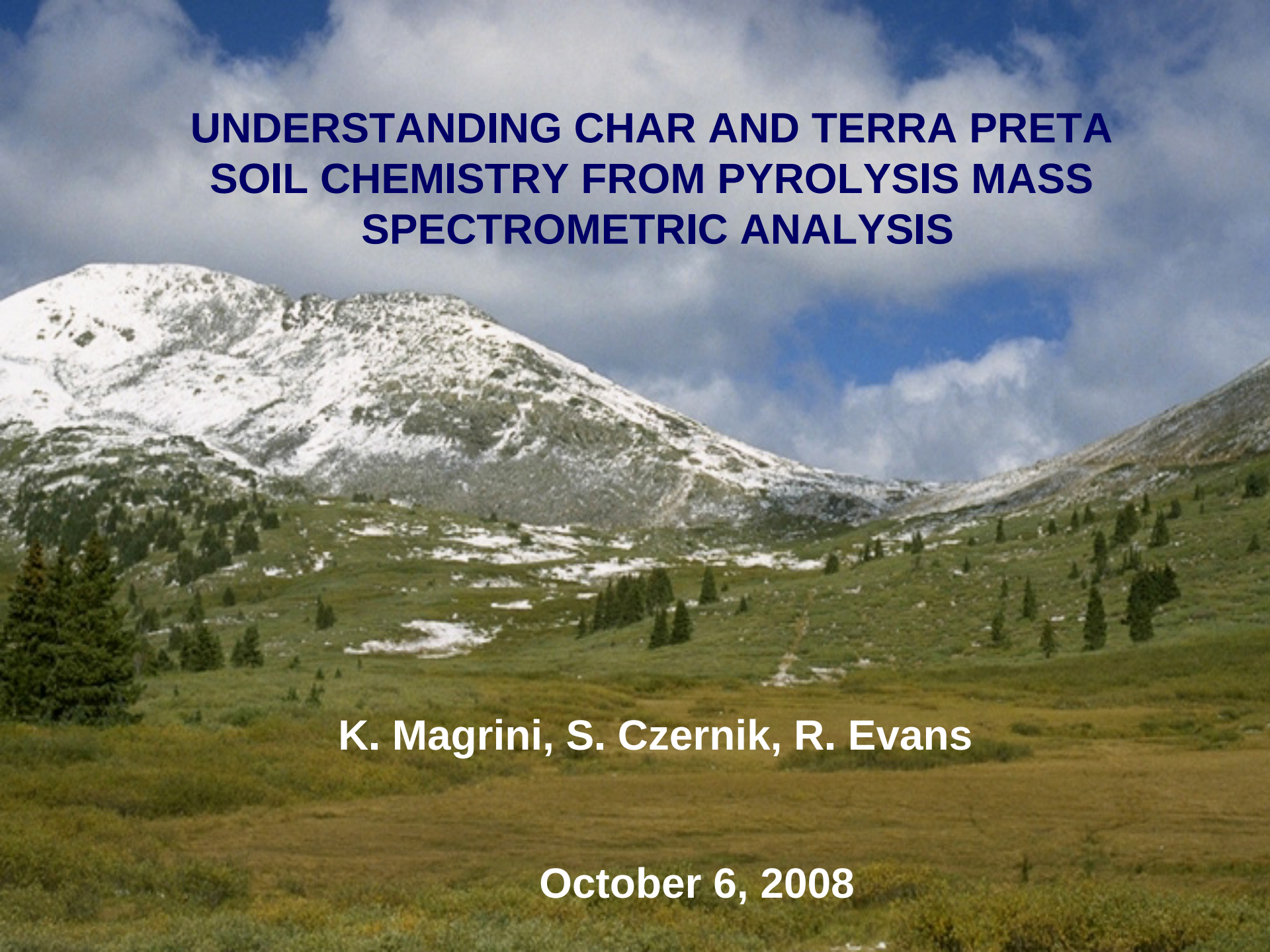

UNDERSTANDING CHAR AND TERRA PRETA SOIL CHEMISTRY FROM PYROLYSIS MASS SPECTROMETRIC ANALYSIS

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October 6, 2008

OUTLINE

Rapid SOC Analysis

- Py-MBMS Instrument and Methods
- Multivariate Analysis

Results

- Characterized and Managed Soils
- Terra Preta Soils

Conclusions

MOLECULAR BEAM MASS SPECTROMETRY

- Combustion mode provides

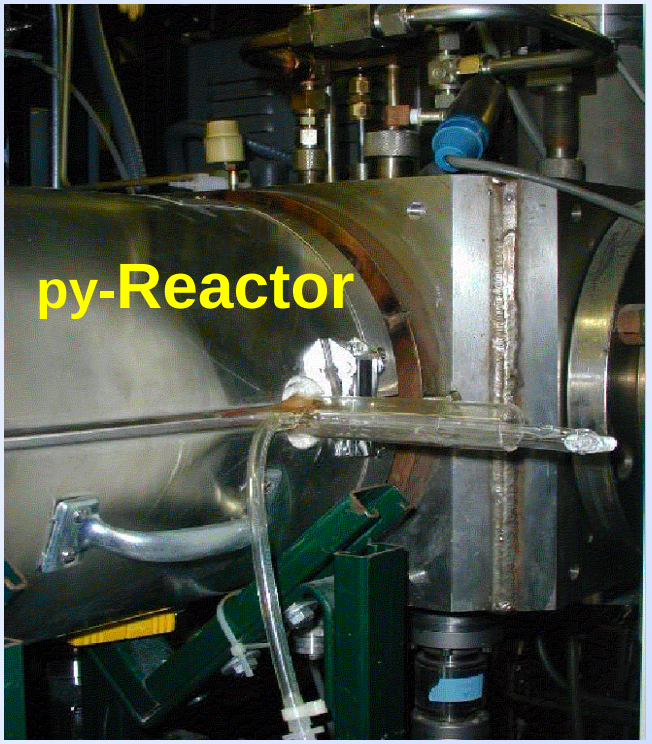
  C, N, and S concentrations

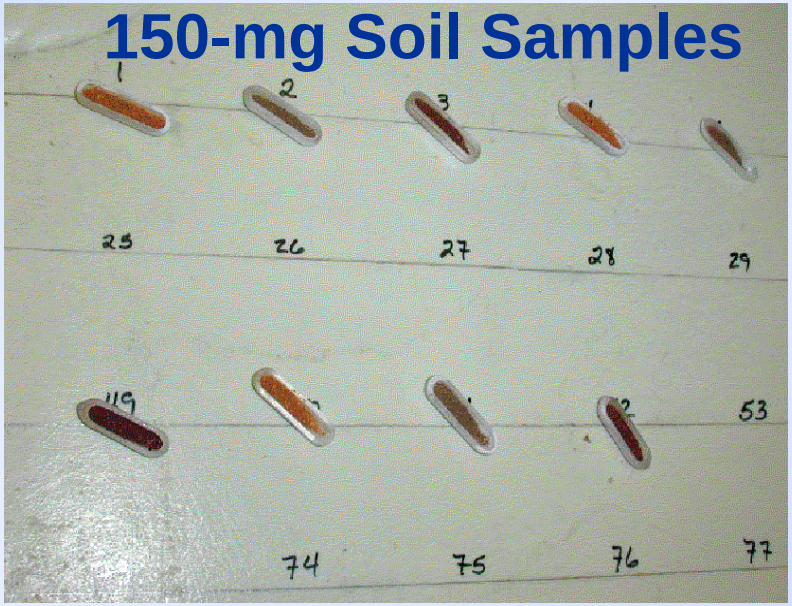
- Pyrolysis mode provides

  SOC chemistry

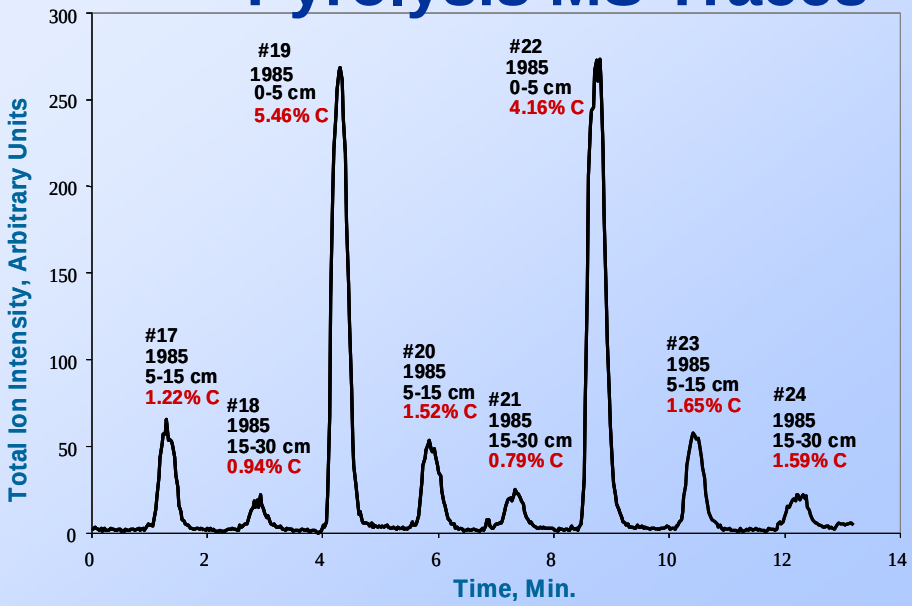
- Handles large number of samples (100-300 samples/day)

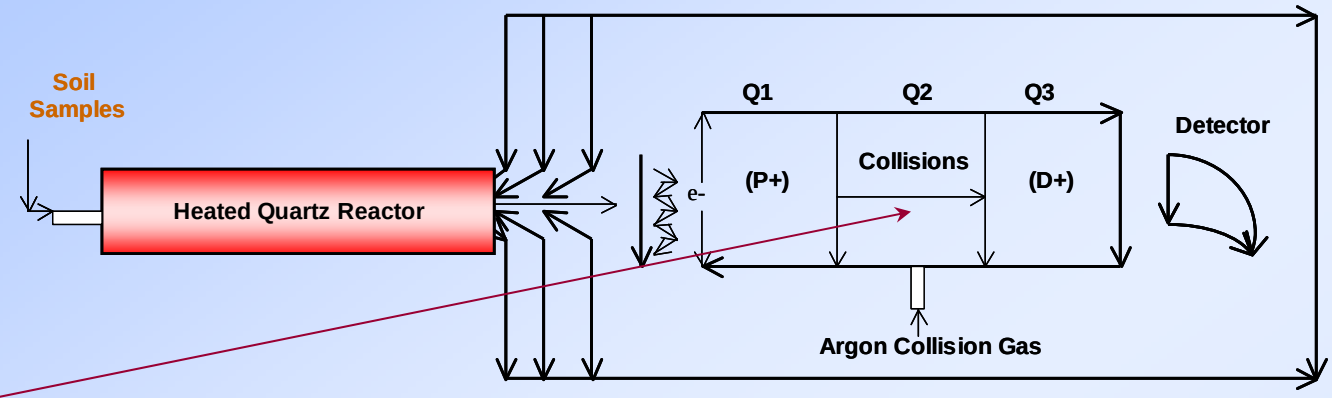
- Analysis time is short (2-5 minutes)



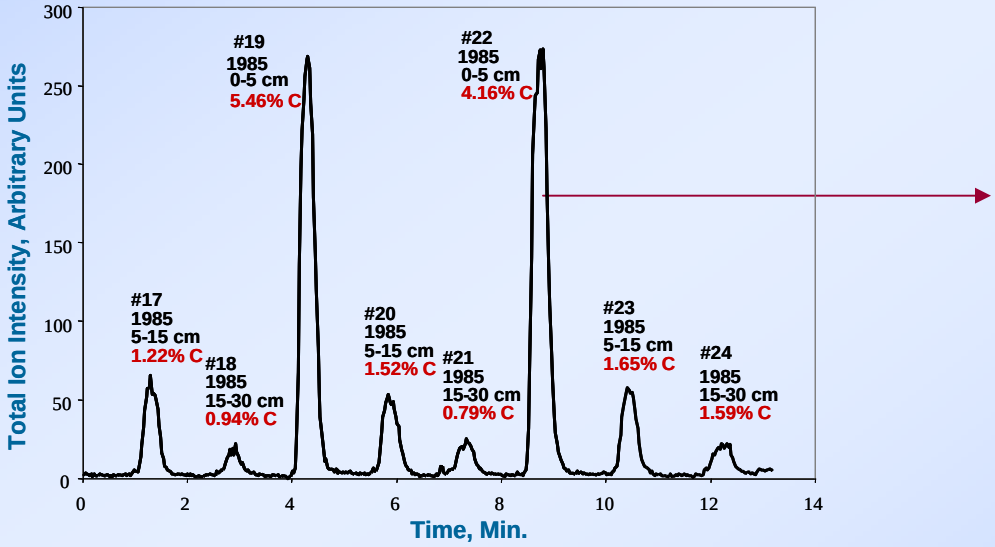


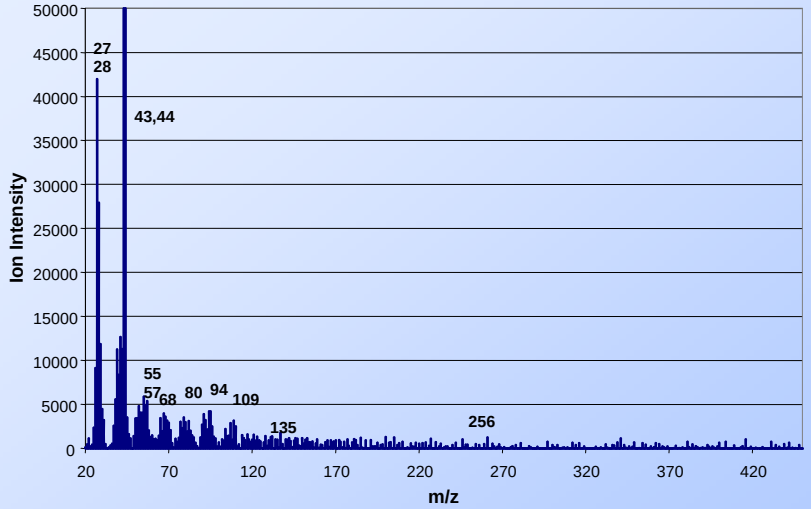
Pyrolysis MS Traces





CID provides a mass spectrum of a specific fragment ion for unique identification
i.e. Mass 396 is fragmented to identify ergosterol as the parent species





- Correlate with other spectroscopic techniques MIR, NIR, DRIFTS
- Correlate with other characterization data
- Build comprehensive SOC database for research use

PRINCIPAL COMPONENT ANALYSIS AND PLS MODELING

A projection method that helps to visualize information

- PCA helps to determine which samples are different and which variables are contributing
- to the difference
- Helps to determine groupings
- Helps quantify the amount of useful information
- PLS builds predictive models with quantitative information

Py-MBMS SOC ANALYSIS

- Analytical pyrolysis coupled with molecular beam mass spectrometry (py-MBMS) and multivariate statistics for rapid soil organic carbon (SOC) chemistry analysis of varied, characterized soils to establish breadth of application

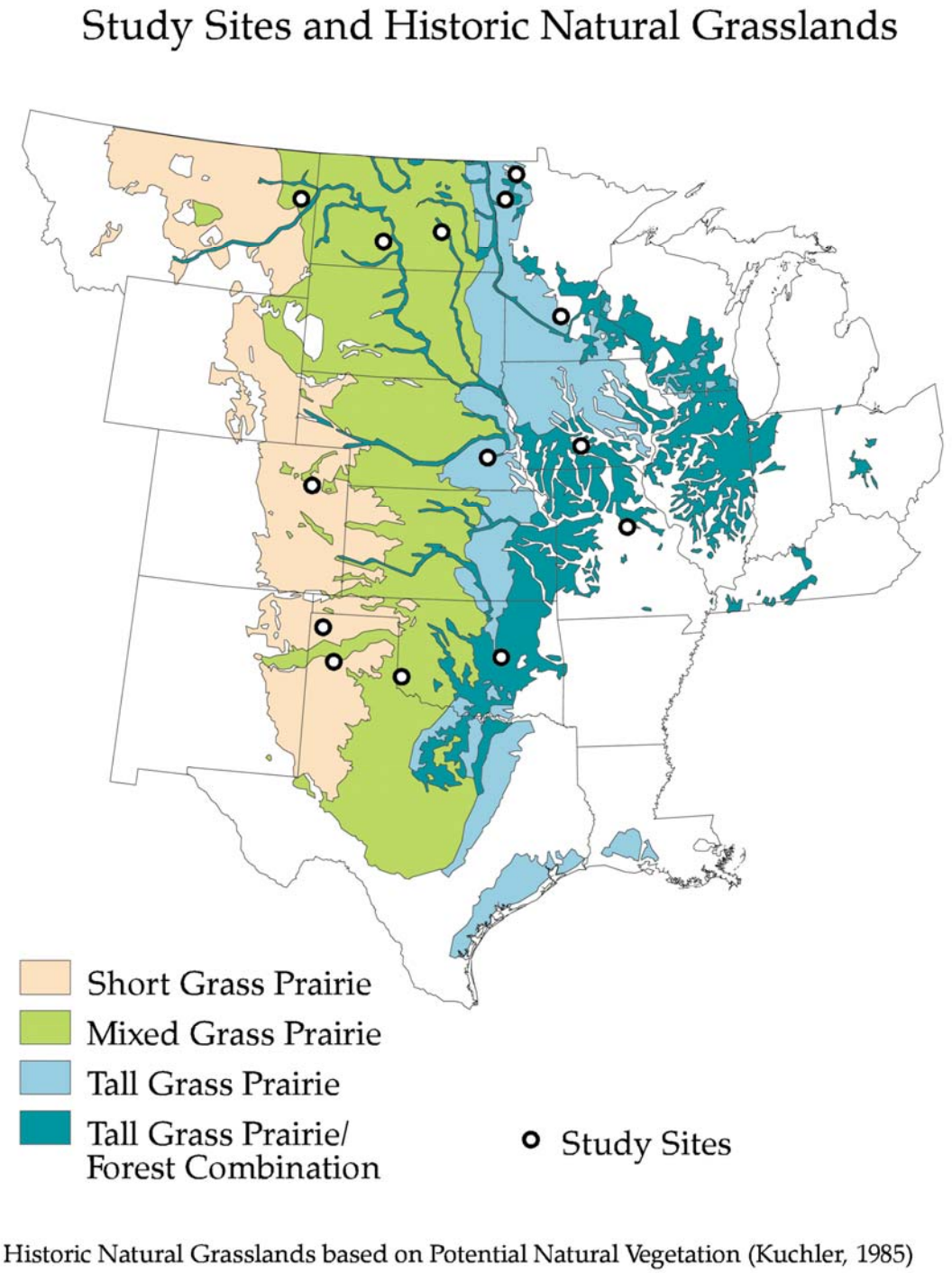
RESULTS

- Forest soils: distinguish disturbance,depth and location
- Agro forest: SOC accumulation with poplar rotation (litter and root inputs with depth)
- Grassland CRP soils: distinguish management impacts
- Native prairie soils: quantitating SMBC, SOC, POM C, Cmin, fractions
- Agricultural management for SOC accumulation (switchgrass)
- Terra preta chemistry

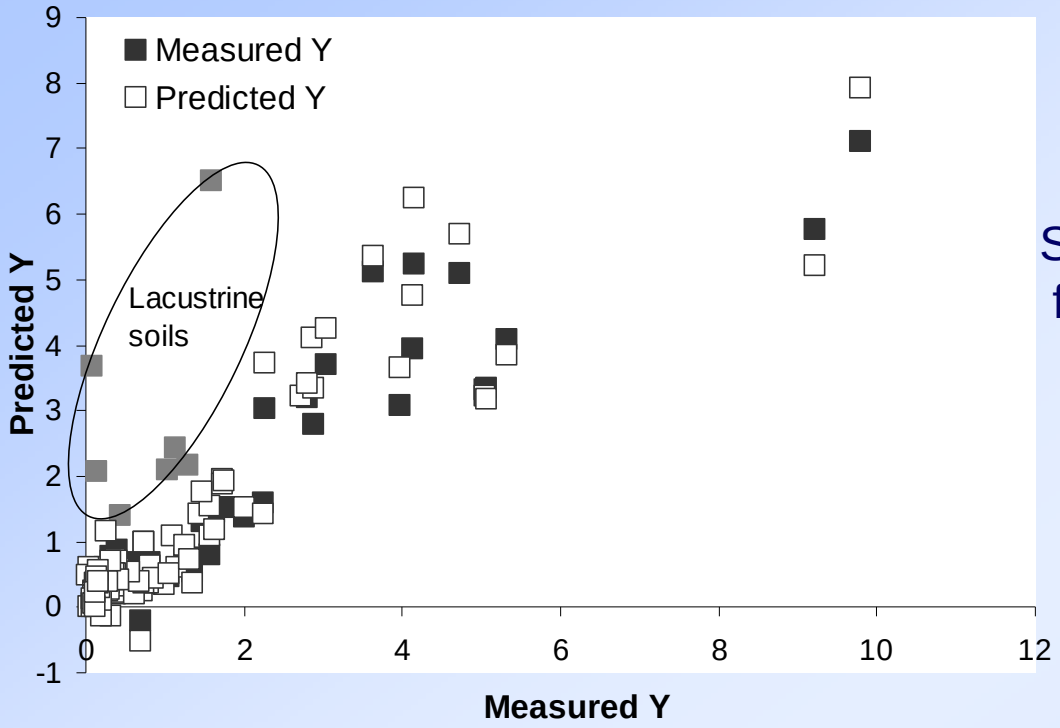
Native prairie soils: quantitating SMBC, SOC, POM C, C min

Soil characterization data

PARAMETER	RANGE
Depth (cm)	0-225
SOC (wt %)	0.02-9.8
SMBC (µg/g soil)	3.6-4933
POM C (g/g soil)	0.01-7.73
Cmin C (g/g soil)	0.61-1.16
Calendar Age (YBP)	0-16157 yrs

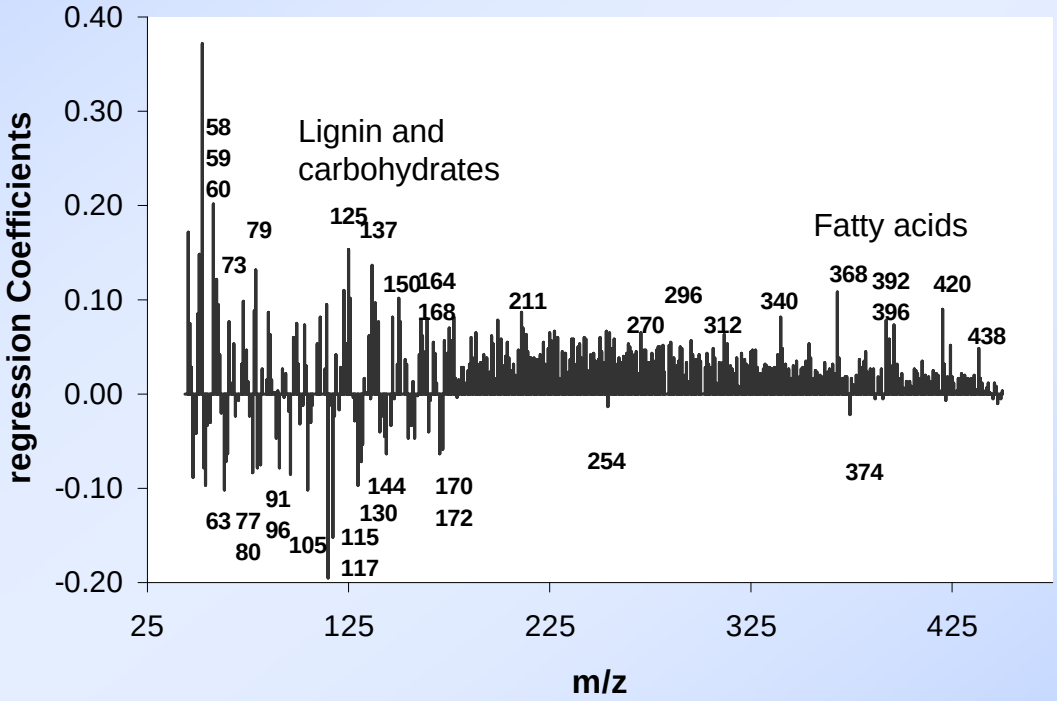


ESTIMATING SOC



SOC PLS 1 model for all samples

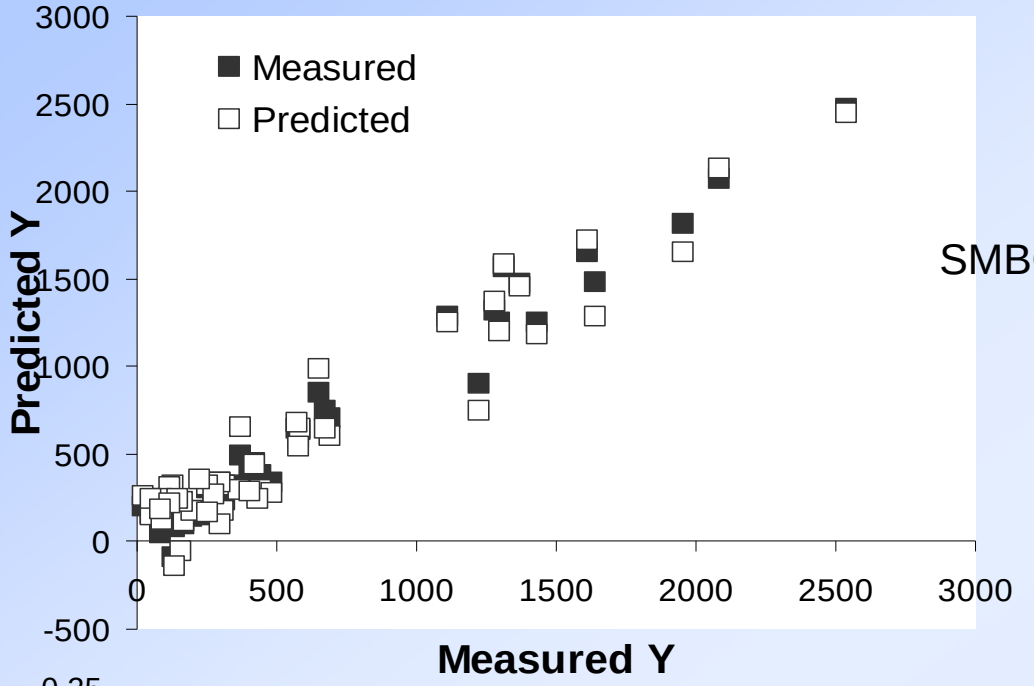
- Lacustrine soils different
- Complex SOC spectra containing lignin, fatty acids ergosterol, and carbohydrate species



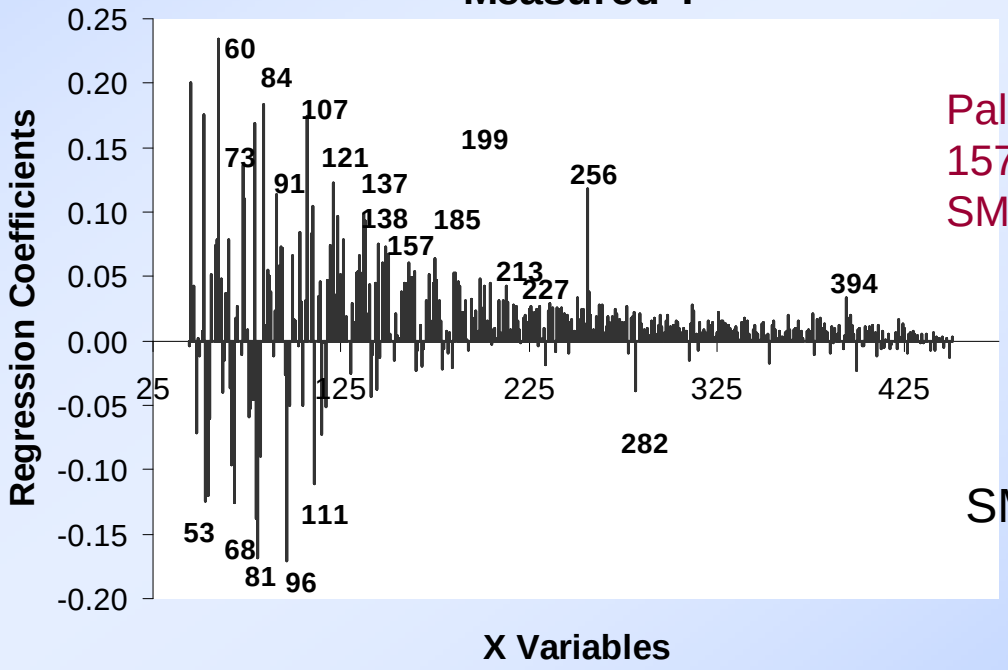
SOC model regression coefficients

Magrini et al., 2007.

ESTIMATING SMBC



SMBC PLS 1 model for all samples

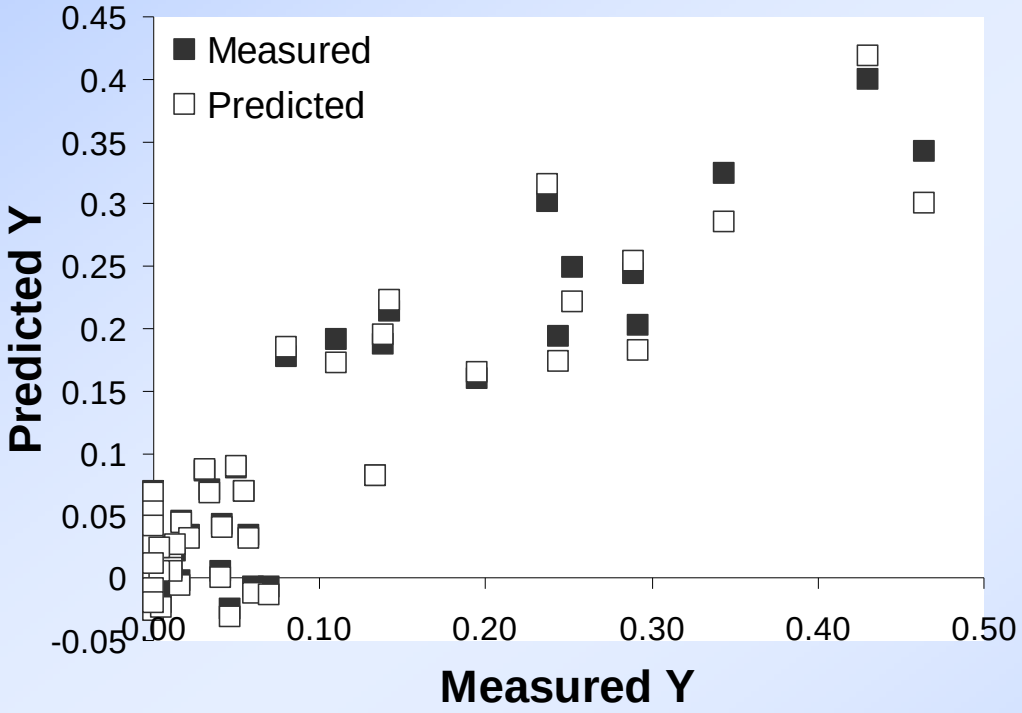


Palmitic acid: 74, 87, 101, 115, 129, 143, 157, 171, 185, 199, 213, 227, 256
SMBC biomarker

SMBC model regression coefficients

Magrini et al., 2007.

ESTIMATING SMBC FROM MASS 256



PLS1 model regressing SMBC vs. mass 256

Single mass has potential to be used as an SMBC biomarker

Magrini et al., 2007.

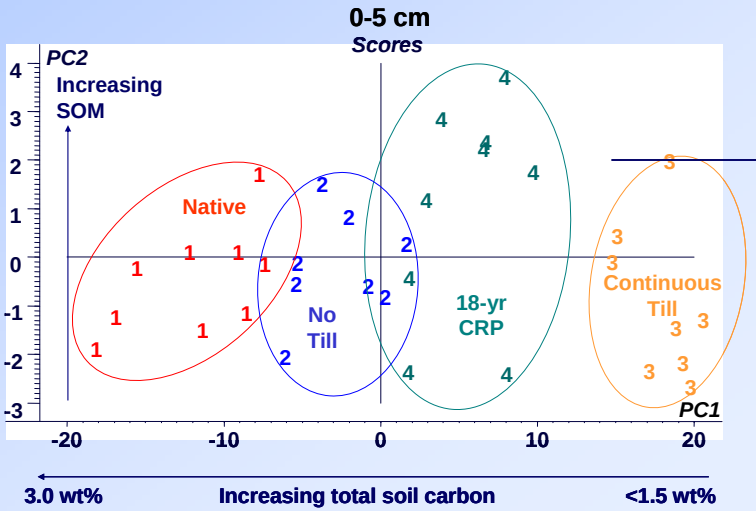
SUMMARY OF PLS MODELS CONSRUCTED WITH SAMPLE CHARACTERIZATION DATA

Variable	# of Samples	Correlation	# Principal Components	Slope	RMSEP
% Carbon	90	0.96	6	0.92	0.37
POM C	27	0.96	3	0.92	0.61
C min	28	0.92	1	0.83	0.53
SMBC	48	0.96	6	0.97	173
^{14}C Calendar Age	20	0.91	2	0.83	2210

Depth	0-225 cm
SOC	0.02-9.8 wt%
SMBC	3.6-4900 µg/g
POM C	0.01-7.7 µg/g
C min	0.6-1.2 g/g
Calendar Age	0-16000 yrs

K. A. Magrini, R. F. Follett, J. Kimble, M. F. Davis, and E. Pruessner.2007. Soil Science.

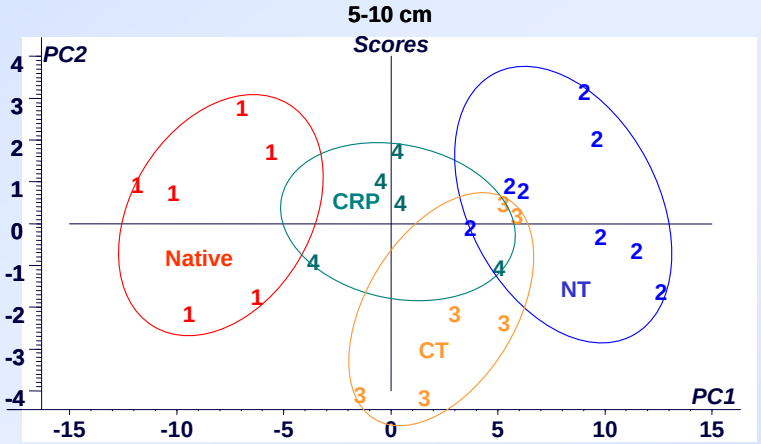
Can we determine sequestration potentials of soil types and management impacts?



Samples from Idaho farm in CRP 18 years.

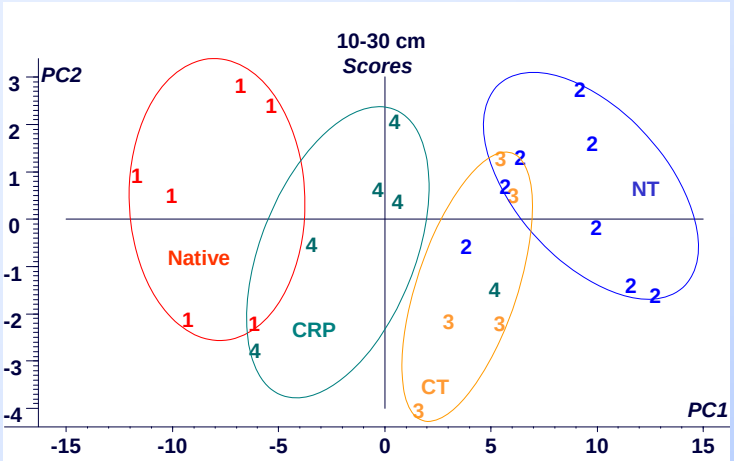
PCA shows land may need to be in CRP longer to recover to native standard SOC levels.

CRP Impacts on SOC
Kimble 2003



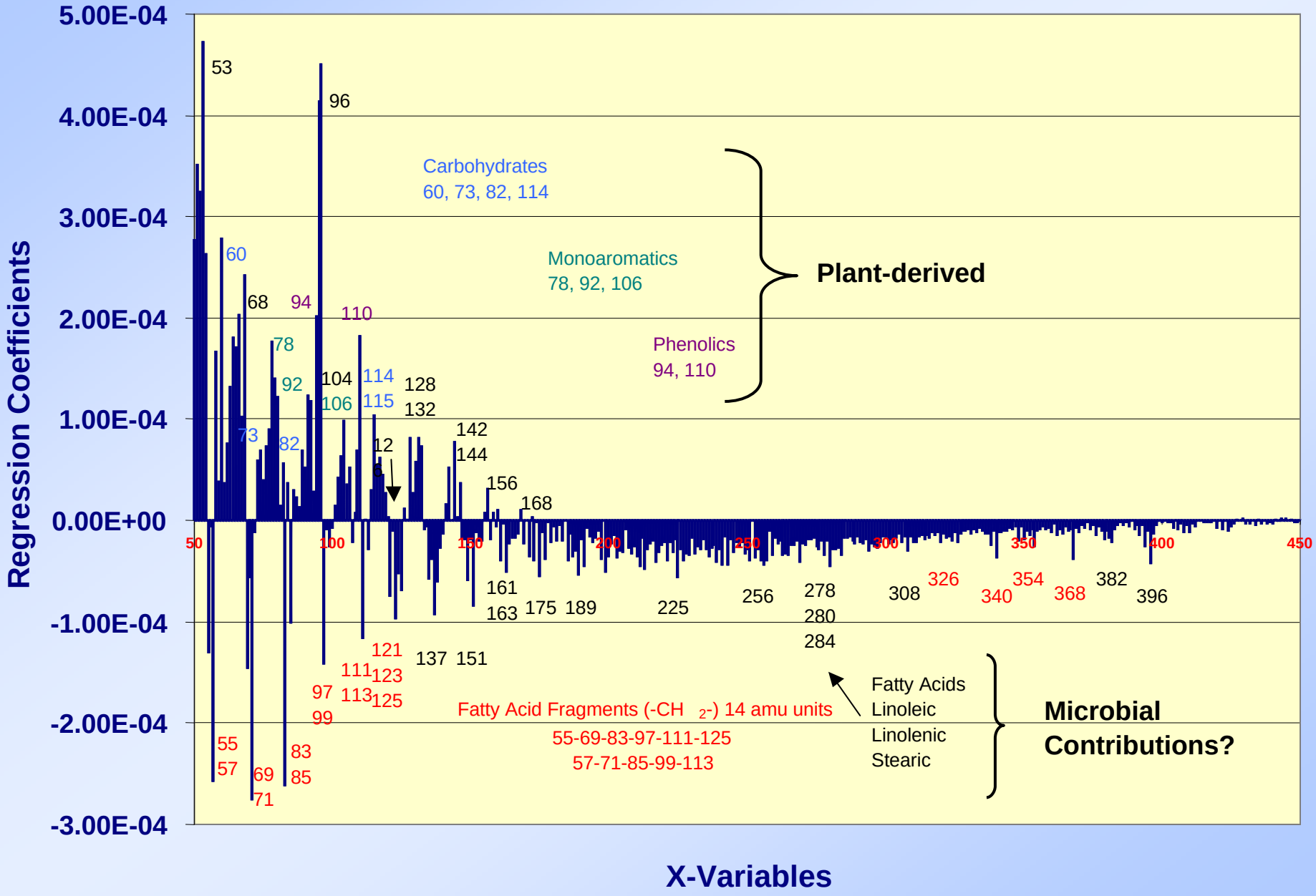
CRP and CT soils likely influenced by specific crop roots at 5-10 cm

- NT and CT: corn (shorter roots)
- CRP: switchgrass (longer roots)

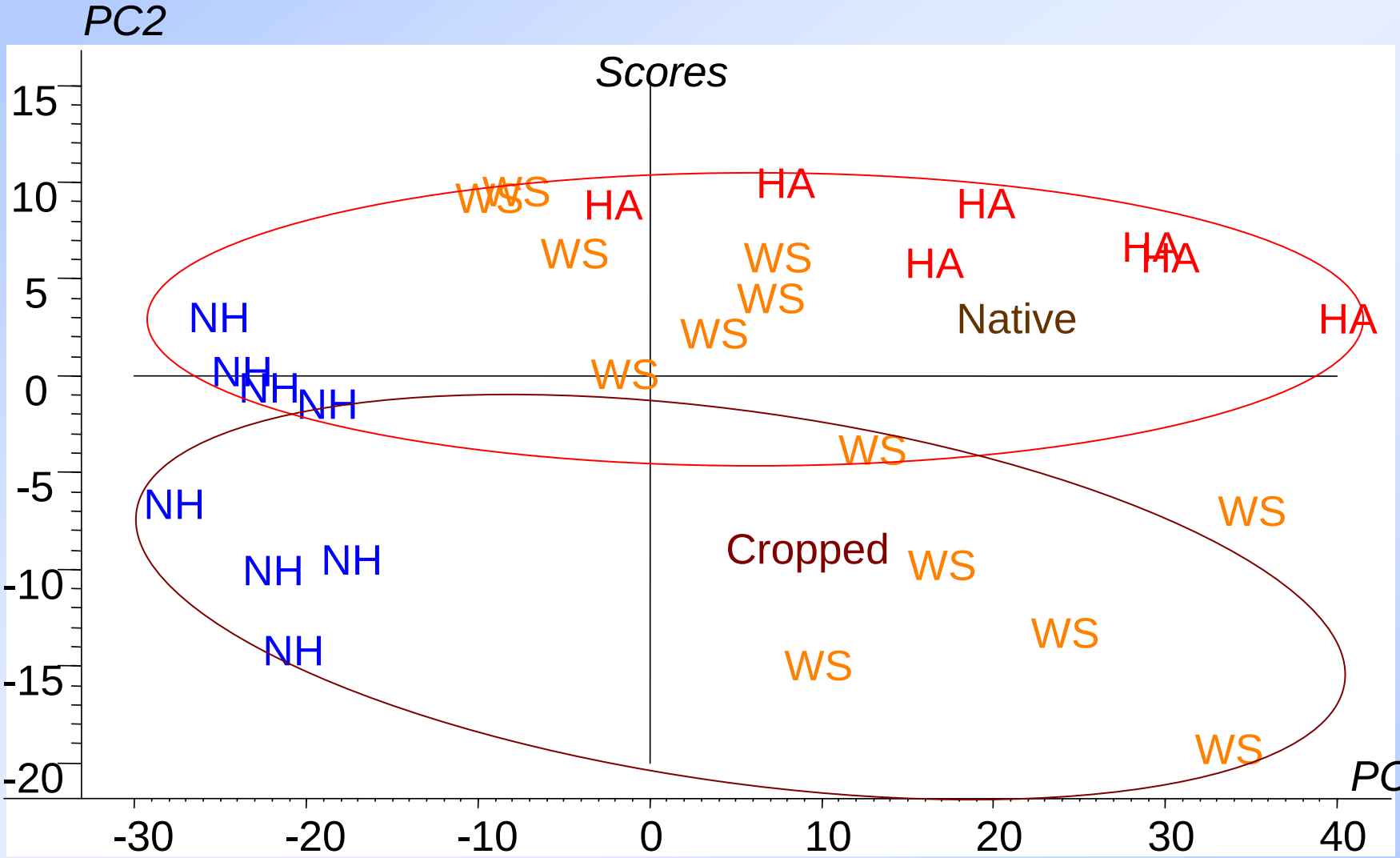


AT 10-30 cm, CT and CRP soils have (CT-short roots) and switchgrass (CRP-long roots) crops. Possibly seeing SOC inputs from each root type

Model for SOC ESTIMATION IN CRP SOILS



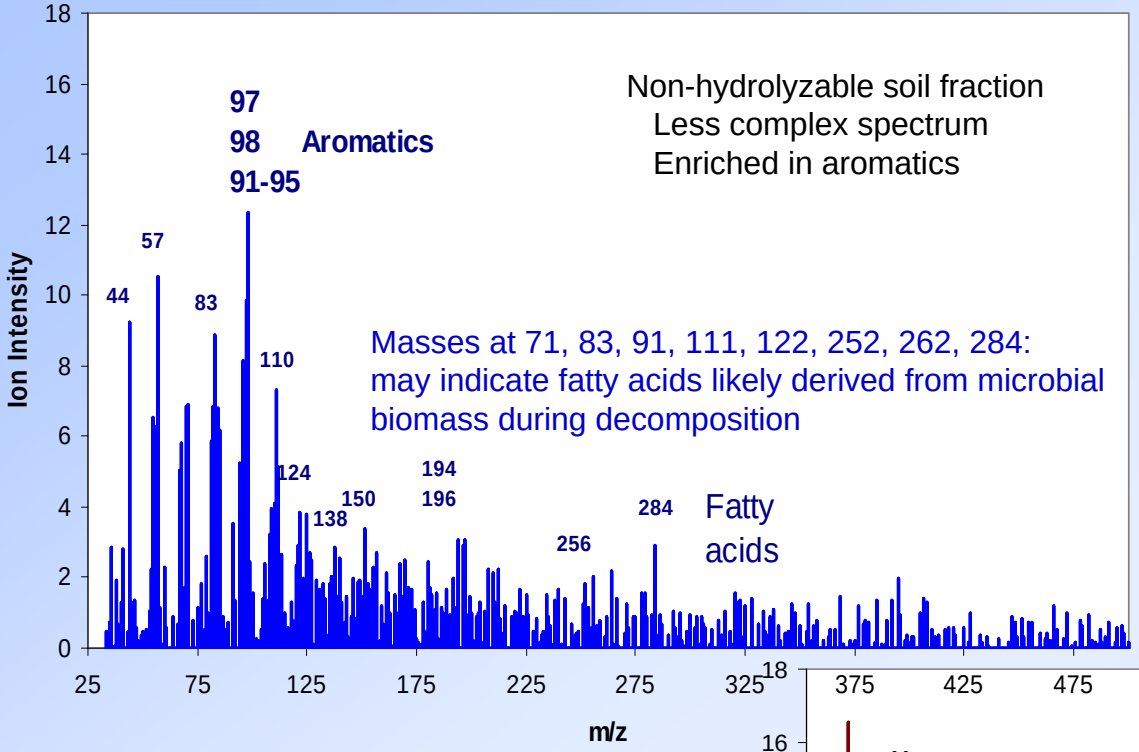
AKRON, CO SOIL FRACTIONS

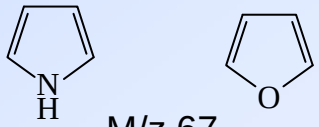


X-expl: 56%,9%

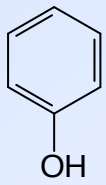
WS: whole soil
HA: humic acid
NH: non hydrolyzable

Mass spectra of Akron, CO whole soil and non hydrolysable fraction

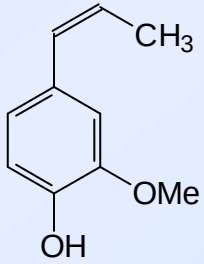




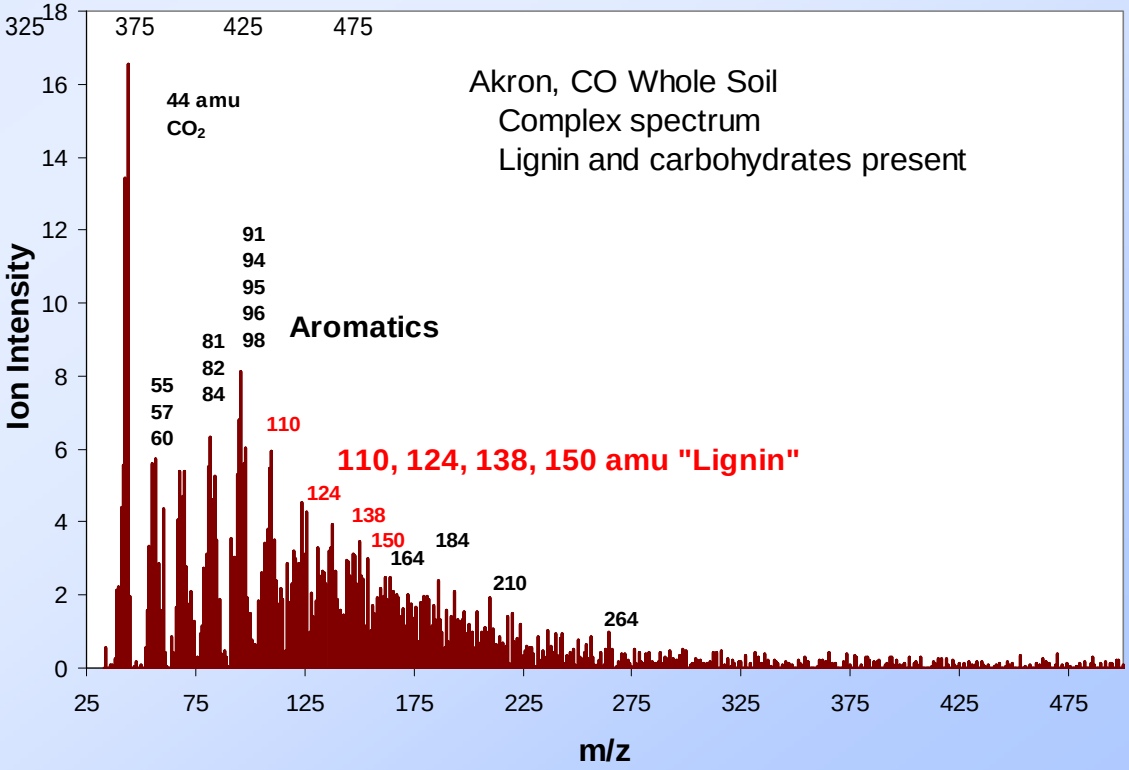
M/z 67



m/z 94



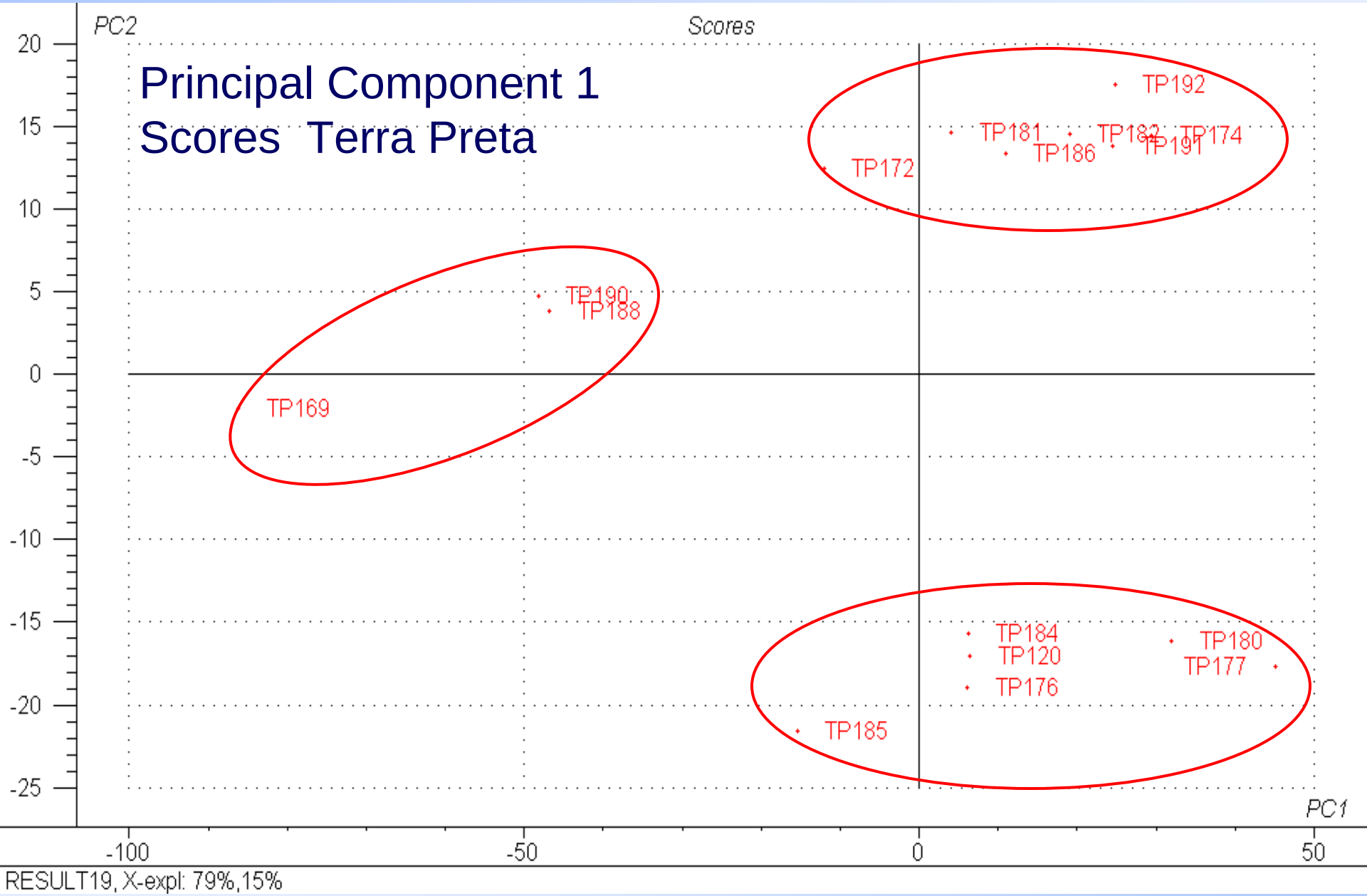
M/z 164



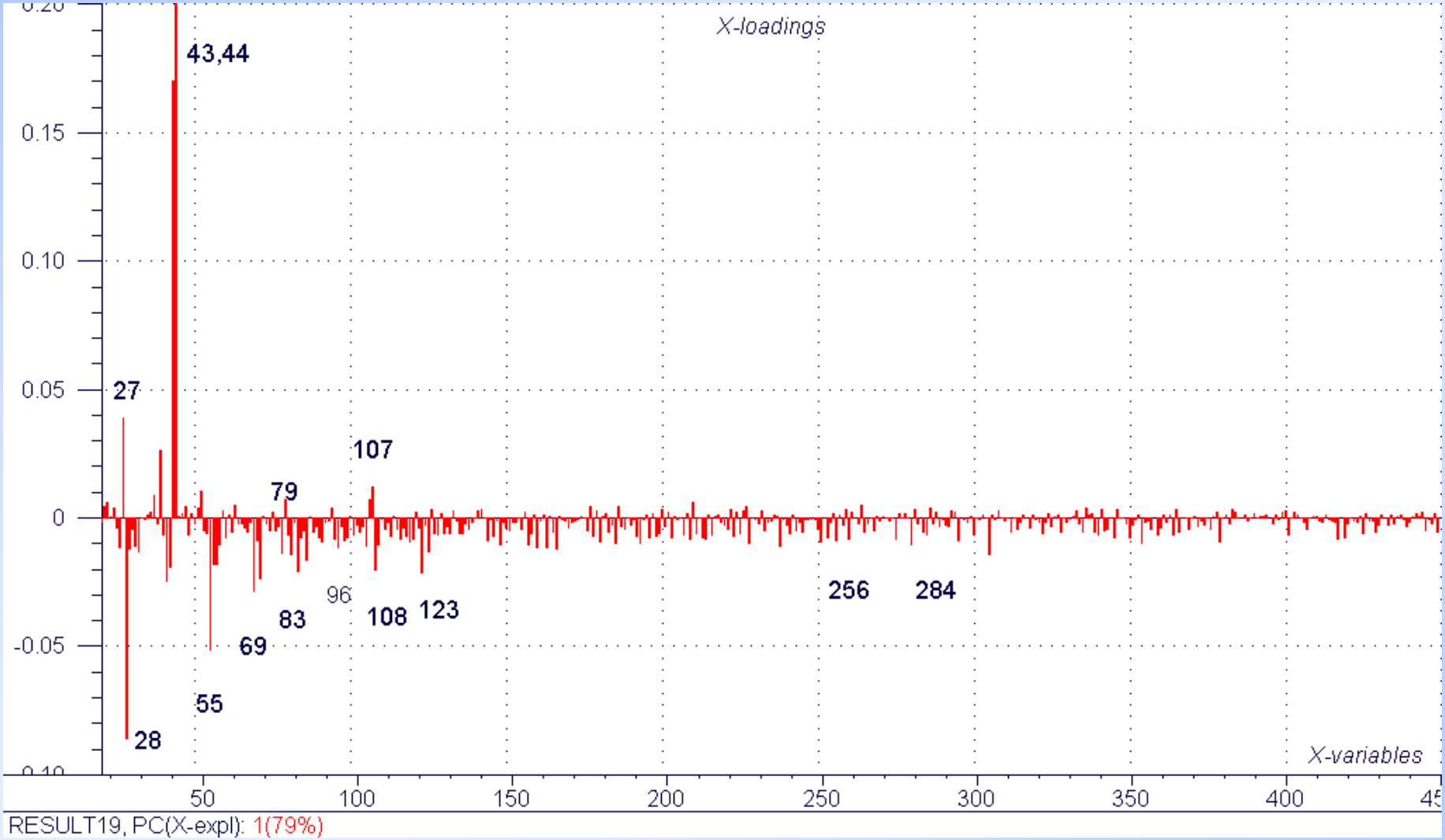
Py-MBMS SHOWS:

- Fractions have different chemistry
- Humic acid similar spectrum to whole soil; enriched mass 91
- Lignin fragments and microbial products present in whole soil, humic acid, and humin fractions
- Non acid hydrolyzable fraction contains fatty acids. Less complex spectra than the whole soil and other fractions – similar to terra preta

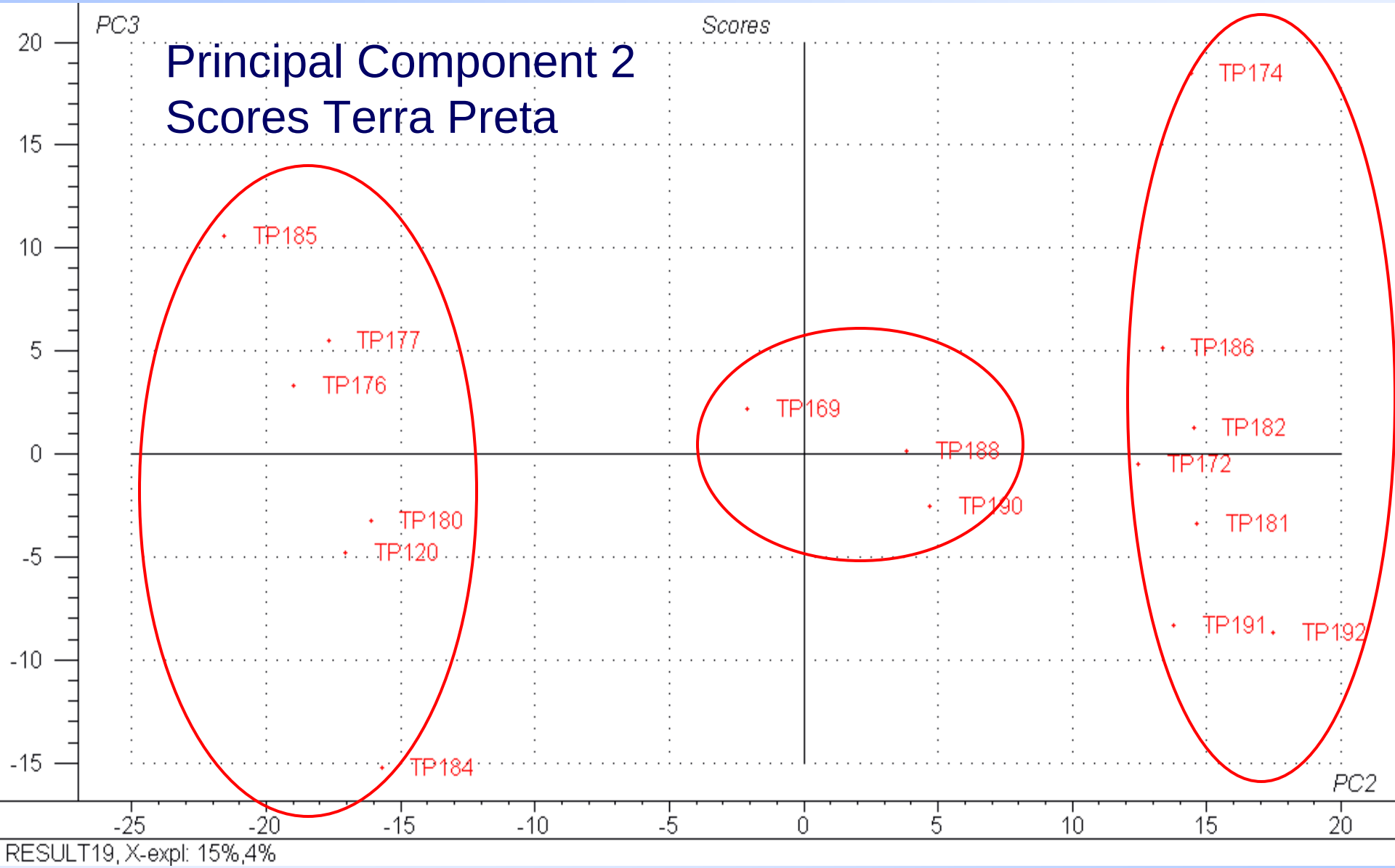
Principal Component 1
Scores Terra Preta



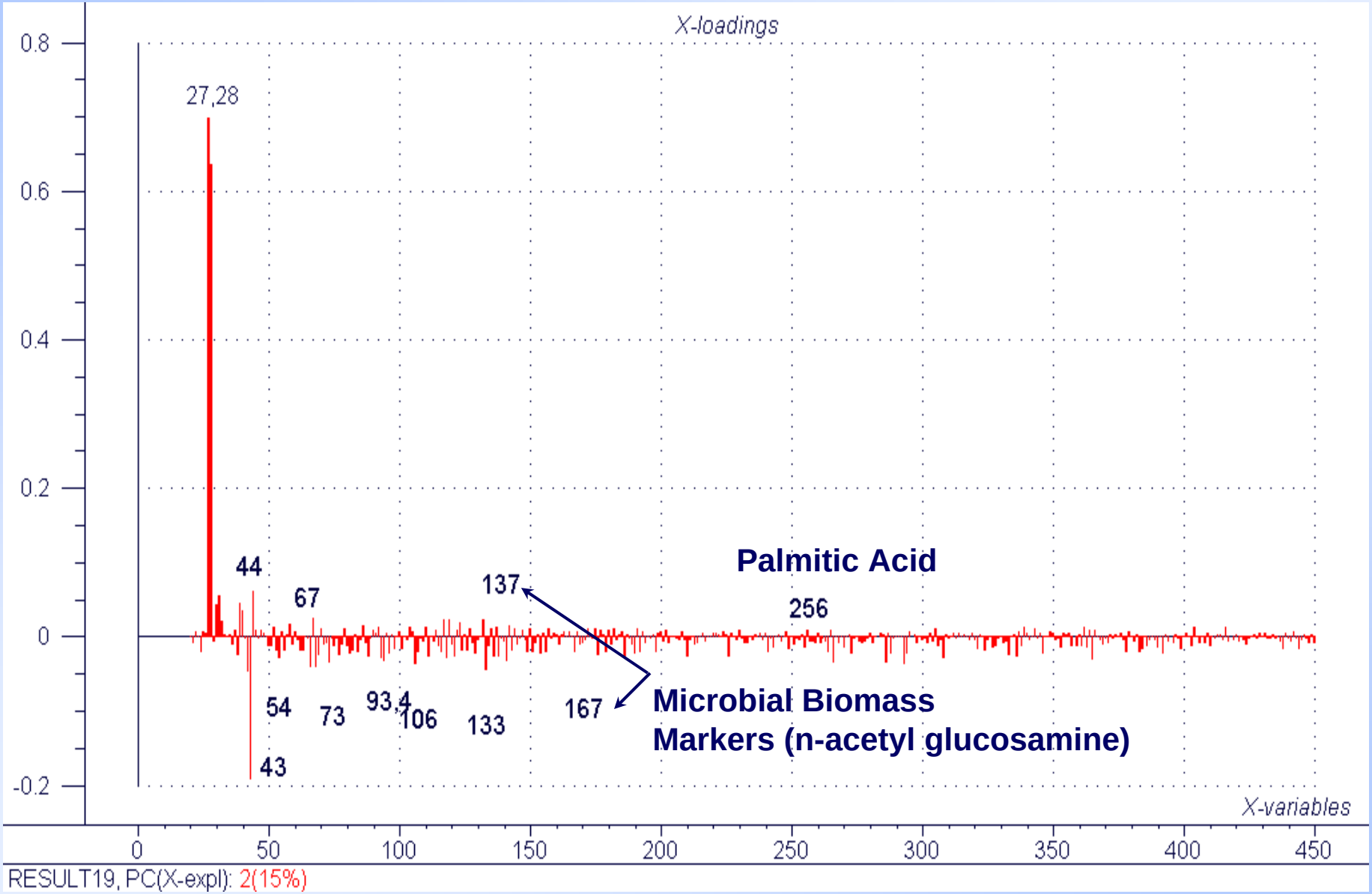
Principal Component 1 Loadings – Terra Preta



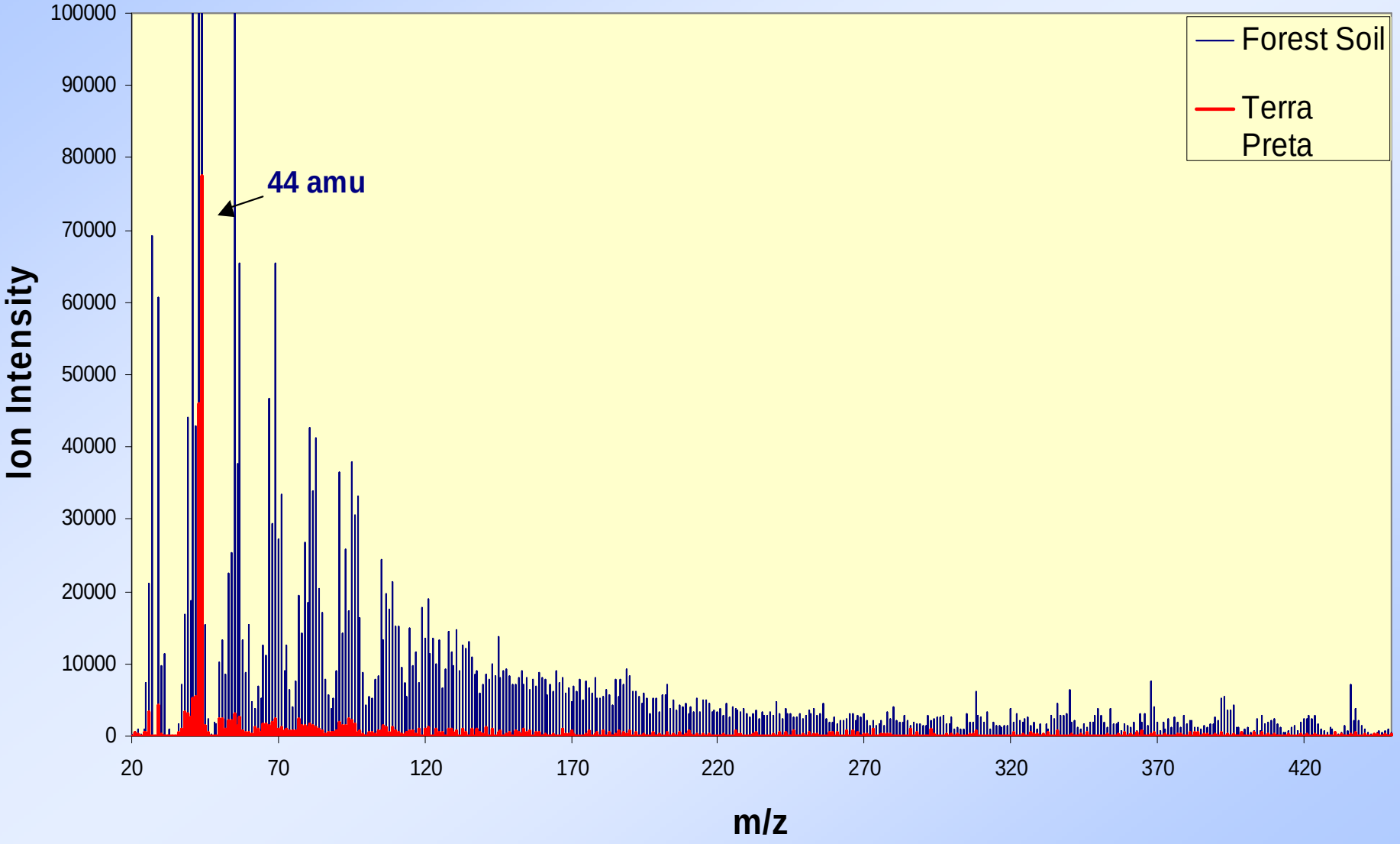
Principal Component 2 Scores Terra Preta



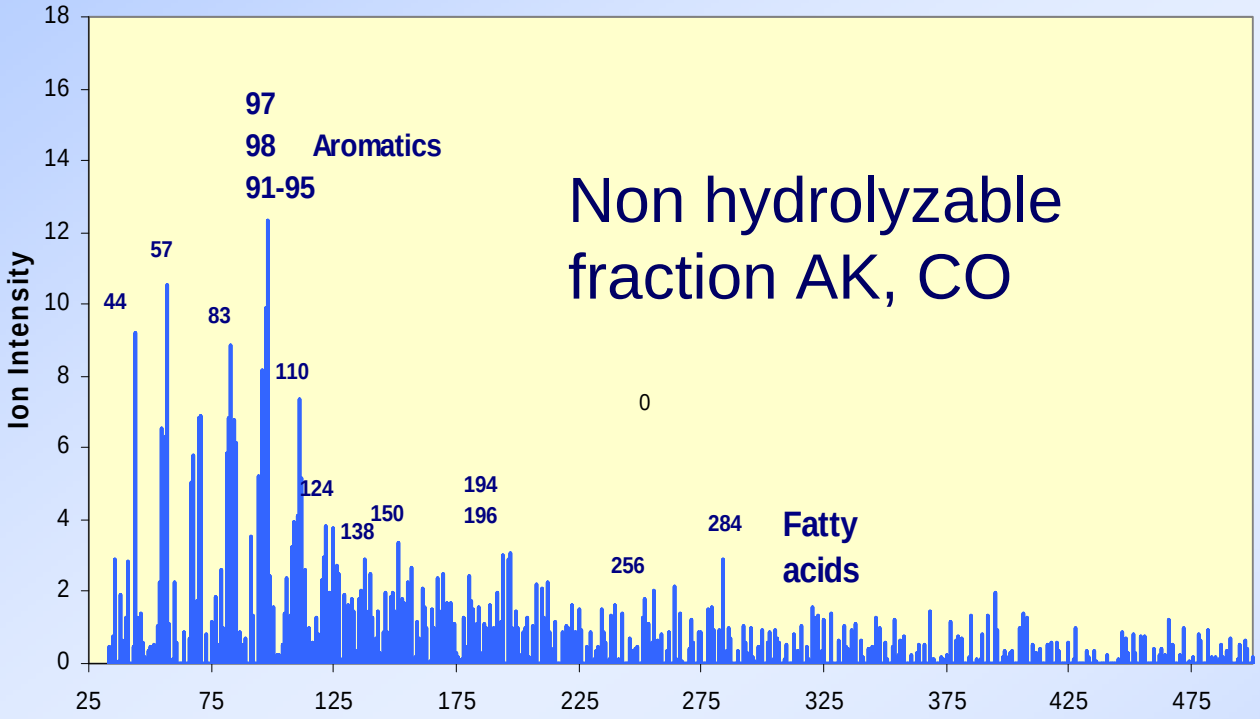
Principal Component 2 Loadings – Terra Preta

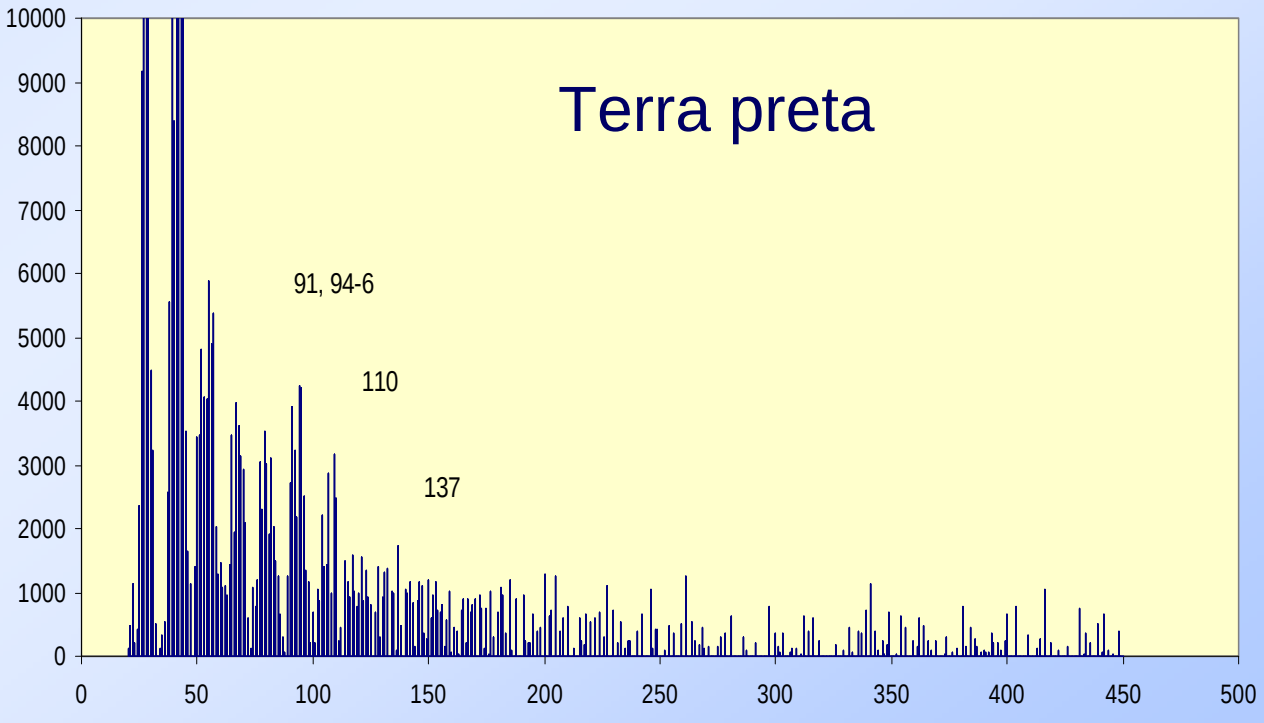


Terra Preta and Forest Soils

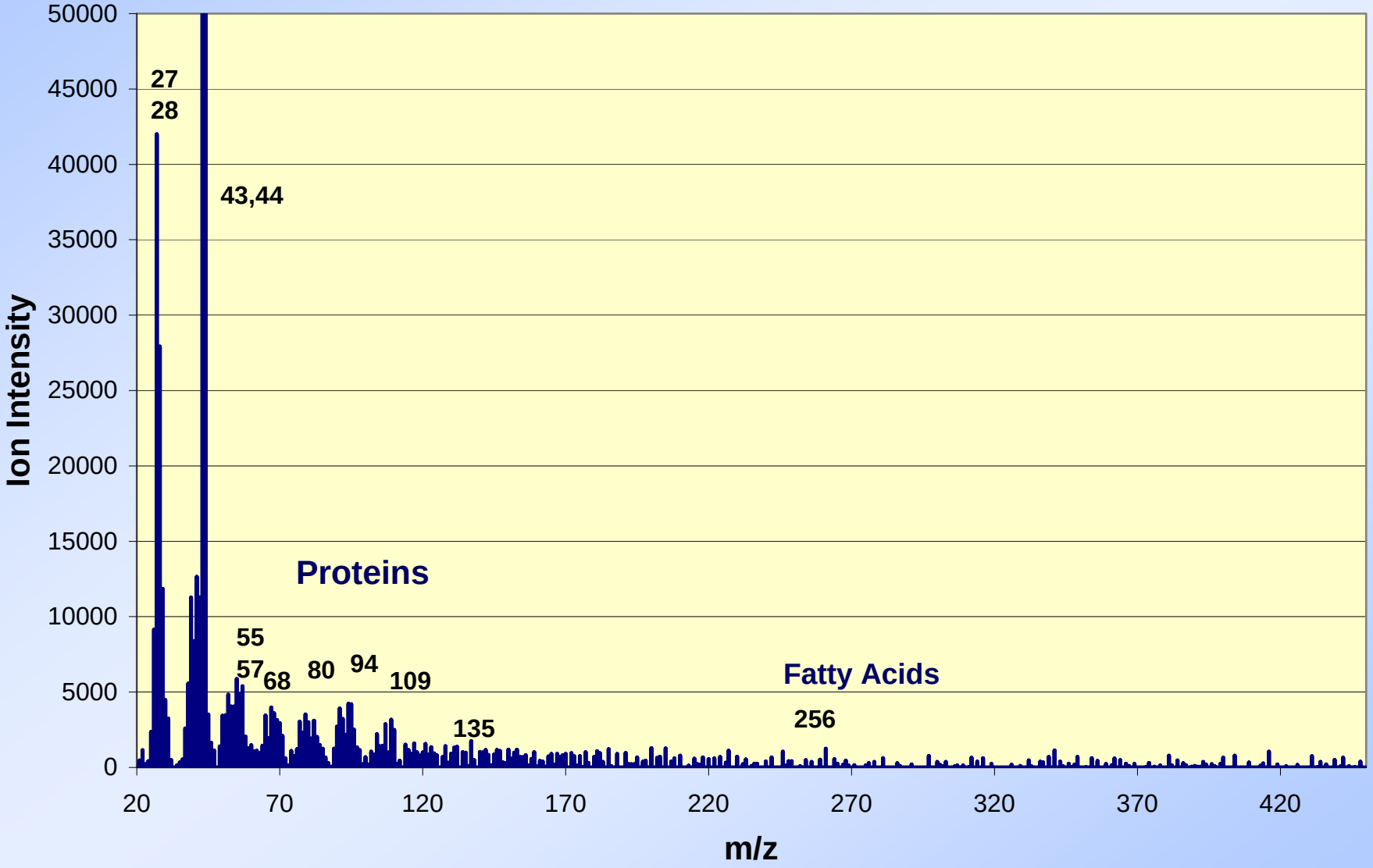


NH and TP spectra are similar to each other and to highly charred biomass





TERRA PRETA MASS SPECTRUM



CONCLUSIONS

- Py-MBS rapidly characterizes SOC species
- Data can be used to estimate SOC and SMB contents
- Terra Preta soils have less SOM complexity and are similar to non hydrolyzable soil fractions
- Working on characterizing “black carbon”

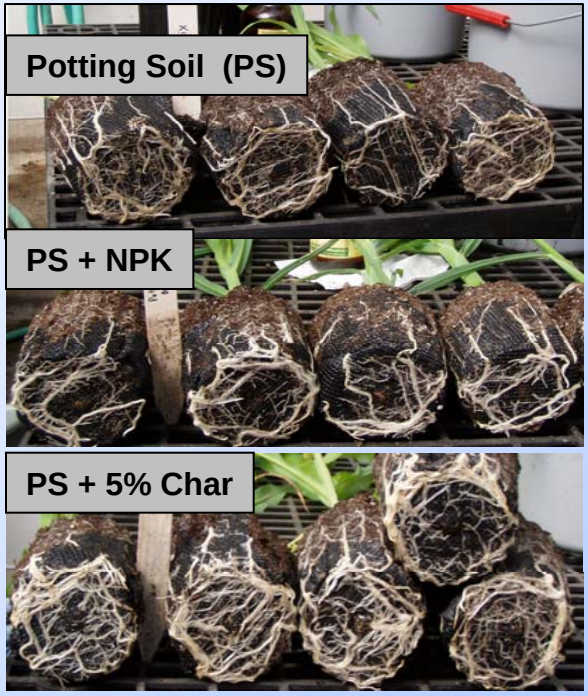


Figure 1: Corn plant roots 35 days post germination in potting soil (PS), PS and NPK addition, PS and 5% peanut char.

NREL

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