

Using LOI and Other Soil Measures to Monitor SOC Stocks for the Carbon Credit Market

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What is soil organic matter?

- Residues of once living organisms in soil -- in various stages of decomposition
- Ranges from poorly decomposed to highly decomposed (chemically and physically transformed)
- Most soil organic matter is colloidal and is highly transformed.

What is soil organic matter?

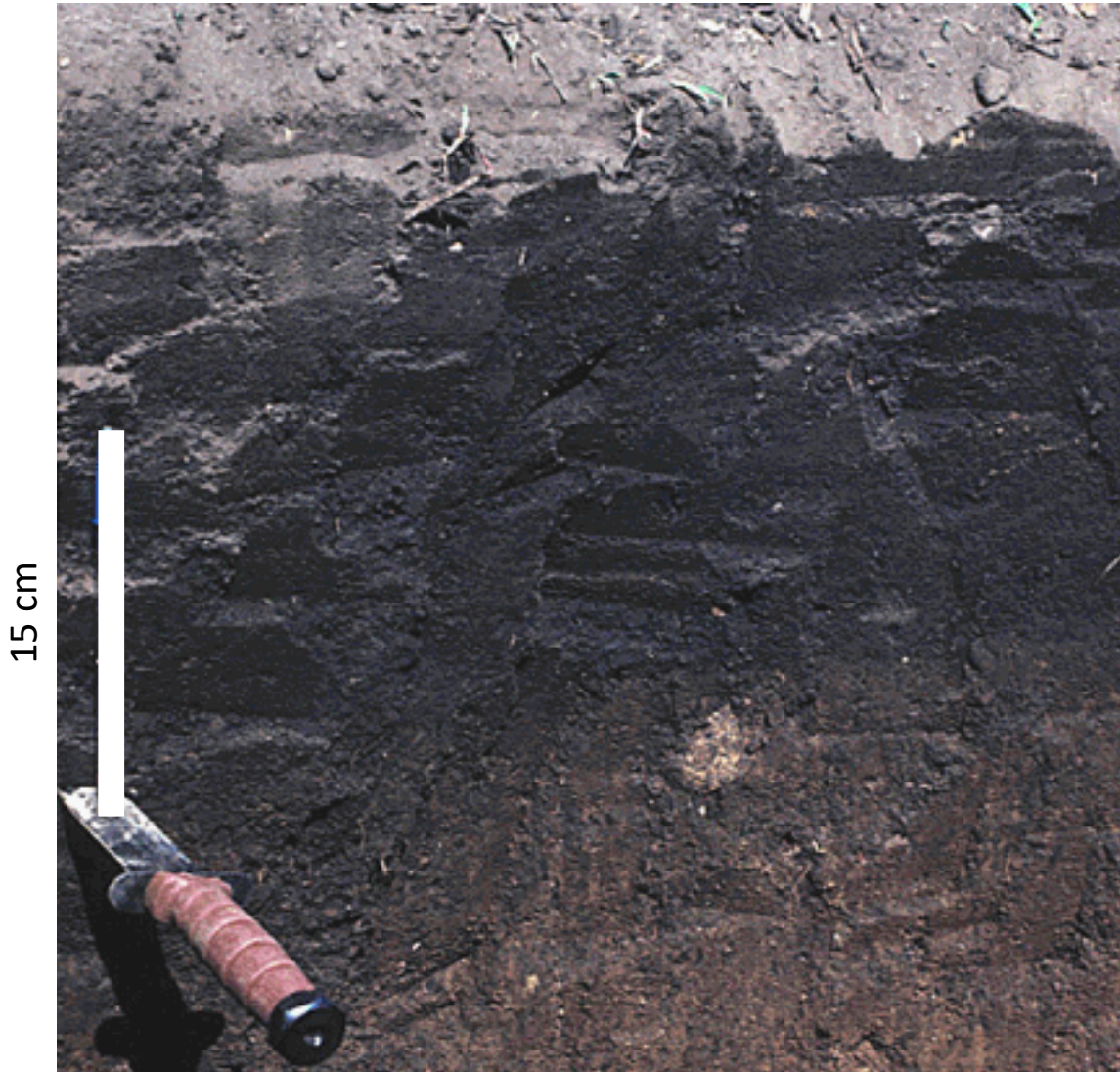
Soils in the US Midwest are well known for their abundant organic matter.

There are several ways to classify soil organic matter.

The simplest is “big” and “small.”

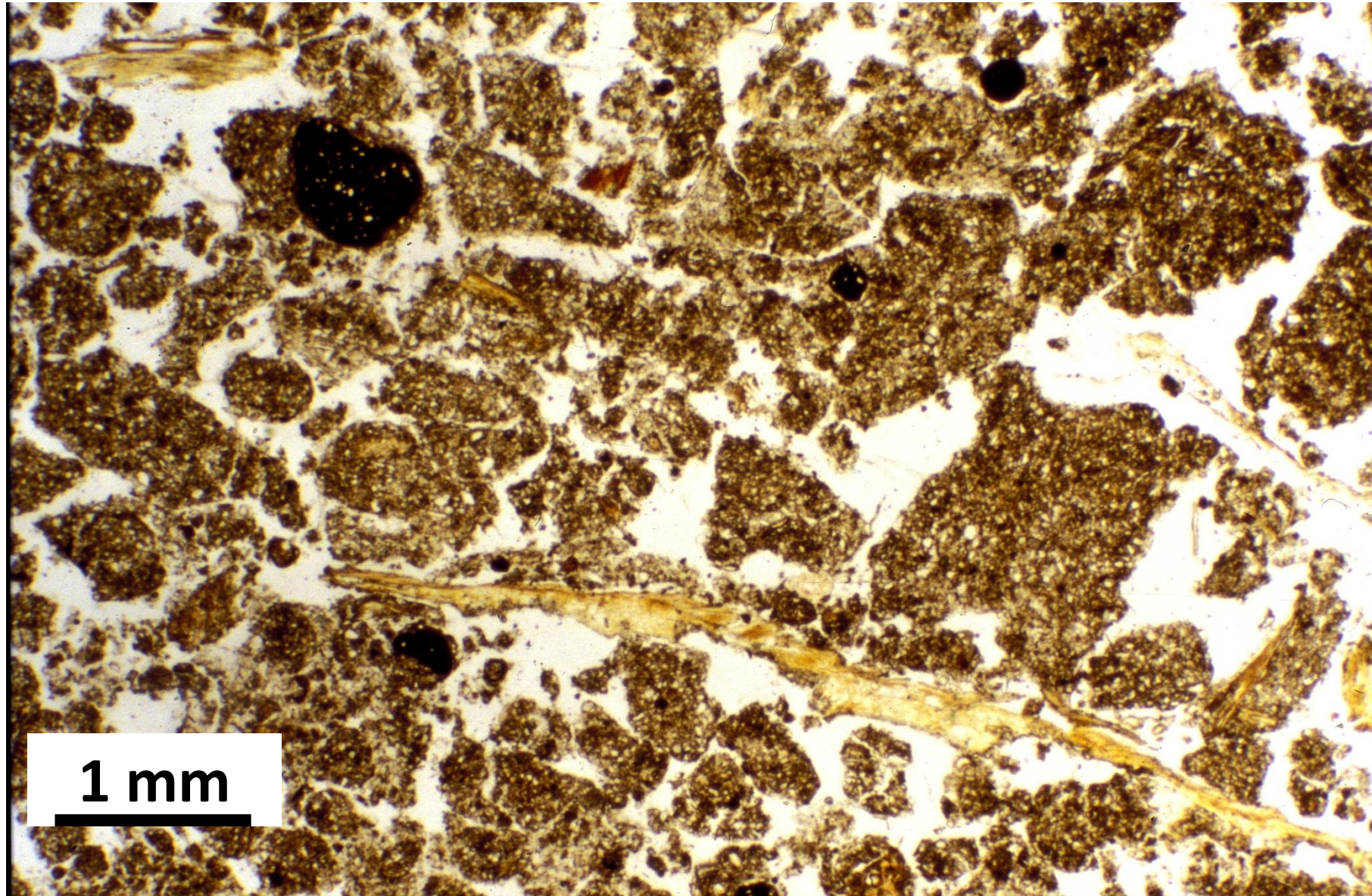
Particulate organic matter consists of poorly decomposed plant residues that are greater than about 50 μm in diameter.

Mineral-associated organic matter is everything else.

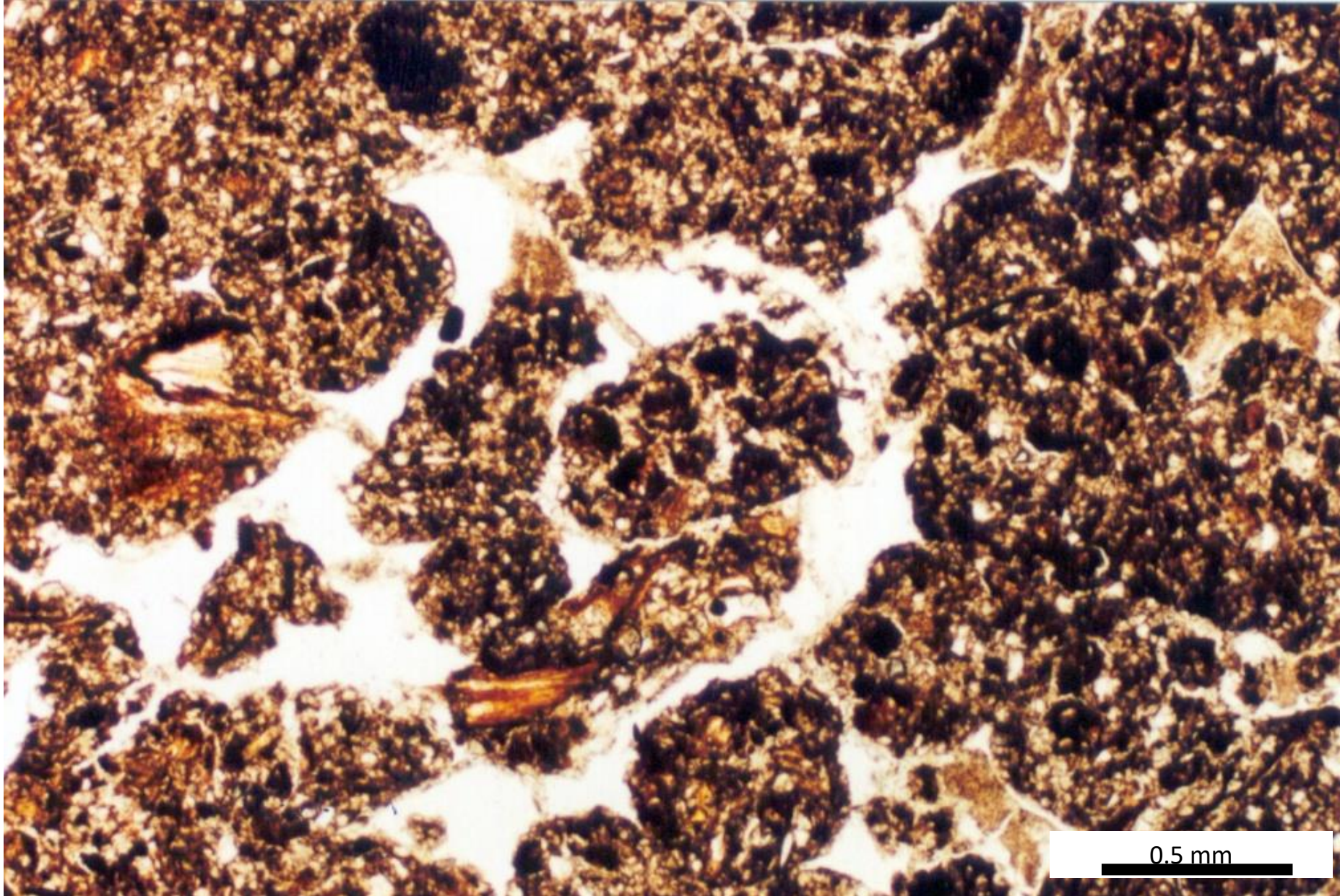


Particulate Organic Matter –

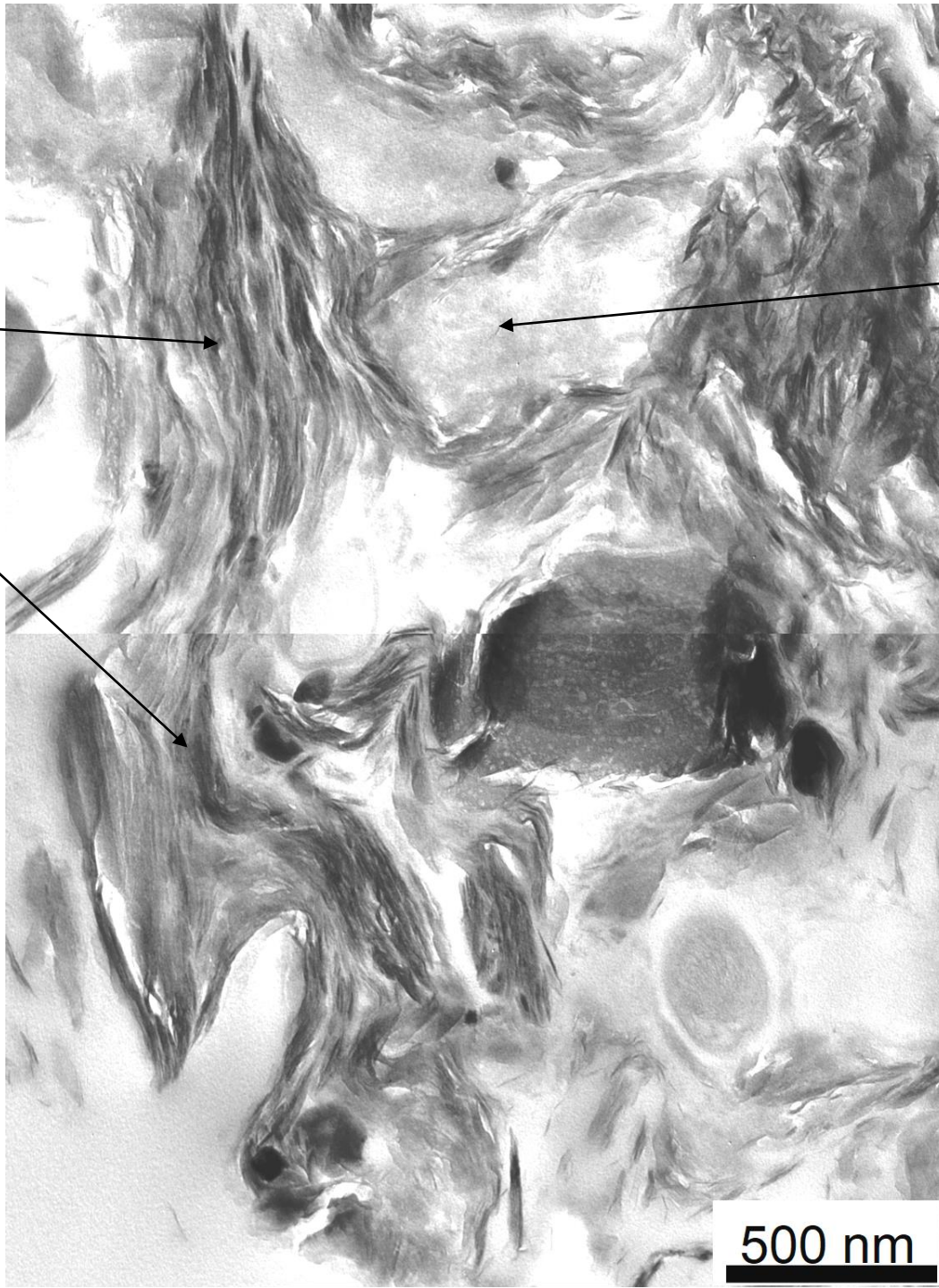
Partially decomposed residues of roots, leaves, and stems



Mineral-Associated Organic Matter



Clay



**Clay-
protected
OM**

500 nm

Chemical components of SOM

1. Microbial biomass and necromass

- Amino sugars in cell walls of bacteria and fungi

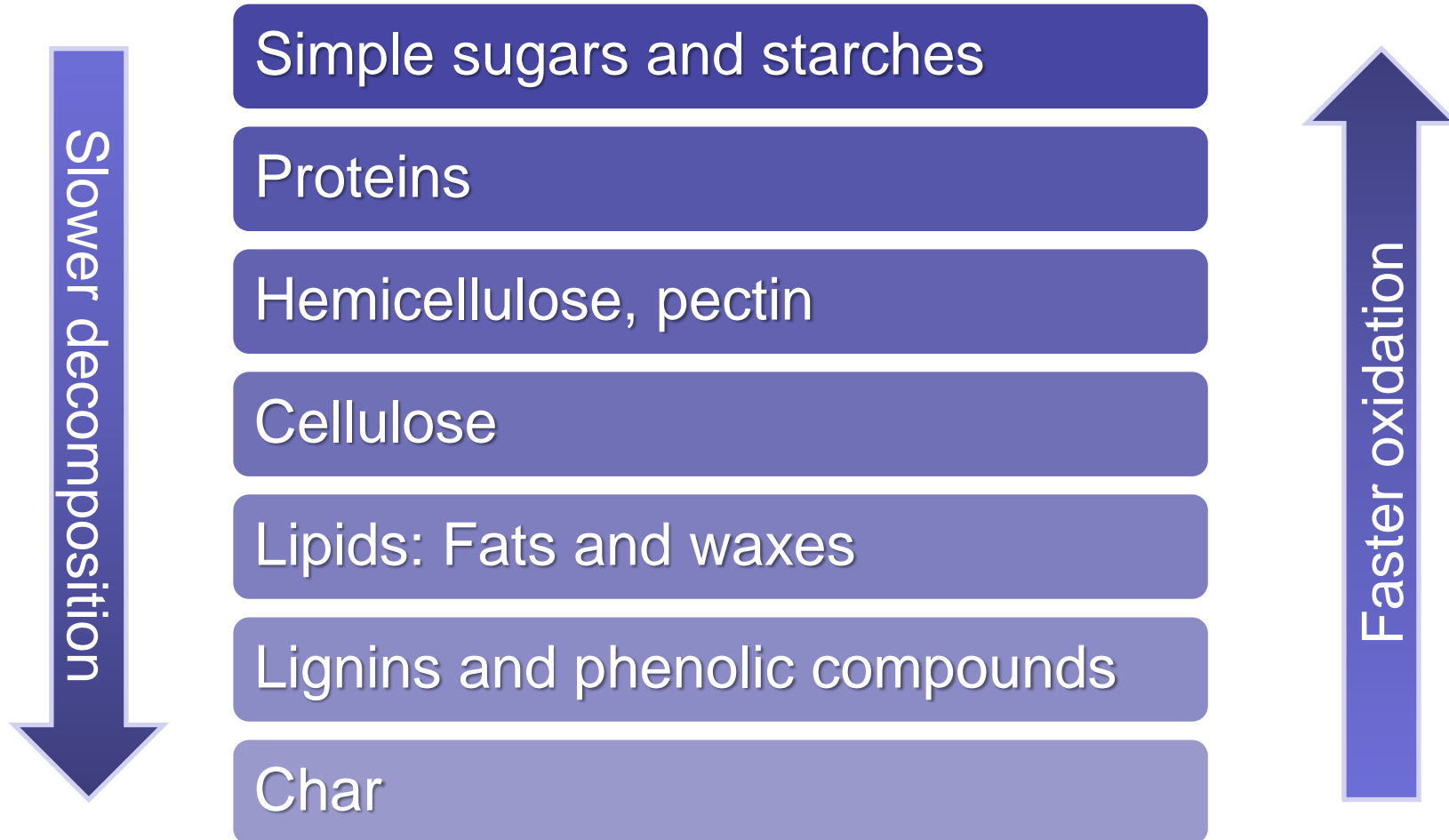
2. Plant residues

- Carbohydrate residues (simple and complex sugars)
- Lignin residues (phenols)
- Lipid residues (fats and waxes)
- Protein residues (peptides and amino acids)

3. Char (black carbon) residues (and potentially biochar)

4. Humified compounds (transformed residues)

Decomposition rates of free plant residues



What is the **elemental** composition of soil organic matter?

- Sulfur: Less than 1 %
- Phosphorus: Up to 1-2%
- Hydrogen contributes <8% by mass
- **SON** = soil organic nitrogen: ~5% of SOM is N
- **SOC** = soil organic carbon: ~50 – 60% of SOM

Carbon markets and soil organic carbon

- If we can store more carbon in the soil, less will be in the atmosphere to contribute to greenhouse gases like CO₂ and CH₄.
- Land management influences the loss or accumulation of carbon in soils.

Management practices have the potential to maintain or increase the amount of carbon stored in soils.

• minimize tillage	• limit drainage of poorly drained soils	• include cover crops in cropping systems
• increase the abundance of perennial crops	• limit wind and water erosion	

- Carbon markets are a way to pay land managers to adopt practices that store more carbon in soils.

Carbon markets require determination of carbon **stocks**, not just carbon **concentrations**

- To demonstrate that a **change** in SOC has occurred as a result of different management, carbon markets need to know the mass of SOC in a unit **volume** of soil to be managed because over time bulk density can change, too.

Example: How much carbon is present in one hectare to a depth of 20 cm?

(Assume that the mass concentration of C is 20 g kg^{-1} (2%) and the bulk density is 1.3 Mg m^{-3} (1.3 g cm^{-3})).

$$\begin{aligned} \frac{20 \text{ g C}}{\text{kg soil}} \times \frac{1.35 \text{ Mg}}{\text{m}^3} \times 0.2 \text{ m depth} \times \frac{10^4 \text{ m}^2}{\text{ha}} \times \frac{1 \text{ kg}}{10^3 \text{ g}} \times \frac{10^3 \text{ kg}}{\text{Mg}} \\ = 54 \times 10^3 \frac{\text{kg C}}{\text{ha}} = 54 \frac{\text{metric T of C}}{\text{ha}} \end{aligned}$$

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Example: How much carbon is present in one hectare to a depth of 20 cm?

(Assume that the mass concentration of C is 20 g kg^{-1} (2%) and the bulk density is 1.30 Mg m^{-3} (1.30 g cm^{-3})).

$$\frac{20 \text{ g C}}{\text{kg soil}} \times \frac{1.35 \text{ Mg}}{\text{m}^3} \times 0.2 \text{ m depth} \times \frac{10^4 \text{ m}^2}{\text{ha}} \times \frac{1 \text{ kg}}{10^3 \text{ g}} \times \frac{10^3 \text{ kg}}{\text{Mg}}$$
$$= 54 \times 10^3 \frac{\text{kg C}}{\text{ha}} = 54 \frac{\text{metric T of C}}{\text{ha}}$$

Uncertainty of carbon stock calculations

- Take a soil with BD of 1.35 Mg m^{-3} and organic carbon concentration of $2.0 \pm 0.1\%$. The analytical uncertainty of 0.1% OC ($1.9 - 2.1 \%$) in the determination of organic carbon concentration leads to a **$\pm 5\%$ uncertainty in the calculated stock of carbon.**
- Even if that soil's organic carbon concentration were known to be exactly 2.00% , then an uncertainty of 0.10 Mg m^{-3} in the BD value leads to an **uncertainty of $\pm 7\%$ in the calculated stock of carbon.**
- Since (in reality) we are uncertain of the true value of **both** organic carbon concentration **and** bulk density, the total uncertainty in carbon stock is the **sum** of the two relative uncertainties (12%): $54 \pm 6.7 \text{ MT ha}^{-1}$.
- These are *analytical* (measurement) uncertainties **only**, not uncertainty due to *sampling* different locations in a field.

Dry combustion analysis of soil carbon

Principle

- Heat sample to at least 900 deg C to oxidize carbon.
- Measure CO₂ released by using an infrared detector.
- Result is *total carbon concentration*, not organic carbon.
- Total N can be measured with the same instrument.

Issues of concern

- Equipment is *expensive* to purchase and maintain.
- Separate determination of inorganic carbon is required for calcareous samples.
- Replicate analyses: $\pm 0.1 - 0.2$ % organic C (e.g., 2.5% OC ± 0.15 %)



Loss-on-ignition is a determination of soil organic matter (SOM) concentration

1. The LOI method is based on the idea that temperatures greater than about 350 deg C will combust (ignite) the organic matter in a soil.
2. The oxidized products (mostly CO₂ gas) are volatile and evaporate from the sample.
3. The difference in mass before and after heating is assumed to result from the loss of **organic matter, not just carbon**.

Loss-on-ignition is a determination of soil organic matter (SOM) concentration

Soil organic matter concentration is estimated by the change in mass of a sample (that has been dried at 105°C) when it is heated at ~400°C for 16 hours.

1. Mass of soil sample before heating = 10 g.
2. Mass of soil sample after heating at 400°C for 16 hours = 9.6 g
3. Mass loss = SOM oxidation = $10 - 9.6 = 0.4$ g
4. Therefore: SOM concentration = $0.4 / 10 = 0.04 \rightarrow 4\%$ or 40 g kg^{-1} .

Loss-on-ignition as a prediction of soil organic carbon (SOC) concentration

1. Plant materials range in C concentration from ~35 – 45%, i.e., 0.35 – 0.45 g g⁻¹.
2. Most soil organic matter is derived from plant residues, and as those residues decompose, elements like O and N are lost from the system faster than C. So the C concentration of SOM is higher than that in plants.
3. Most studies have reported SOM to be about 50 – 60% carbon. The value that is most often cited is 58%.
4. That value comes from the determination of C in extracted soil organic matter by using a wet chemical oxidation procedure.
5. Multiply %LOI-SOM by 0.58 to get %SOC.

LOI – Issues of concern

- Protocols
- Interferences
- Omissions
- Conversion to carbon concentration

LOI – Protocols are not well-standardized

Drying to remove water – must remove water by oven-drying the sample at 105 deg C, not less, to remove water associated with cations in clay mineral interlayers

(SSSA Methods of Soil Analysis: 24 hours)

Temperature of combustion – must be high enough to combust the organic matter; protocols usually range from 300 to 500 deg C

(SSSA Methods of Soil Analysis: 400 deg C)

Period of heating – protocols range from 2 hours to overnight

(SSSA Methods of Soil Analysis: 16 hours)

LOI – Common mineral interferences

Kaolinite – loses 14% of its mass at temperatures greater than **450** deg C; so temperatures greater than 400 will likely count kaolinite as organic matter

Smectite – loses ~5% of its mass at temperatures between **100 and 250** deg C; LOI temperatures greater than 250 will likely count smectite as organic matter

Iron and aluminum oxides – lose 10-30% of their mass at temperatures greater than **350** deg C; so temperatures greater than 350 will likely count oxide minerals as organic matter

Gypsum – will lose 21% of its mass at temperatures greater than **100-200** deg C; so temperatures greater than that will likely count gypsum as organic matter

Calcite – will start to lose mass at temperatures greater than **500** deg C; so temperatures greater than 500 may count some calcite as organic matter

LOI – One common omission

Char residues (black carbon)

Many soils contain residues of incompletely burned plant materials, due to natural fires (lightening), Native American fires used to drive game, or cropland fires used to remove excess crop residues.

Char residues are likely to be stable to approximately 500 - 800 deg C. So LOI methods will not oxidize them, and they will not be included in the estimate of organic matter (or organic carbon).

Highly variable, but char carbon is likely to comprise 20 – 30 % of organic carbon in many Iowa soils.

Impacts of interferences and omissions

- Remember how LOI-SOM is calculated:

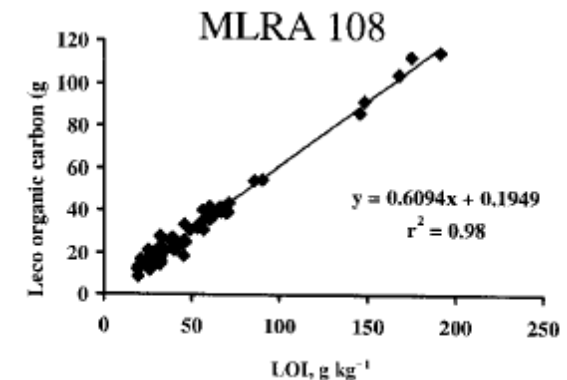
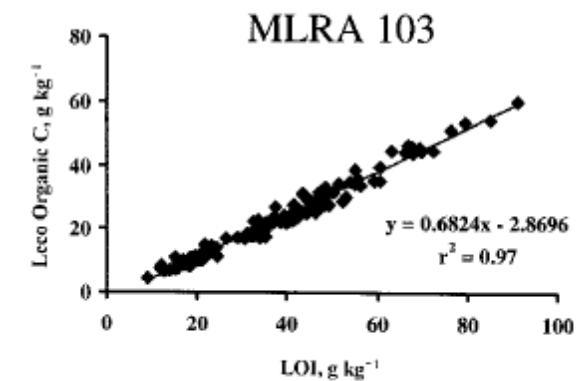
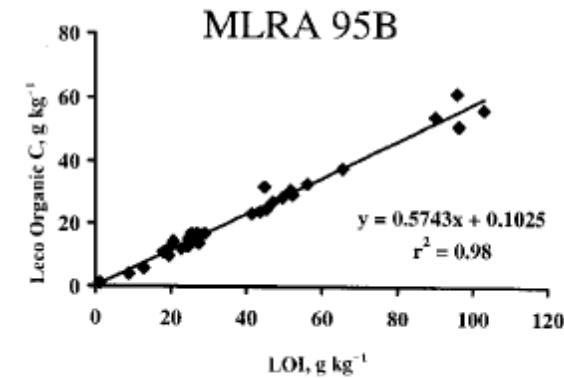
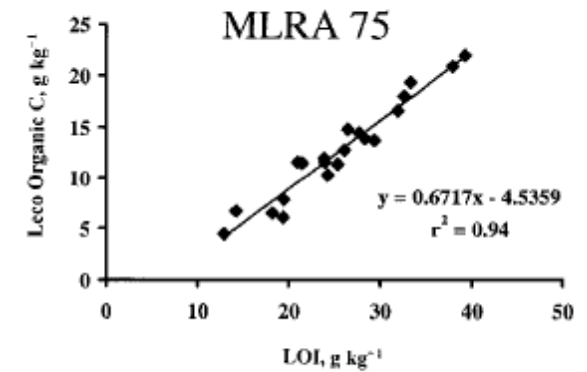
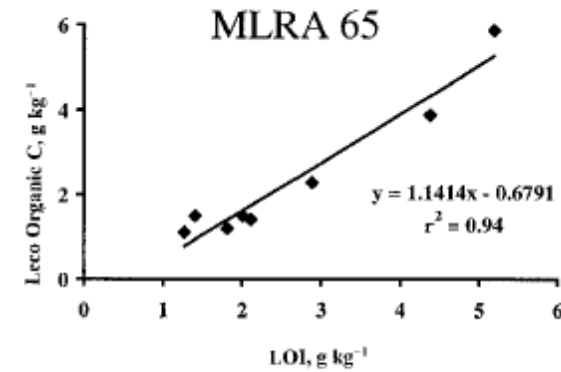
Mass loss = SOM (?) oxidation = $10 - 9.6 = 0.4$ g

Therefore: SOM concentration (?) = $0.4 / 10 = 0.04 \rightarrow 4\%$ or 40 g kg^{-1} .

- If this were a soil with 30% clay and if 25% of the clay were **kaolinite**, then the mass loss due to dehydroxylation would be 10.5 g kg^{-1} of soil. More than $\frac{1}{4}$ of the mass loss in the example would be loss from kaolinite, not SOM. **Keep temperatures at or below 400 deg C.**
- **Smectite** concentrations are much greater than kaolinite concentrations in most Iowa soils (e.g., 60-65% of clay fraction). The mass loss due to smectite in an Iowa soil sample will be about the same or even more than that due to kaolinite, depending on the concentration of clay. **No workaround for this error.**
- If 25% of the SOM in this soil were **char residues**, the true organic matter concentration would be 5.3% (53 g kg^{-1}). But the LOI-SOM (4%) would underestimate the true value by 1.3% (because the temperature was not high enough) – missing one-fourth of the soil organic matter (and carbon) that is actually there. **No workaround for this this error.**

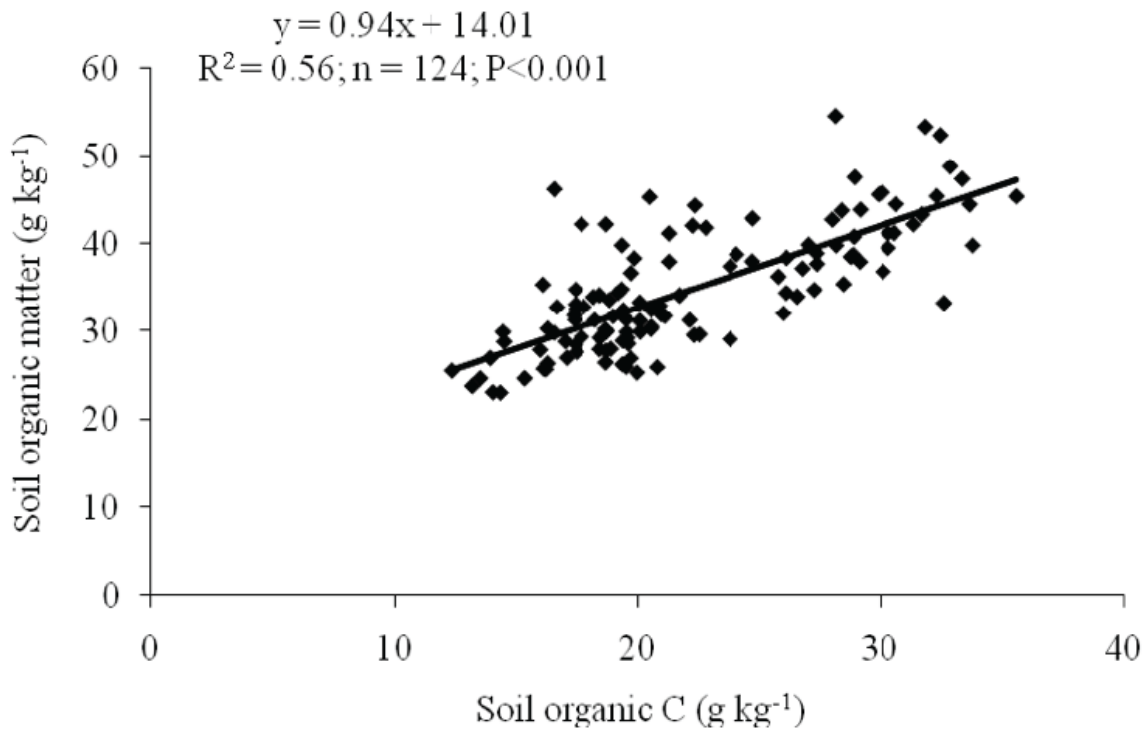
LOI-SOM correlates with dry combustion SOC, but the prediction error depends on soil characteristics (esp. mineralogy and char).

- Correlation graphs for soils in five soil regions in the Midwest (MLRAs).
- Slopes and intercepts differ considerably.

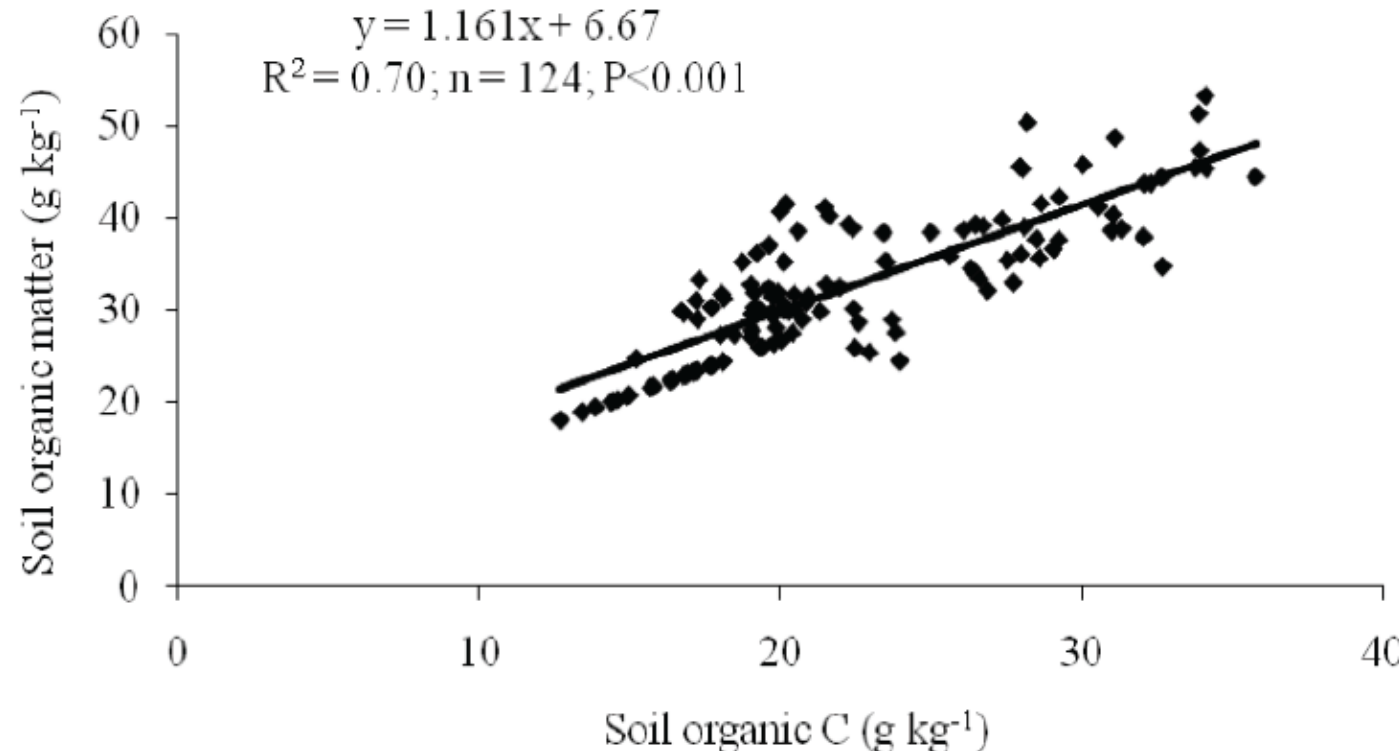


Sampling variation affects the uncertainty of prediction, too.

- Regression of LOI-SOM and SOC for 124 plots sampled in **2007**



- Same 124 plots sampled in **2009**
- Slope, intercept, and R^2 differ



Conversion of LOI-SOM to SOC is disputed

- The most common factor cited is that SOM is 58% SOC. So if you know SOM, you could in theory calculate SOC easily (multiply by 0.58).
- But that conversion (~200 years ago) was derived from some samples of highly decomposed, base-extractable organic matter rather than all soil organic matter.
- In addition, the method most commonly used to determine soil carbon for over 100 years, wet oxidation, was known not to oxidize all organic carbon very well, especially carbon in char residues.
- Today we recognize that there is no single conversion factor that is accurate for all soils. Some soil scientists argue that the *median* concentration of carbon in SOM is ~50%, not 58%.
- But should we ignore char residues? I think not. We need to count that as stored carbon and recognize its value. I am inclined to stick with the conversion factor of 0.58.

LOI – SOM is still useful to know as a general *soil health index and to predict trends in soil behavior*

- **Structure and bulk density:** SOM binds clay and silt particles into aggregates, preventing *erosion*, increasing *water-holding capacity*, providing space for *root growth*, promoting *gas movement* in soil
- **Cation exchange capacity** of SOM: Negative charge arising from ionization of weak-acid functional groups
- Source of **plant macronutrients** – especially N, P, and S
- Retention of **micronutrient metals**
- Adsorption of **pesticides and organic contaminants**

Alternatives to LOI to determine organic carbon concentration in soil

- Wet oxidation: organic carbon
- Infrared spectroscopy: organic carbon (and other soil properties)

Wet oxidation

Principle

- Use a strong chemical oxidant (potassium dichromate) in solution and at 170 deg C for 30 min.
- Use an autotitrator to measure the amount of Cr that was reduced as a reflection of the carbon that was oxidized.
- An experienced analyst could run 100 samples per day.
- The removal of inorganic carbon before analysis is simplified.

Issues of concern

- Samples must be heated uniformly during digestion (use a block digester).
- Chromium is toxic and the cost of waste disposal may be high.



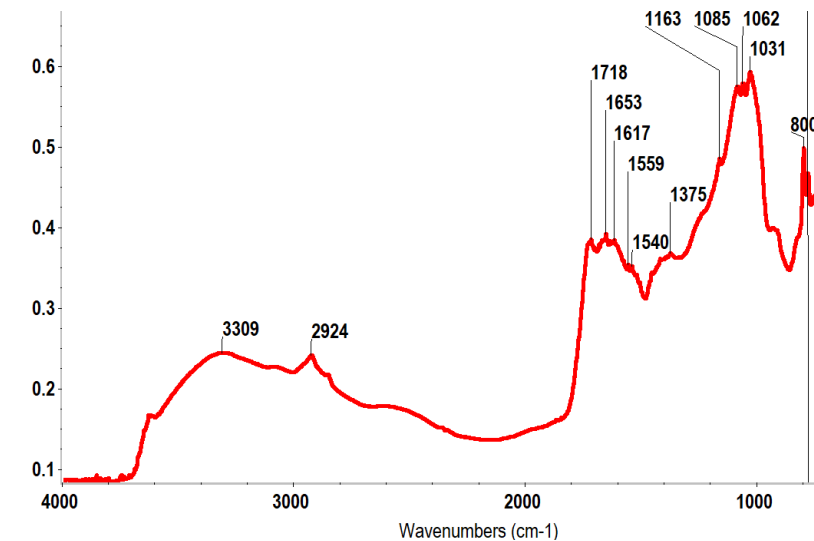
Diffuse reflectance infrared spectroscopy

Principle

- Peaks on the infrared spectrum are associated with specific organic functional groups.
- Functional groups are indicative of organic compounds.
- Absorbance values can be statistically correlated with amount of organic carbon in the sample, allowing prediction for unknown samples.

Practice

- Soil samples are dried, ground, and placed in a small sample cup. High throughput can be achieved with 96-well microplates. Some procedures include mixing the sample with KBr.
- Collecting a spectrum requires a few minutes per sample. Usually, many scans are averaged. Replicate samples are also averaged.



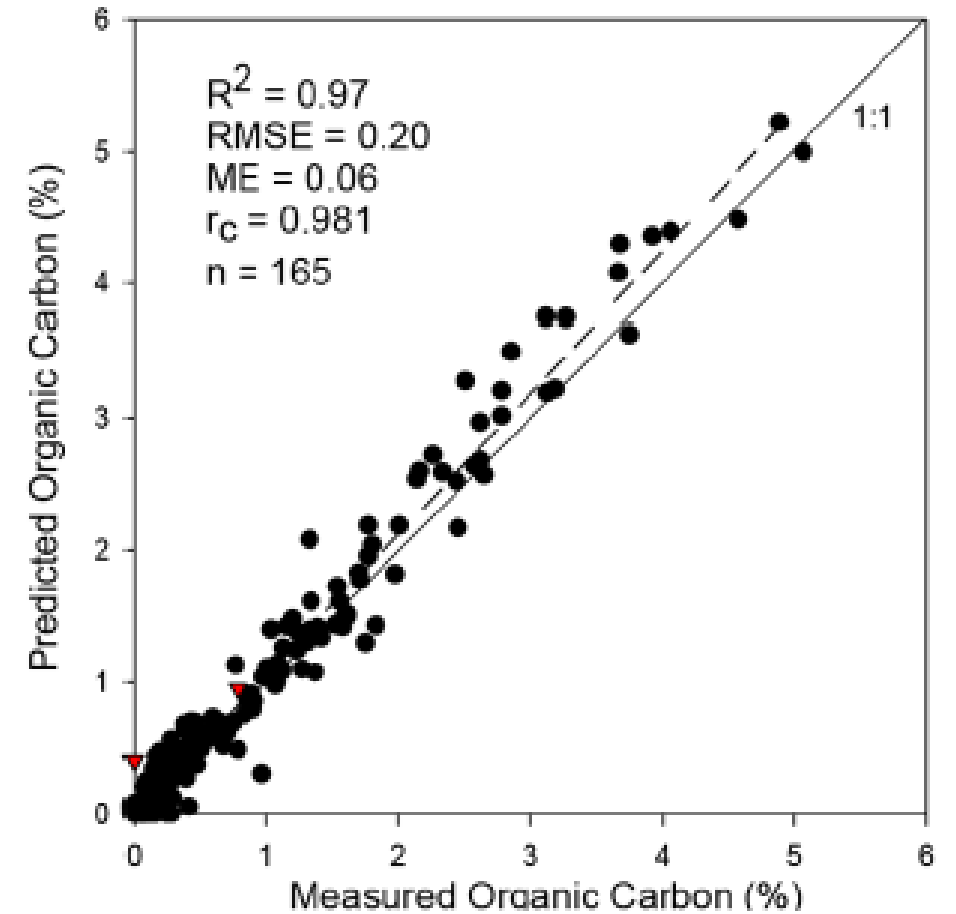
Empirical method

The method depends on organic carbon measurements of a calibration set of samples, ideally soils that are closely related to the unknown samples.

Spectra are processed with chemometric procedures and machine learning techniques to make predictions of organic carbon.

Prediction errors can be in the same range as the analytical error, as the mean error (ME) value (0.06%) at right suggests.

Analytical methods, instrumentation, and statistical techniques need to be standardized for this to be a practical tool for routine characterization of organic carbon.

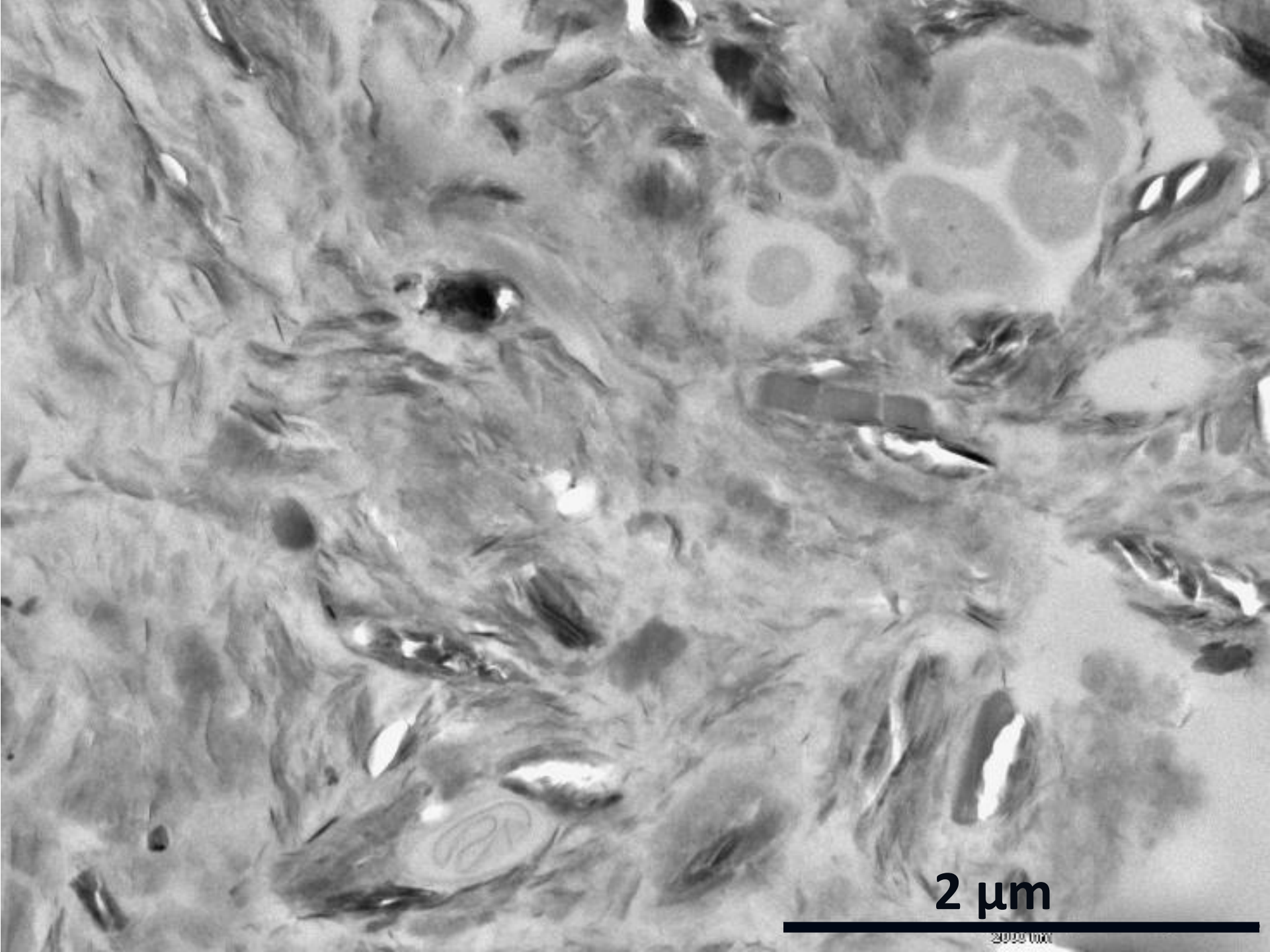


195 soil samples of mostly loess-derived soils in Kansas. Predictions were made using a calibration model based on ~3000 Mollisols in 15 US states.

Seybold et al. 2019. Soil Sci. Soc. Am. J. 83:1746–1759. doi:10.2136/sssaj2019.06.0205

Summary

- **Analytical uncertainty** in organic carbon analyses has an important impact on the calculation of carbon stocks.
- **Dry combustion** is the best method for determination of organic carbon concentrations, although analytical uncertainty remains.
- **Loss-on-ignition can be used to *estimate* soil organic matter**, but there are common interferences and omissions that lead to error.
- **LOI-SOM concentration is not sufficiently accurate or precise to predict soil organic carbon concentration for carbon market calculations.**

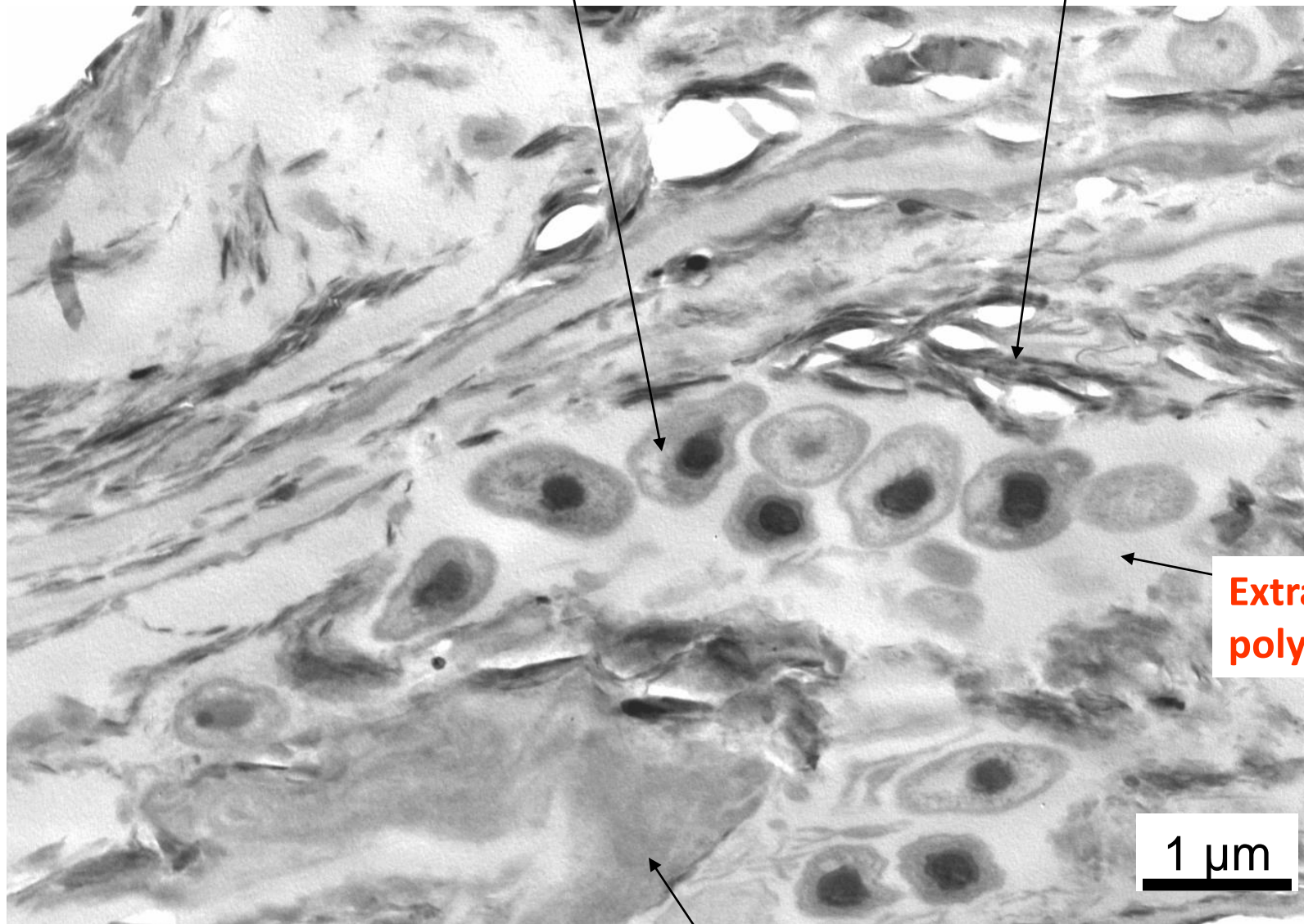


2 μm

2008 1000

microorganisms

layer silicate clay



**Extracellular
polysaccharide**

1 μm

humified organic matter

Why is soil organic matter important?

- **Structure and bulk density:** SOM binds clay and silt particles into aggregates, preventing *erosion*, increasing *water-holding capacity*, providing space for *root growth*, promoting *gas movement* in soil
- **Cation exchange capacity** of SOM: Largely a negative charge arising from ionization of O-containing groups.
- Source of **plant macronutrients** – especially N, P, and S
- Retention / binding of **micronutrient metals**
- Retention / binding of **pesticides and organic contaminants**
- **Carbon storage** in soils – SOM keeps carbon out of the atmosphere

What affects the concentration of SOM in a soil?

SOM is higher in soils with:

- Greater biomass inputs
 - Perennial plants
 - Fast plant growth
- Reduced erosion
 - Less tillage
 - Perennial plants
- Soil environment
 - High clay soil
 - Low disturbance
 - Less tillage, shrink swell
 - Lower temperature

SOM is lower in soils with:

- Lower biomass inputs
 - Annual plants
 - Slow plant growth
- Greater erosion
 - More tillage
 - Annual plants
- Soil environment
 - Sandy soil
 - High disturbance
 - More tillage, shrink-swell
 - Higher temperature