Food and Agriculture Organization of the United Nations

GLOSOLAN
Soil spectroscopy training workshops

Soil sample preparation for MIR measurement; Is fine grinding necessary for accurate MIR predictions?

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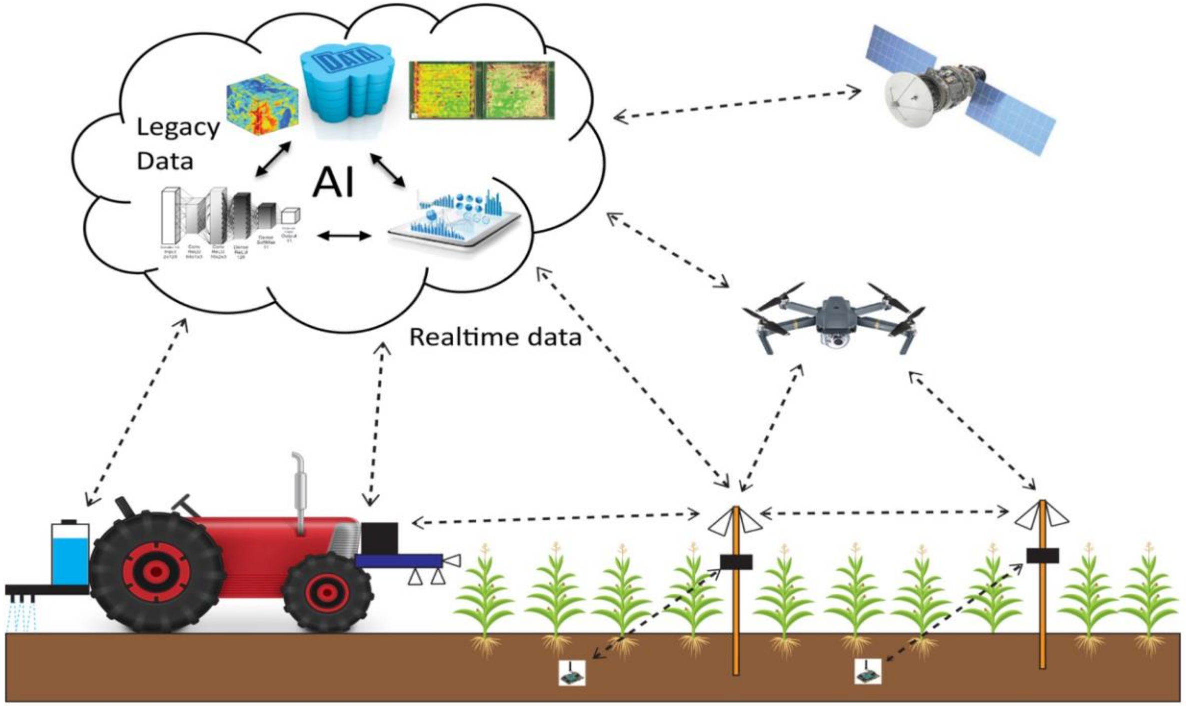
Online webinars

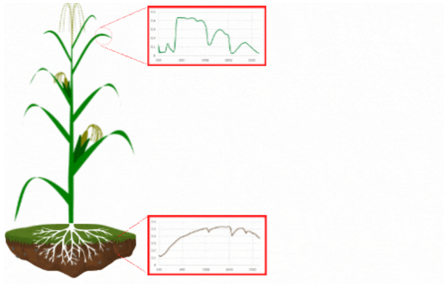
GLOBAL SOIL PARTNERSHIP

Advanced Plant & Soil Sensing Laboratory



Precision agriculture applications in soils & plants

Field soil sampling at North Farm, MSU in summer 2022



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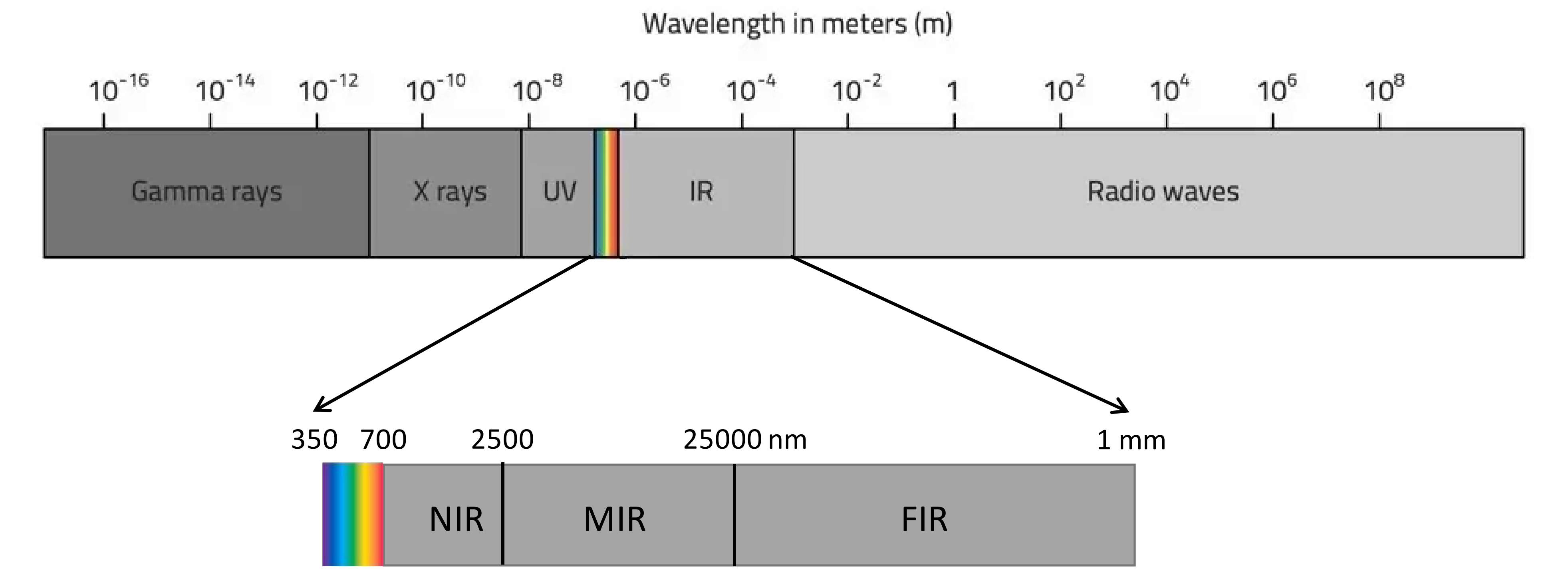
Outline

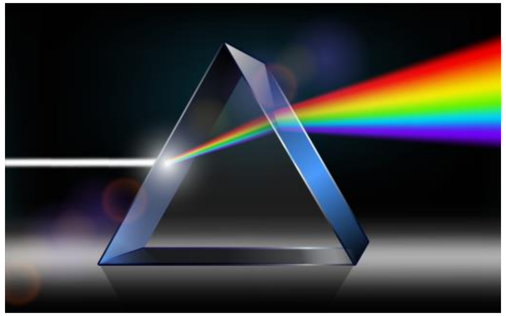
- MIR spectroscopy
- Sample pre-processing
- Why fine-grind?
- Why study fine-grinding effect
- Objectives
- MIR spectral library
- Subset selection for the study
- Data Analysis
- Results
- Conclusions
- Discussion

MIR spectroscopy

- Electromagnetic spectrum
  - Near infrared: 700-2500 nm
  - Mid infrared: 2500-25000 nm



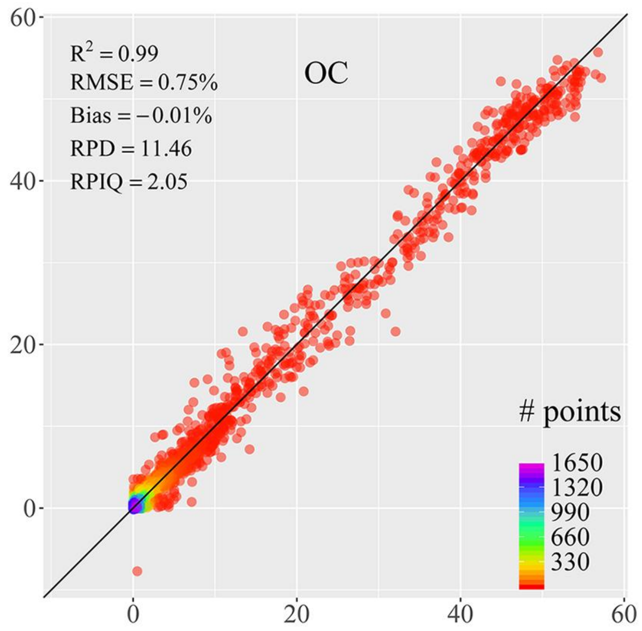
- Why spectroscopy?
  - Rapid
  - Non-destructive
  - Less-expensive
  - No need of expensive and time-consuming sample pre-processing
  - Less harmful to environment
  - Single spectrum → multiple properties
  - Efficient when large number of samples needed
  - Potential for field use



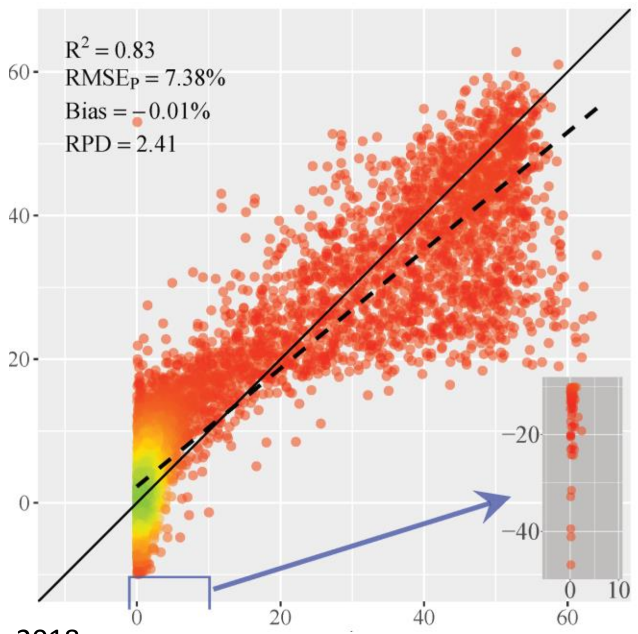
https://leverageedu.com/blog/what-is-spectroscopy/

- VisNIR vs MIR

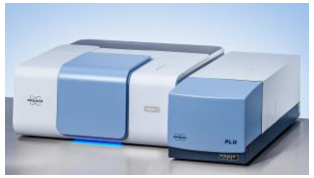
MIR	VisNIR
Primary absorption bands	Mostly overtones, combinational bands
High accuracy	Comparatively low accuracy
Expensive spectrometers	Cheap spectrometers available
Limited field use (on-the-go)	Easily adaptable for field use



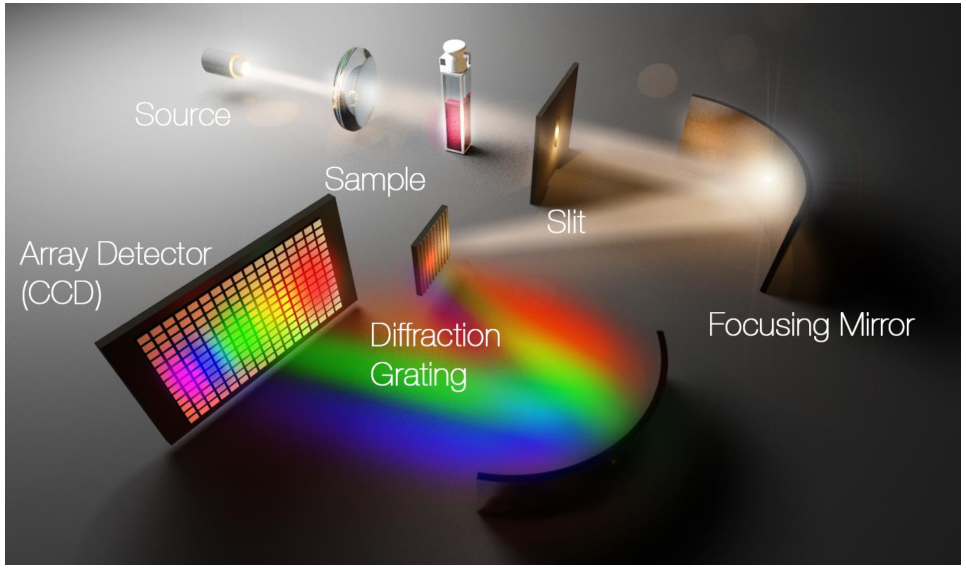
Organic Carbon Prediction

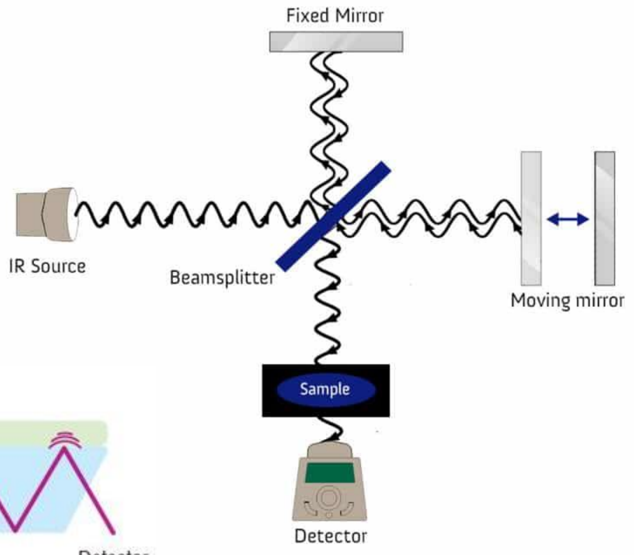


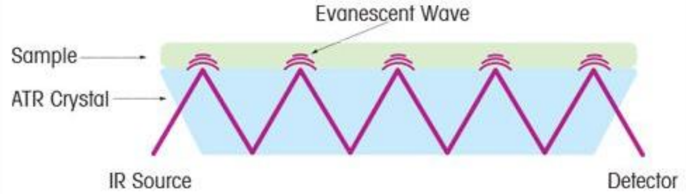
Wijewardane et al., 2016; 2018



- Spectrometers
  - Dispersive
  - Fourier transform (FTIR)
    - Higher signal-to-noise ratio
    - Higher sensitivity
    - Higher speed
    - Sampling techniques
      - Transmission
      - Attenuated Total Reflection (ATR)
      - Specular Reflection
      - Diffuse Reflectance
  - Different manufacturers and models
  - Laboratory and portable

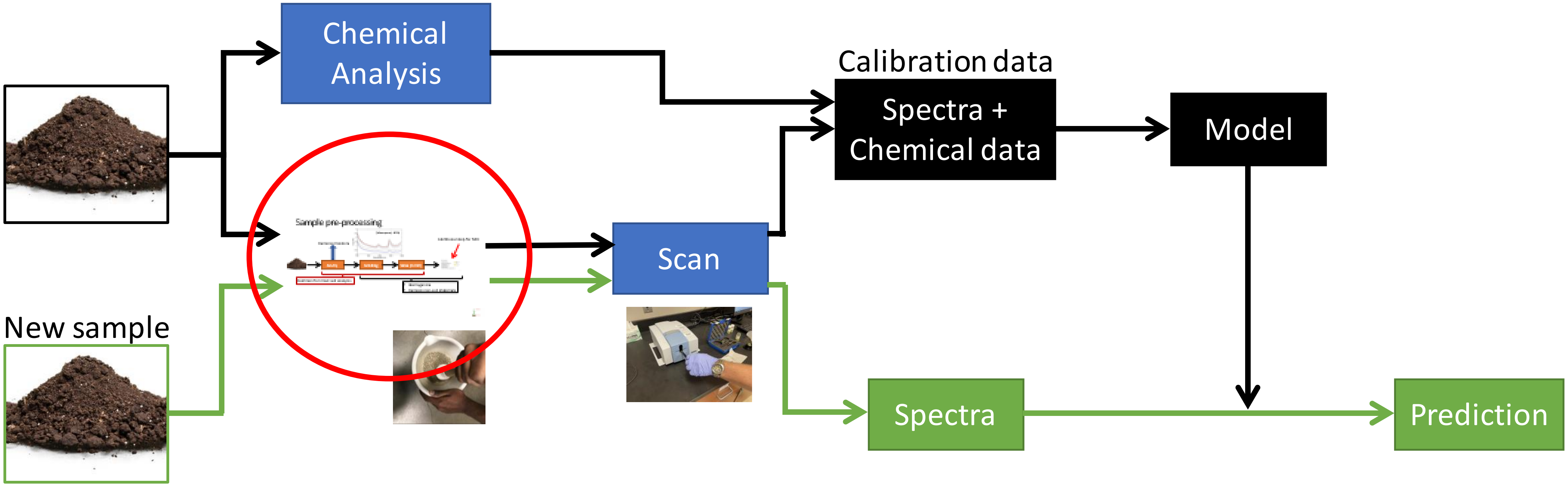






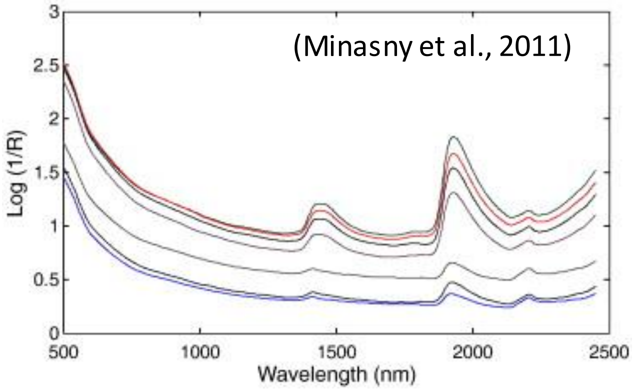
https://www.innovatechlabs.com/newsroom/672/stuff-works-ftir-analysis/
https://www.optecks.com/Portal/index.php/knowledge-center/spectroscopy-root/spect1
https://www.mt.com/my/en/home/products/L1_AutochemProducts/ReactIR/attenuated-total-reflectance-atr.html

• How spectroscopy works



Sample pre-processing

Remove moisture



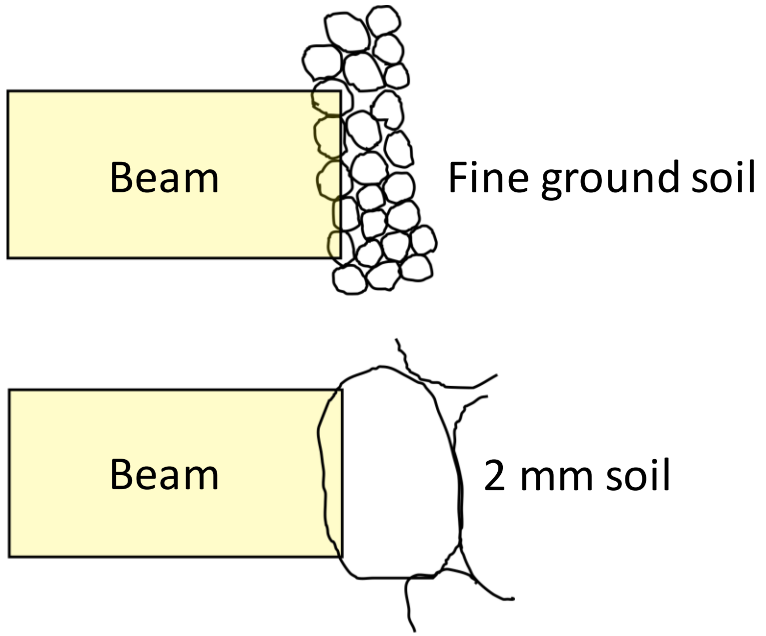
Air-dry → Grinding → Sieve (2 mm) →

Additional step for MIR

Common for most soil analysis

- Homogenize
- Remove non-soil materials

Why fine-grind?



- Homogenize sample
- Beam size and scan surface area
- Prevent specular reflections
- Higher reflectance
- Remove spectral artifacts
- Defined absorptions
- Expose more materials by aggregate breakup

- Higher accuracy - literature

Study	Fine grinding level	Conclusion
Stumpe et al., 2011	2 min	Up to 38 % increase in R^2 for pH and OC
Le Guillou et al., 2015	< 1mm	Up to 9% increase in R^2 for OC and texture
Barthès et al., 2016	< 0.2 mm	13% increase in R^2 for organic C
Janik et al., 2016	< 0.1 mm	Up to 33% increase in R^2 for Clay and Sand. 24% decrease in R^2 for Silt.
Deiss et al., 2020	< 0.5 mm	Up to 10% increase in R^2 for texture, pH, OC, and POXC

- Drawback
  - May break important chemical bonds
  - Change particle size distribution
- High cost, time, and labor involvement
  - Need a mill
  - Labor for sample loading, cleaning, instrument operation
  - 15 min grinding + cleaning time

Why study fine-grinding effect?

- Previous studies
  - Limited number of samples
  - Soils from a regions
  - Limited soil types
  - Variable results depending on soil property and sample set
  - Did not evaluate uncertainty of model predictions
- Impact on spectral libraries
- Can fine-ground (FG) spectra predict for non-fine-ground (NG)?

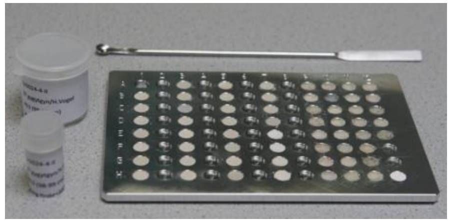
Objectives

- Compare FG and NG on model performance for 8 soil properties: TC, OC, TN, CEC, pH, and texture, using PLS and ANN
- Evaluate the performance of FG spectral library models to predict for FG versus NG sample spectra
- Evaluate the uncertainty of model predictions

MIR spectral library

- Open to public
- Generated & compiled by USDA-NSSC-KSSL
- Soil samples collected under different projects
- ~50,000 samples
- Pre-processing
    - Air-dry (30-35^{o}C for 3-7 days) → grind → sieve (2 mm) → fine grind (ball mill, <0.18 mm particles) → loaded into sample wells (6 mm diameter and 1.3 mm deep)
- 8 soil properties: TC, OC, TN, CEC, pH, clay, sand, and silt

- Scanning
  - Using Bruker Vertex 70 with HTS-XS accessory
  - 4000-600 cm^{-1} range
  - 4 cm^{-1} resolution
  - 4 replicates (loaded in 4 wells in spot plate)
  - 32 co-added instantaneous scans
  - Reference (empty well) before every scan
  - OPUS software to acquire spectra

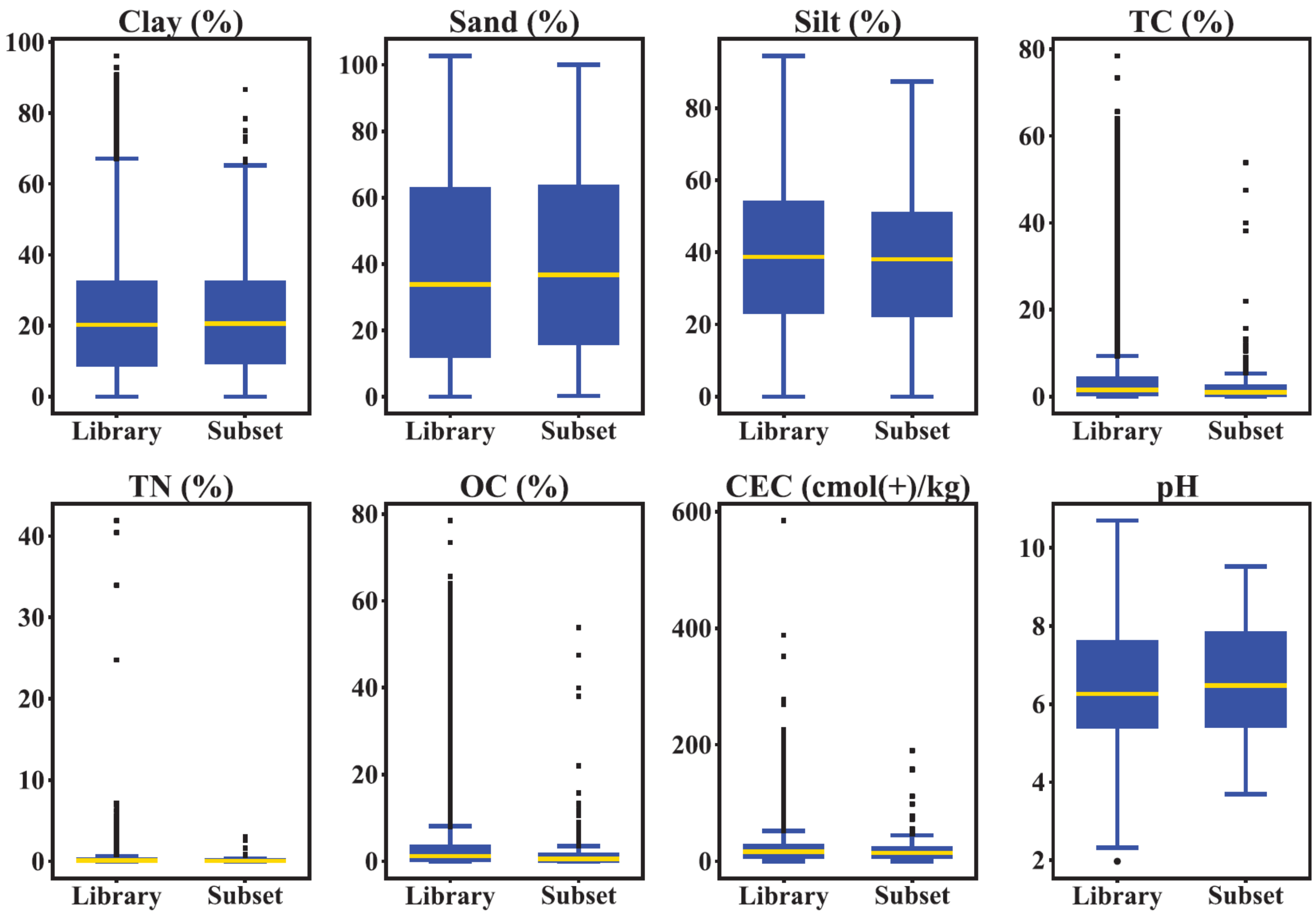


https://www.bruker.com/en/products-and-solutions/infrared-and-raman/ft-ir-routine-spectrometer/hts-xt-microplate-reader.html

Subset selection for the study

- Selected from spectral library
- Using stratified random sampling
  - Stratified on major horizon and taxonomic order
- ~500 samples in total
- Scan without fine-grinding (2 mm)
- Diverse sample set
  - Major horizons: O, A, B, C, and E
  - Taxonomic orders: Andisols, Entisols, Mollisols, Alfisols, Inceptisols, Ultisols, Aridisols, Spodosols, Vertisols, Histosols, and Gelisols

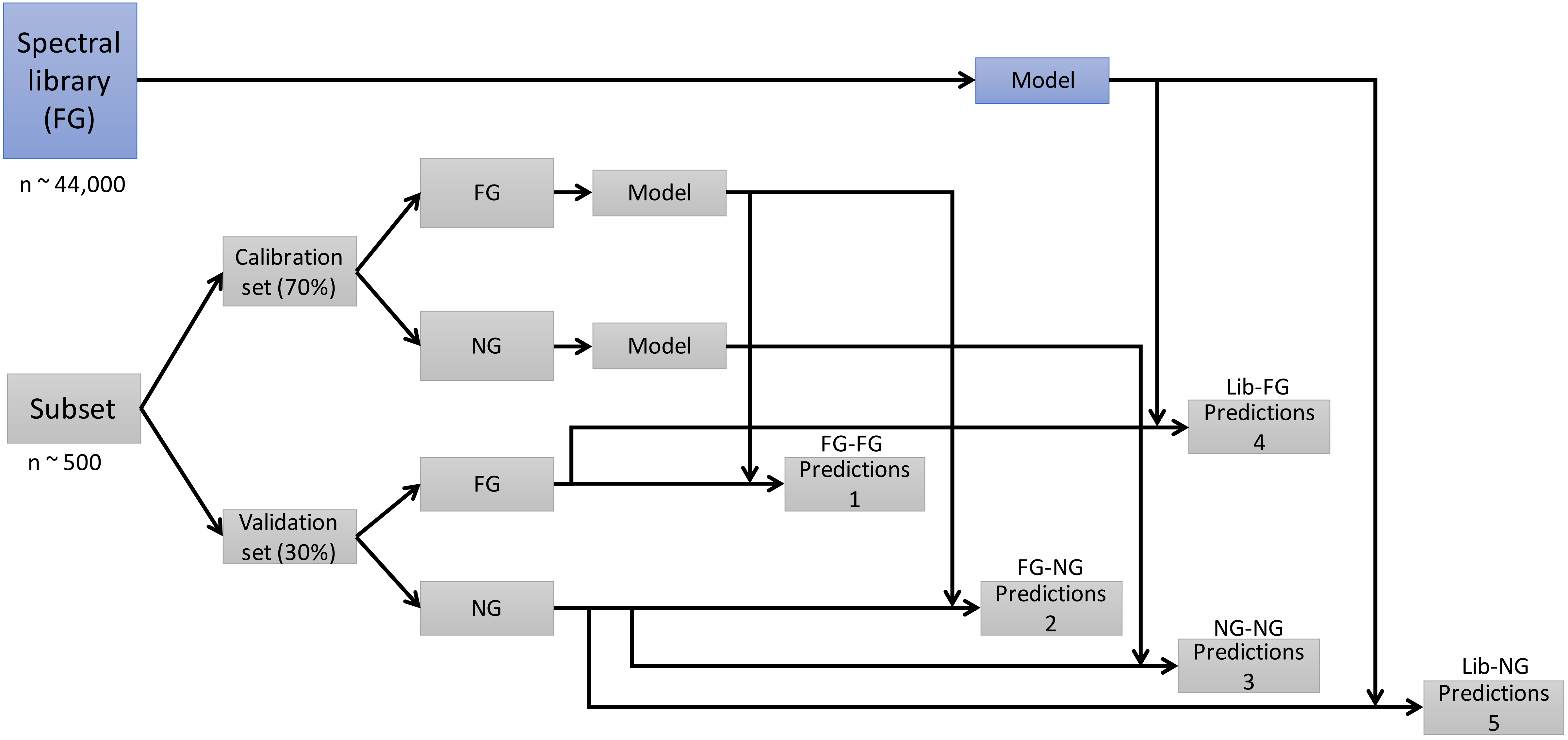
- Distribution of the eight soil properties



Data Analysis

- Spectral differences among spectra - Levene's test on PCs
- Randomly split subset: calibration – 70% and validation – 30%
- Five different model calibration-validation schemes
- Two modeling techniques: PLS and ANN
  - 10-fold cross-validation for model tuning
- Repeat with different calibration/validation splits to evaluate uncertainty
- Calculate prediction statistics: R^2, RMSE, and Bias

- Model calibration-validation schemes



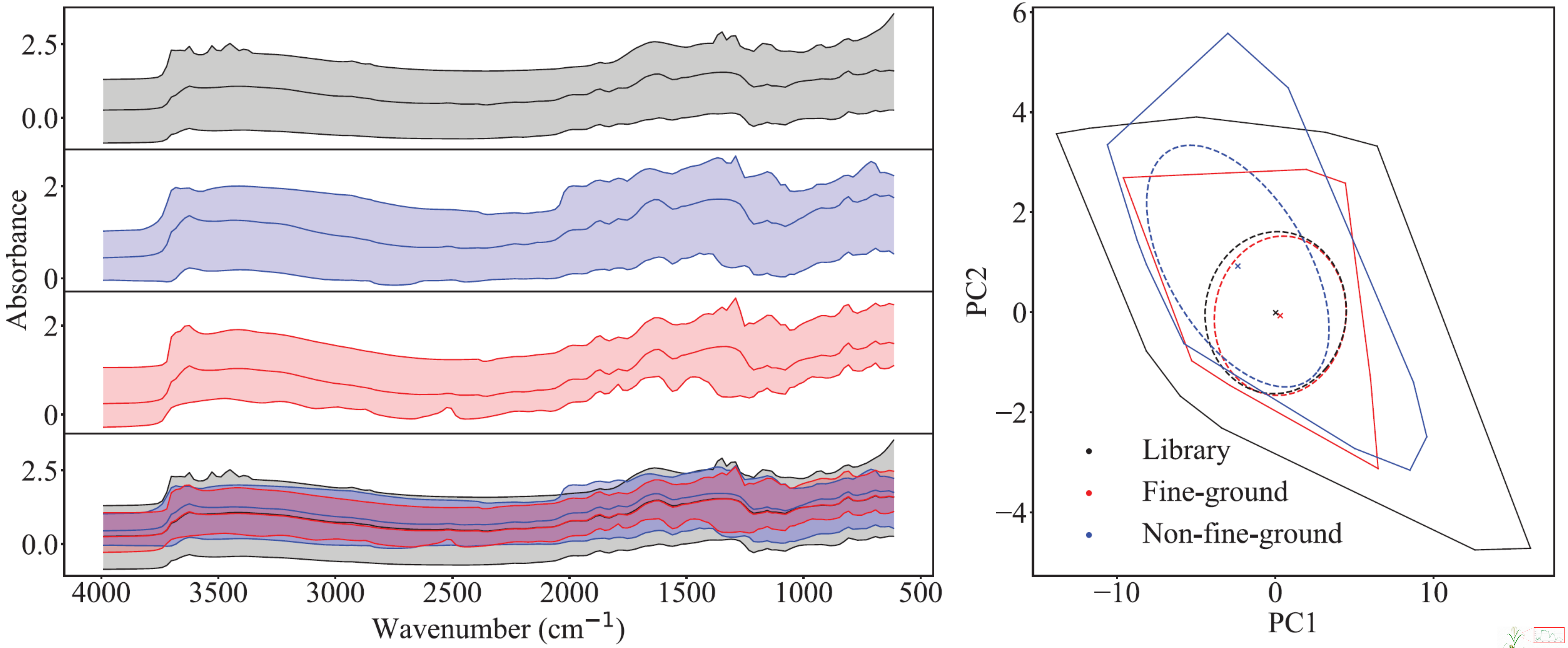
Results

- Spectral discrepancies among FG/NG/Lib
  - Different variances for both PC1 and PC2 for all except Lib vs FG
  - NG significantly deviating from FG

Spectral groups	PC1	PC2	Conclusion
	p value		
Library vs. FG	.13	.98	same variances
Library vs. NG	<.001	<.001	different variances
FG vs. NG	<.001	<.001	different variances
Library vs. FG vs. NG	<.001	<.001	different variances

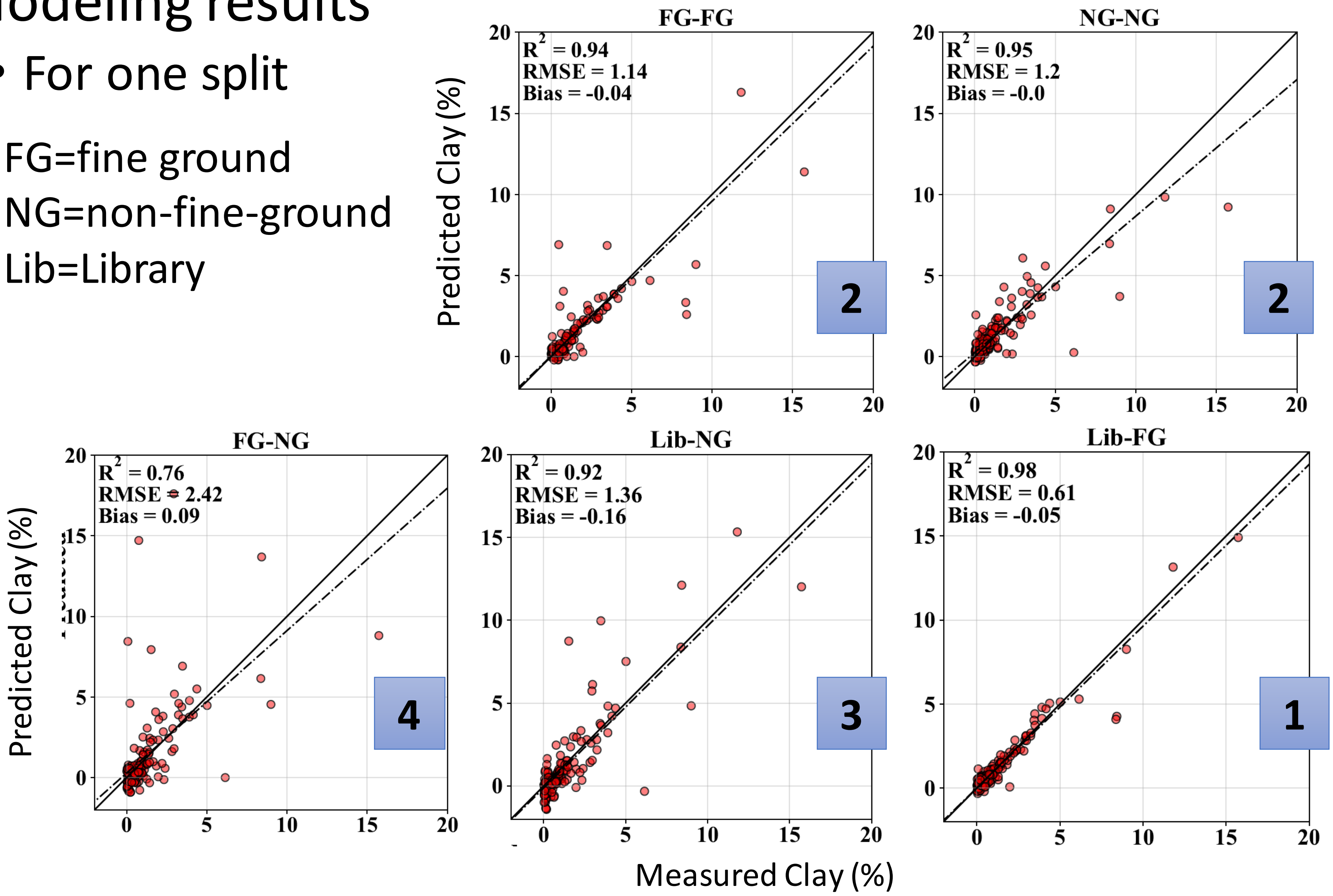
Note. FG, fine-ground; NG, non-fine ground.

- Convex hulls
  - Grinding reduce spectral variation – Guillou et al, 2015

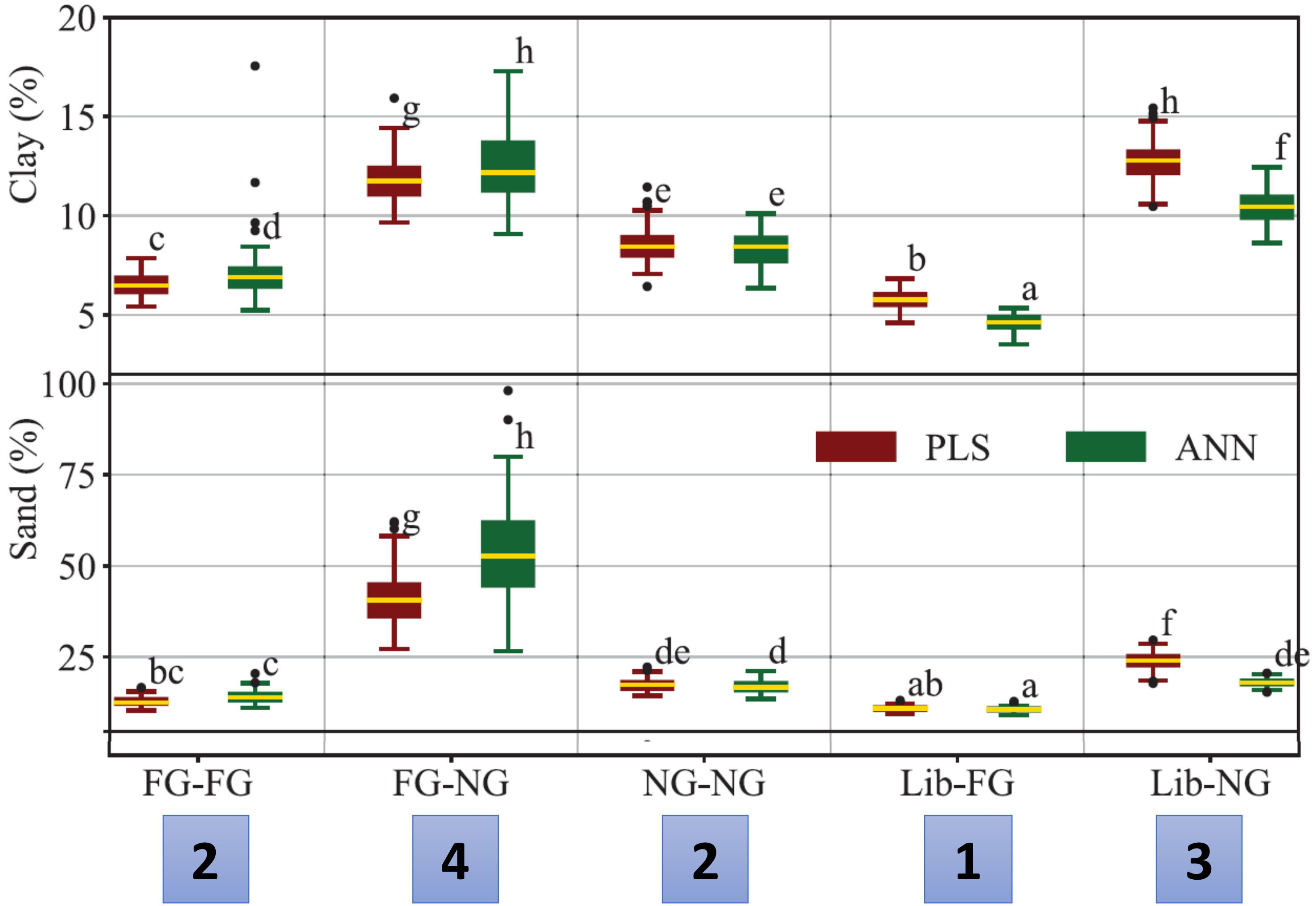


- Modeling results
  - For one split

- FG=fine ground
- NG=non-fine-ground
- Lib=Library

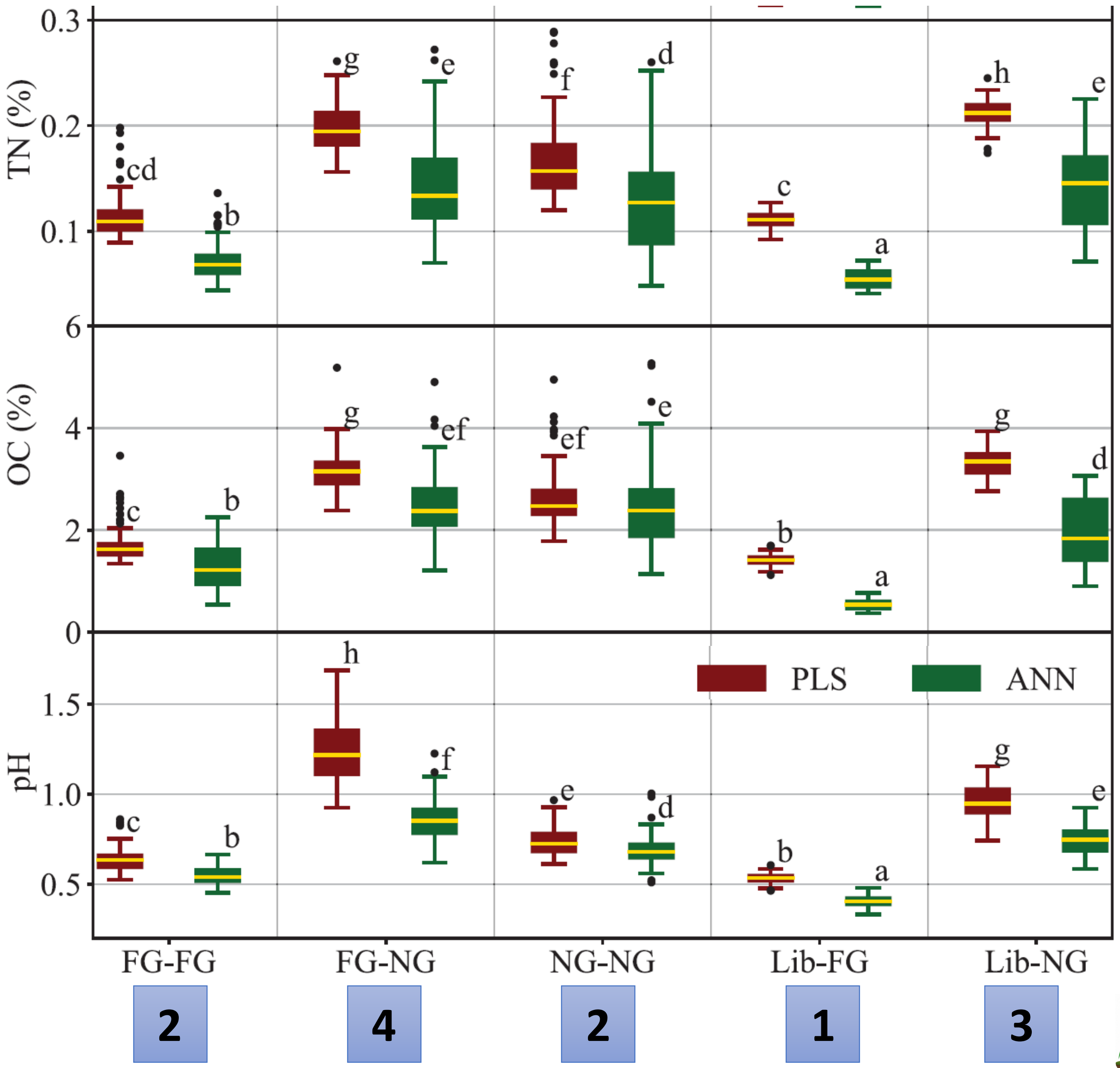


- Model uncertainty comparisons – RMSE
  - Significance letters: compare within same modeling tech
  - Library to FG: best
  - FG to NG: worse
  - PLS and ANN same conclusions



- Model uncertainty comparisons – RMSE
  - Significance letters: compare within same modeling tech

  - Library to FG: best
  - FG to NG: worse
  - PLS and ANN same conclusions
  - FG-FG: low variance



What we observed?

- Best case scenario: Library to fine-ground
  - Both are fine-ground
  - Robust and accurate models with large number of samples
- RMSE increase when library to non-fine-ground
  - Spectral differences
- PLS perform as good as ANN in smaller dataset (e.g., FG-FG)
- ANN perform better when library used
  - ANN (non-linear) capture local variations compared to PLS

Conclusions

- Mismatched grinding conditions → increase error
  - Spectral differences
- FG-FG is recommended
  - High overall accuracy
- Finer particles
  - Uniform distribution of materials
  - Capture representative spectra
  - Works with smaller scanning area (ATR)
  - Expose interior matrix to MIR beam → more defined spectral signatures

- Breakup highly reflective martials → reduce specular reflections
- Reduce specular reflections from large particles (high specular reflections can mask signatures in diffuse)

- High accuracy with ANN on spectral libraries

Decision on fine-grinding

- Influence by several factors
  - Cost & time
    - Capital cost for ball mill with accessories
    - One sample fine grinding ~$1.00 per sample additional
    - 2.5 min per sample
    - Larger (regional, national, continental) project → higher cost and time
  - Application
    - Field application (intact soils) → fine grinding not possible
    - Lab applications → possible

- Desired accuracy
  - Precision ag → need higher accuracy, high number of samples
  - Global scale studies → may tolerate some error
- Cost and time vs accuracy

Scenario (compared to Lib-FG)	% RMSE increase		
	Min	Average	Max
FG-FG (compared to Lib-FG)	0	17	22
FG-NG (compared to Lib-FG)	82	155	278
Lib-NG (compared to Lib-FG)	80	112	141
NG-NG (compared to Lib-FG)	27	62	97
NG-NG (compared to FG-FG)	8	39	91

- Never use mismatching grinding conditions for modeling

- What we did not try?
  - Non-ground spectral library to non-ground spectra
    - Library not available
    - High cost and time
  - Calibration transfer

- Publication
  - https://acsess.onlinelibrary.wiley.com/doi/full/10.1002/saj2.20194

Soil Science Society of America Journal

SOIL CHEMISTRY

Fine grinding is needed to maintain the high accuracy of mid-infrared diffuse reflectance spectroscopy for soil property estimation

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Abstract

In mid-infrared diffuse reflectance (MIR) soil spectroscopy, grinding is one major step that can have pronounced effects on spectra and model calibrations. The reported literature on the effects of fine grinding on spectroscopic model performance have been inconsistent, likely in part because of limitations in sample set and model calibrations in previous studies. This study was focused on answering the question whether fine grinding is necessary for MIR spectroscopy in order to minimize model uncertainty. The main goal of this study was to compare model performance with and without fine grinding for eight soil properties using two different modeling techniques: partial least squares regression (PLS) and artificial neural networks (ANN).

Thank You