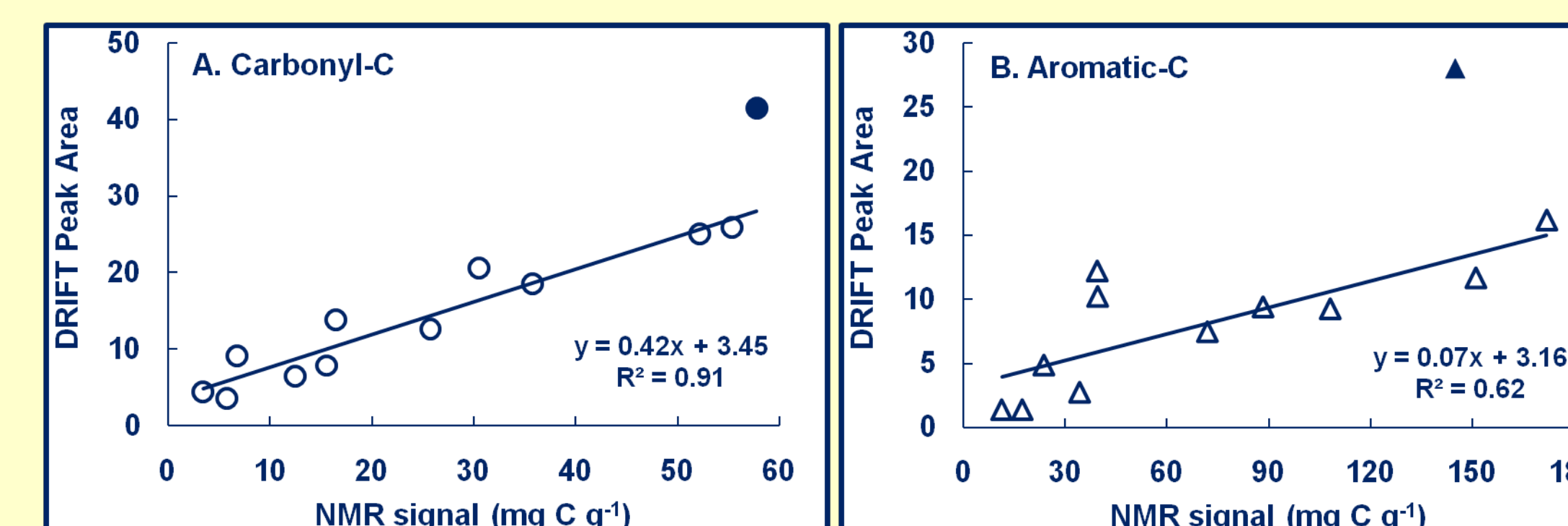


Fig. 2. Correlation plots of peaks areas obtained from DRIFT scans (a) @ 1730-1650 cm⁻¹ against the NMR signal @ 205-160 ppm and (b) @ the 1600-1500 cm⁻¹ against the NMR signal @ 160-100 ppm. Regression lines did not include the outlier (solid fill).

DIFFERENTIAL THERMAL GRAVIMETRY

- Approximately 20 mg of each sample heated @ 10°C min⁻¹ from 25°C to 110°C, and held at 110°C for 60 min to insure evaporation of water.
- Samples heated from 110°C to 800°C @ 10°C min⁻¹ with the heating chamber continuously flushed with air at 200 ml min⁻¹. Mass loss recorded over time.

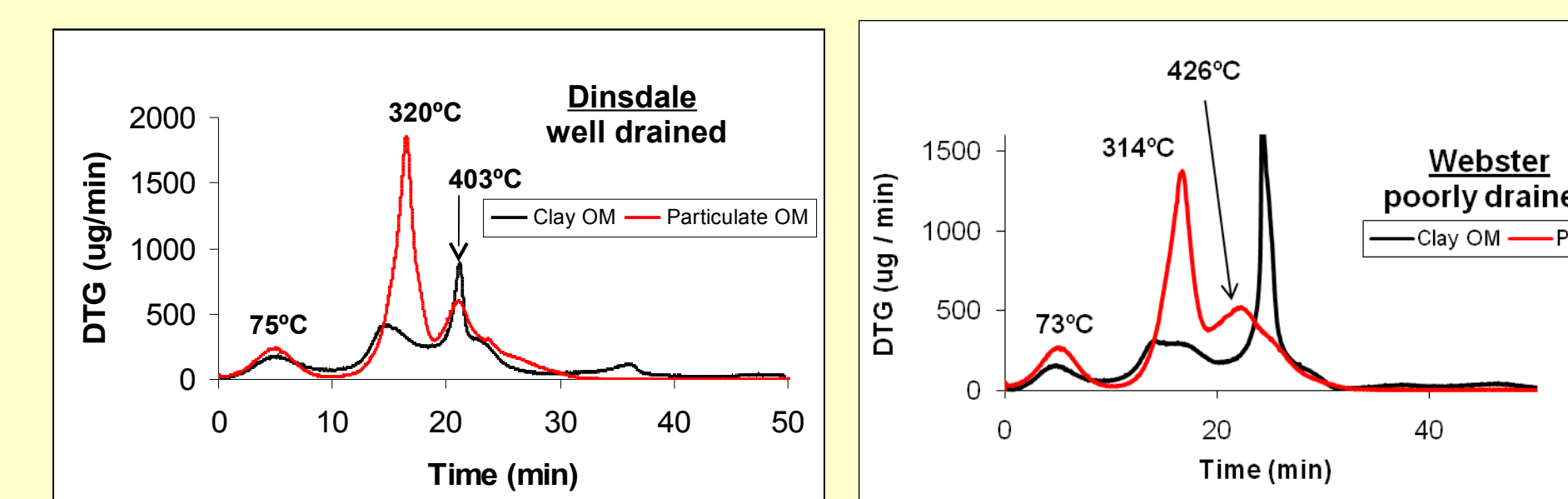


Fig. 3. Differential thermographs of well- and poorly-drained soils.

Table 3. The percent of oxidizable mass loss after heated at indicated temperature range using a heating rate of 10°C min⁻¹.

Temp Range (°C)	150-350	350-450	450-550	550-1000
% Oxidizable Mass				
Soil				
POM				
Dinsdale (W)	50	38	11	2
Clarion (W)	44	34	17	5
Maxfield (P)	53	39	7	1
Webster (P)	49	34	15	2
Canisteo (P)	84	10	3	2
Nicollet (SP)	42	49	5	4
Whole/Unfractionated				
Dinsdale (W)	30	17	23	31
Clarion (W)	26	17	18	38
Maxfield (P)	31	25	21	22
Webster (P)	27	21	24	28
Canisteo (P)	31	22	31	16
Nicollet (SP)	27	17	32	24
Clay				
Dinsdale (W)	35	20	30	15
Clarion (W)	30	13	31	26
Maxfield (P)	31	17	35	18
Webster (P)	30	16	44	11
Canisteo (P)	30	16	44	11
Nicollet (SP)	30	13	29	18
Reference Materials				
Cellulose	30	62	8	0
Lignin	37	48	15	0
Pectin	64	36	5	0
Albumin	61	27	8	5
Eicosane	100	0	0	0
Eicosanoic Acid	62	30	7	0

- Our thermal characterization of model/reference compounds suggests that substantial portions of hemicellulose, protein, and lipids are lost over the temperature range from 110 to 350°C.
- Lignin and cellulose are also oxidized, but not entirely. In the range 350 to ~450°C, oxidation of residues of lignin and cellulose, along with most of the remaining pectin, protein, and lipids occurs.
- At temperatures from ~450 to 550°C, the most resistant lignin residues are oxidized, along with small remnants of cellulose, pectin, protein, and lipids.
- Thermal analysis of the POM fractions reflects that nature of the crop residues that dominated POM at the time of sampling. Readily oxidizable compounds already been removed by decomposition, concentrating lignin in the POM.
- Whole SOM is enriched in difficult to oxidize compounds – probably because most charcoal particles are larger than clay size.
- In contrast to the NMR data, it appears that the well drained soils accumulate difficult-to-oxidize material.

ACKNOWLEDGEMENTS

Mr. Ben Hanisch and Mr. Nicholas Leete, undergraduates, ISU
Ms. Ritushree Chatterjee, Research Associate, Agronomy Dept., ISU
Mr. Brian Hill, Soil Testing Lab./Agronomy Dept., ISU
Dr. Jingdong Mao, Old Dominion University
Mr. Alan Karkosh and Mr. Jim Andrew, landowners