Overview of Handheld XRF Applications for Soil Science

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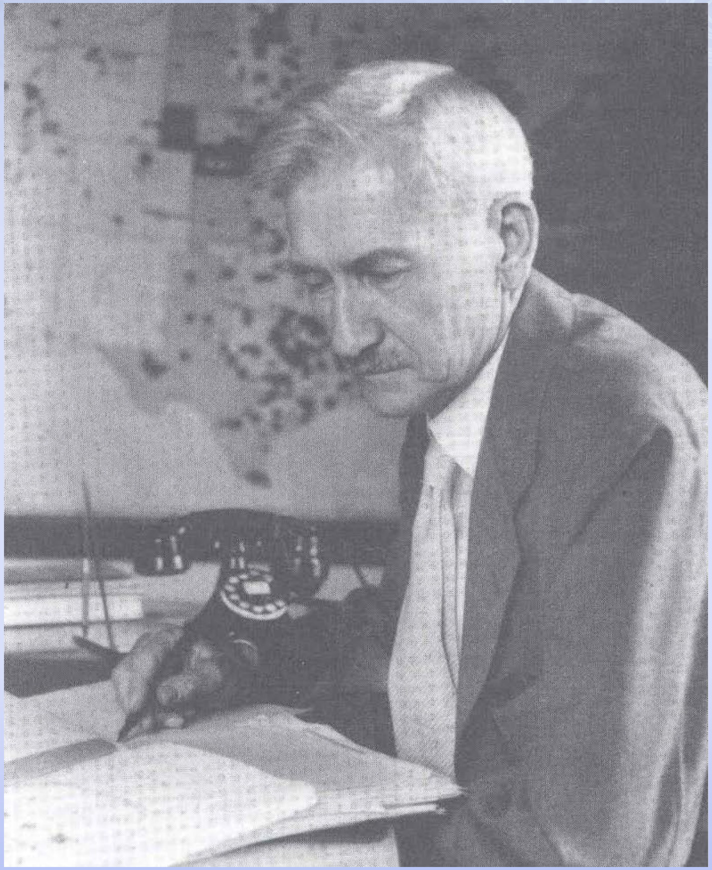
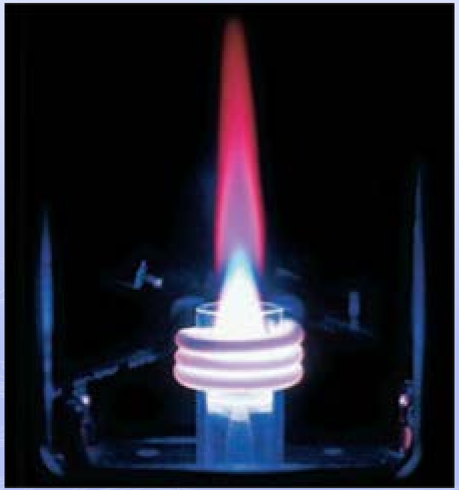
Introduction

- Soil scientists have long differentiated soils based on chemical properties
- Under Curtis Marbut's *Normal Soil* concept two major soils were identified:
  - Pedocals
  - Pedalfers



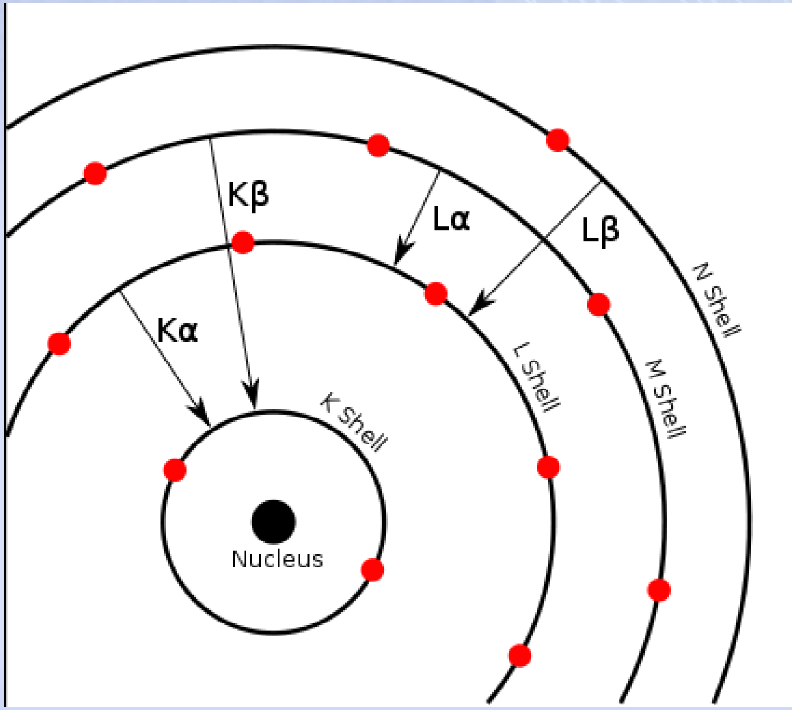


Introduction

- Historically, many chemical determinations were made via titration or colorimetry
- More recently, lab based instruments have offered greater accuracy
  - ICP-AES
  - AA

Field Portable XRF Basics

- Each element has electronic orbitals of characteristic energy
- Essentially, x-rays from the XRF eject an inner sphere electron, allowing an outer shell electron to drop into its place
- There are a limited number of ways in which this can happen:
  - L’ K transition is traditionally called Kα
  - M’ K transition is called Kβ
  - M’ L transition is called Lα
- Each of these transitions yields fluorescent energy unique to each element
  - Intensity is related to elemental abundance



Field Portable XRF Basics

- A battery operated, Innov-X Systems Delta series PXRF (tantalum x-ray tube operated at 35 kV)
- Stainless steel '316' standardization clip is used to standardize the instrument
  - Alloy of Cr, Mn, Fe, Ni, Cu, and Mo
- Instrument was operated with the light element analysis program (LEAP) mode engaged using a software configuration known as *soil mode*
  - Uses a scatter normalization algorithm (per EPA Method 6200) for soil, liquids, and powders allowing for sequential analysis of atomic numbers Z=15 (Phosphorus) to Z=92 (Uranium)
  - Provides optimized tube excitation for increased performance on lighter elements (Ca, K, S, P, Cl, and I)
- Samples were scanned for 30 s per beam through the ~2 cm aperture

Price: ~$30,000

Allows for multiple environmental applications:
- Heavy metals
- Gypsum
- Spodic horizons

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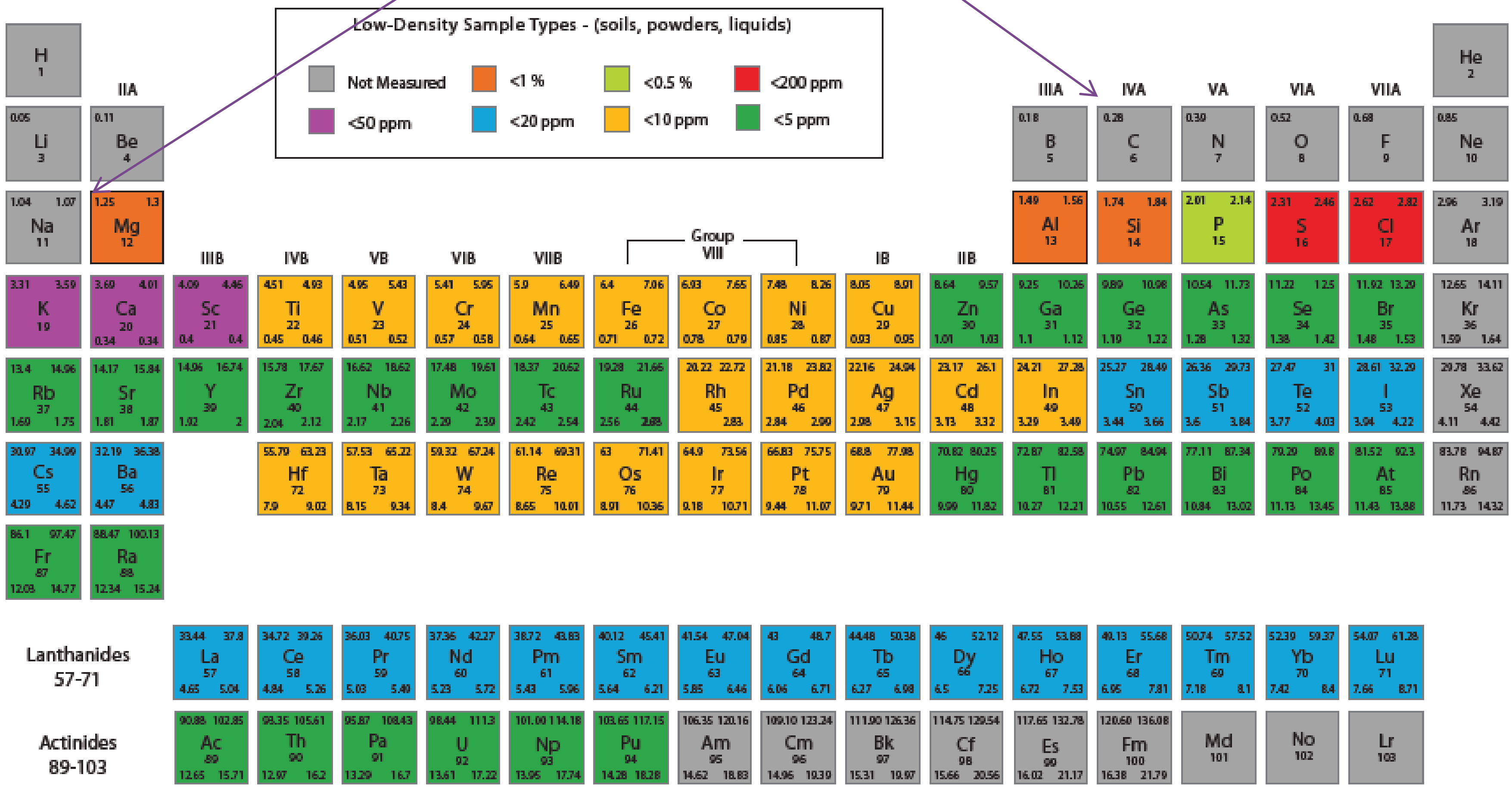
Limitations: cannot detect Na-based salts or carbon

HANDHELD XRF ANALYZERS

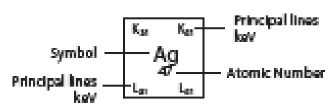
Limits of Detection



Alloy Analysis:

Elements detected: Magnesium (Mg, Z=12) through Sulfur (S, Z=16) and Titanium (Ti, Z=22) through Plutonium (Pu, Z=94).

Please see separate Alloy Analysis LOD Specifications.



INNOV-X

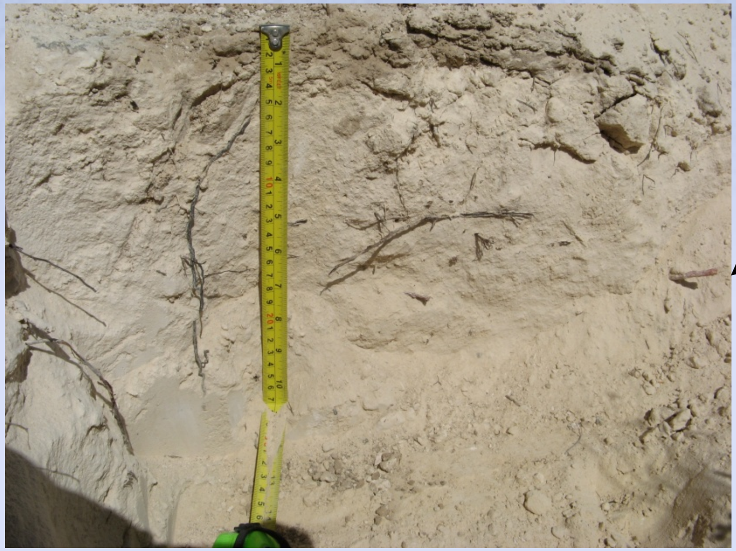
Detection limits are a function of testing time, sample matrix and presence of interfering elements.
Detection limits are estimates based on 1-2 minutes test times and detection confidence of 3σ (99.7% confidence).
Interference-free detection limits are intended as guidelines: please contact Olympus Innov-X to discuss your specific application.

Field Portable XRF Basics

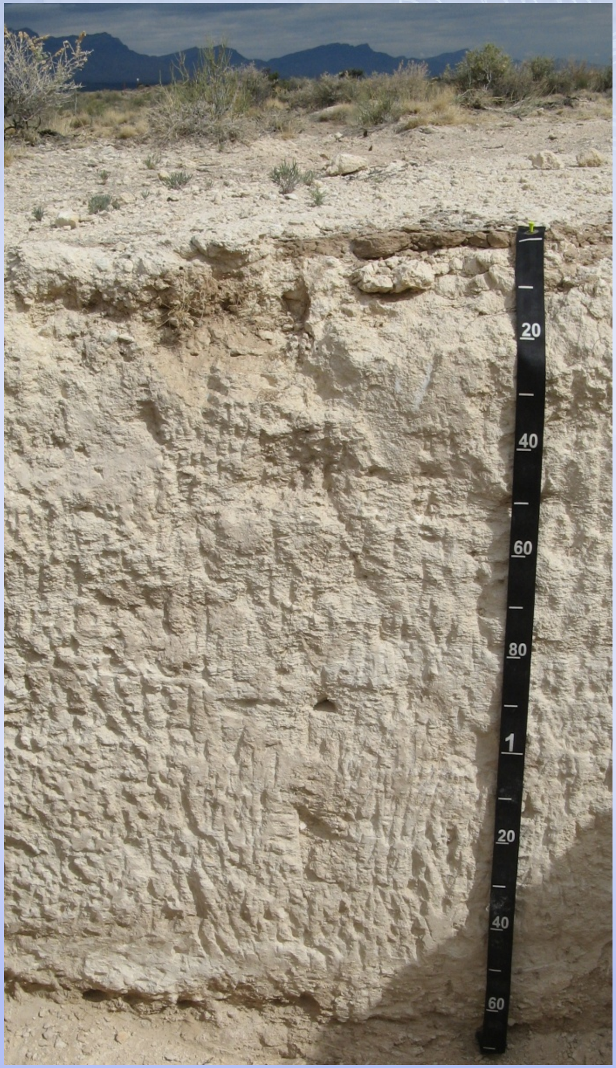
- Data processing includes reporting of the standard error on an individual element basis
- Limit of detection (LOD) is defined as three times the standard error for each element
  - Varies by element, with higher atomic numbered elements generally allowing for lower detection limits
- Logged data is then exported to MS Excel for further analysis such as correlation

➔ Note that PXRF reports total elemental concentration; not ionic species (e.g. Fe^{+2} vs. Fe^{+3}) or compounds (gypsum, calcite, etc.)

Gypsum by PXRF



Leptic Haplogypsids



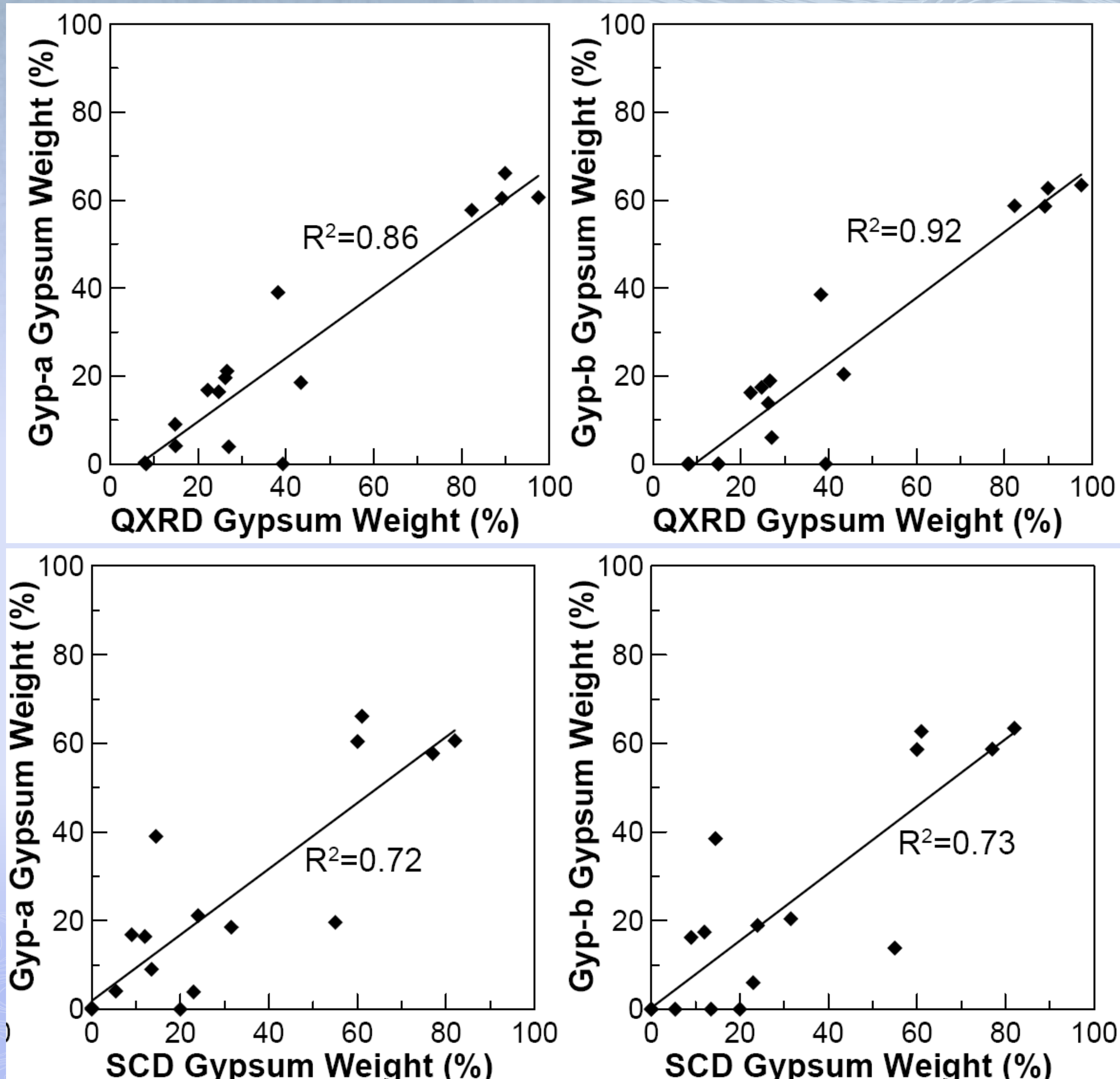
Calcic Argigypsid

Gypsum by PXRF

- Total Ca is quantified by PXRF
- Separately, $CaCO_3$ is quantified by field calcimeter
  - $CaCO_3$ is converted to Ca and subtracted from total PXRF Ca
- Gypsum percentage is calculated from remaining Ca

Gypsum by PXRF

- Research study:
  - Compared gypsum quantification via three different methods:
    - PXRF (Gyp-a, Gyp-b)
    - Soil characterization data (SCD) (Acetone precip.)
    - Quantitative x-ray diffraction (QXRD)
- Results show strong correlations between PXRF and QXRD, decent correlations between PXRF and SCD


Gyp-a Gypsum Weight (%)
QXRD Gypsum Weight (%)
R2=0.86
Gyp-b Gypsum Weight (%)
QXRD Gypsum Weight (%)
R2=0.92
Gyp-a Gypsum Weight (%)
SCD Gypsum Weight (%)
R2=0.72
Gyp-b Gypsum Weight (%)
SCD Gypsum Weight (%)
R2=0.73
0
20
40
60
80
100

Gypsum by PXRF

- Conclusion:
  - PXRF provides a good, rapid, quantifiable measure of gypsum in-situ
  - Future research will utilize S as proxy for gypsum instead of Ca, eliminating the need for field calcimeter work
- Further Reading:

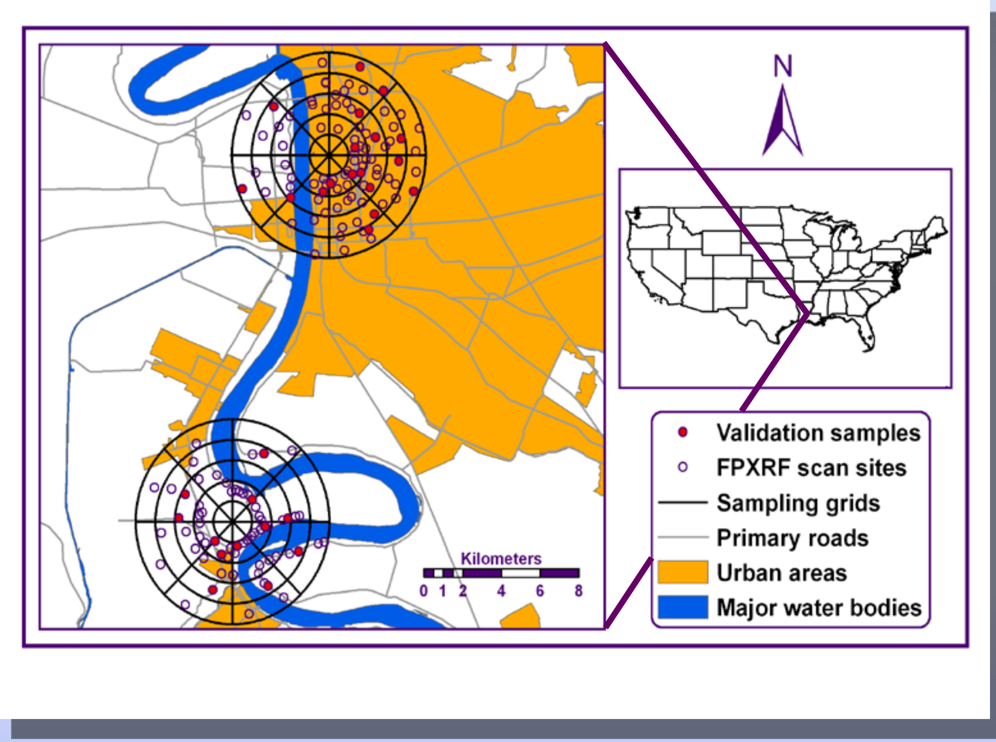
  - Weindorf, D.C., Y. Zhu, R. Ferrell, N. Rolong, T. Barnett, B. Allen, J. Herrero, and W. Hudnall. 2009. Evaluation of portable x-ray fluorescence for gypsum quantification in soils. Soil Sci. 174(10):556-562. doi:10.1097/SS.0b013e3181bbbd0b.
  - Zhu, Y., and D.C. Weindorf. 2009. Determination of soil calcium using field portable x-ray fluorescence. Soil Sci. 174(3):151-155.

Spatial Variability of Heavy Metals in Peri-urban Agriculture

- Agricultural soils near urban/industrial areas have the potential for heavy metal contamination
  - Metallurgy
  - Smelting
  - Petrochemical refineries
- Joint study in Baton Rouge, LA (USA) and Nanjing, China was initiated to assess PXRF utility in mapping heavy metal spatial variability

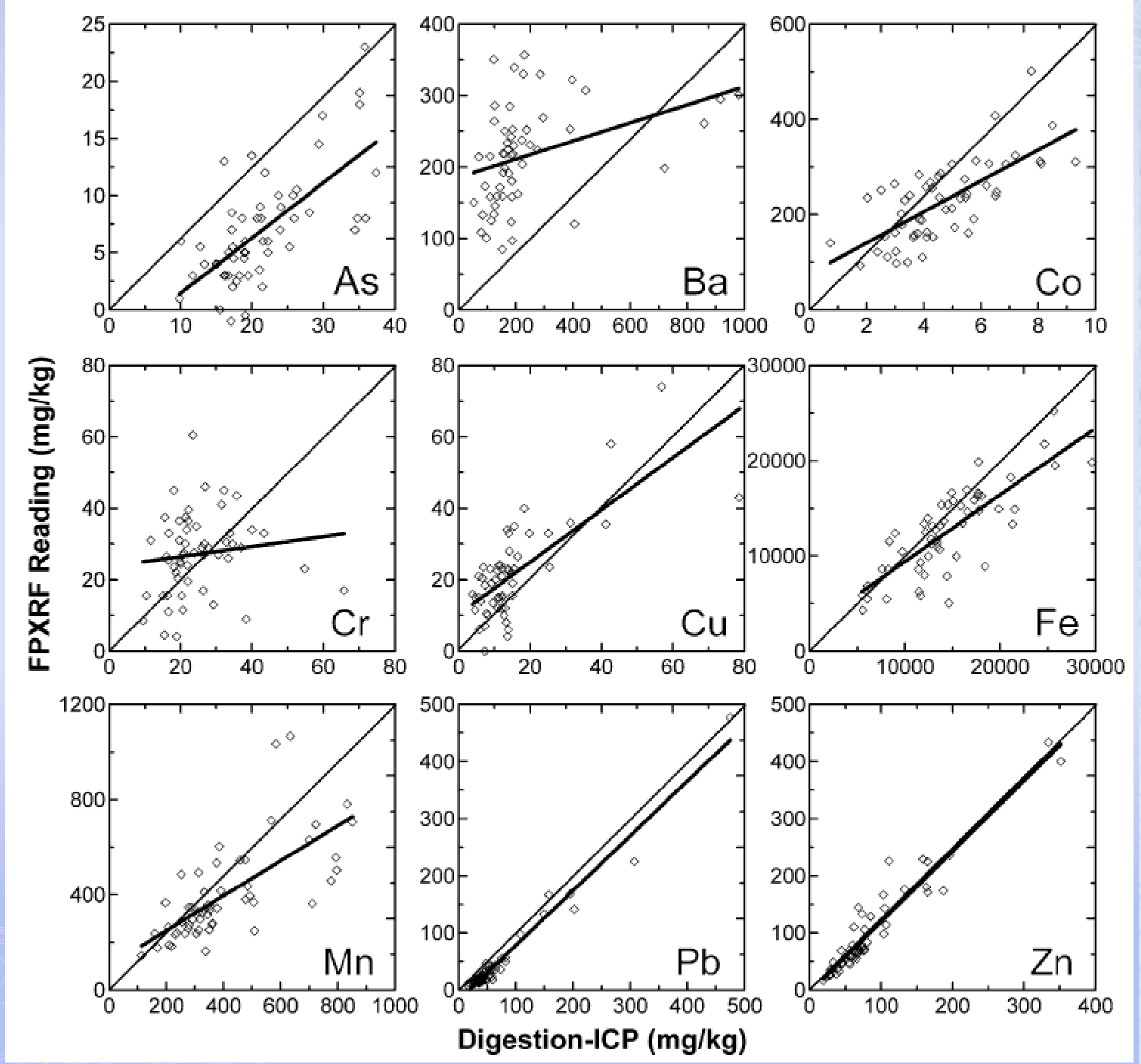
Spatial Variability of Heavy Metals in Peri-urban Agriculture

- In Baton Rouge, two sampling schemes were created in peri-urban sugarcane fields
  - Exxon/Mobil refinery
  - Dow chemical plant
- Scanned with PXRF
- 35% validation via subsampling for ICP-AES analysis (aqua-regia digestion)
- Results were spatially interpolated via ordinary kriging with ESRI ArcGIS

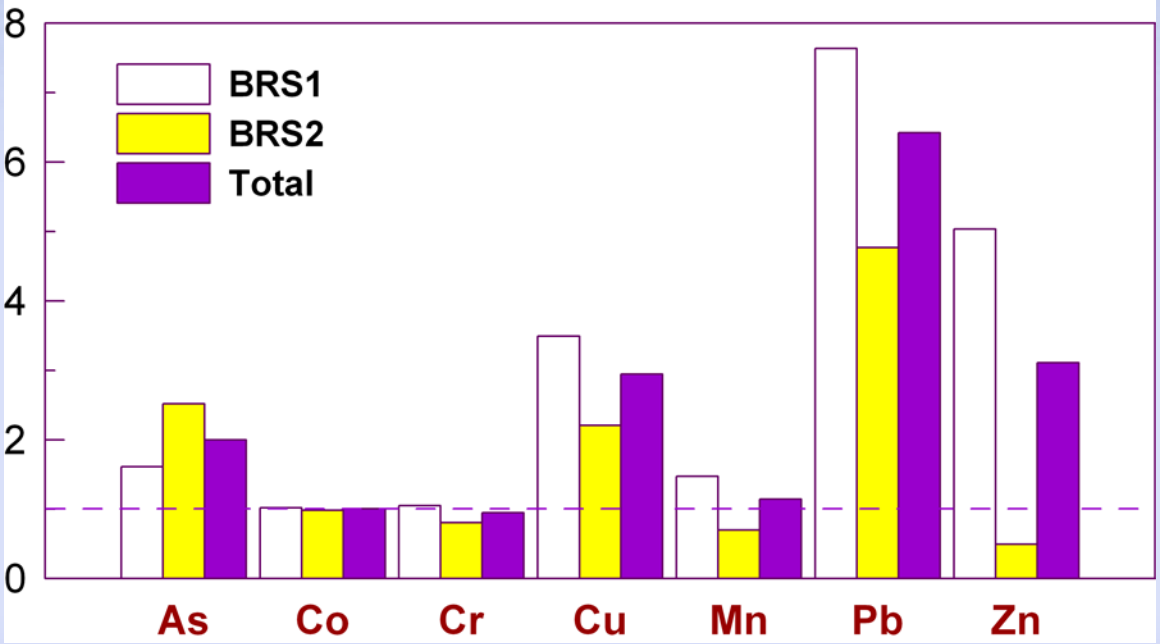


Spatial Variability of Heavy Metals in Peri-urban Agriculture

- Strong, significant ICP-PXRF correlations for many metals
  - R^2
    - Zn: 0.91
    - Pb: 0.97
    - Fe: 0.64
    - Cu: 0.54
  - Lower R^2 values linked to incomplete digestion



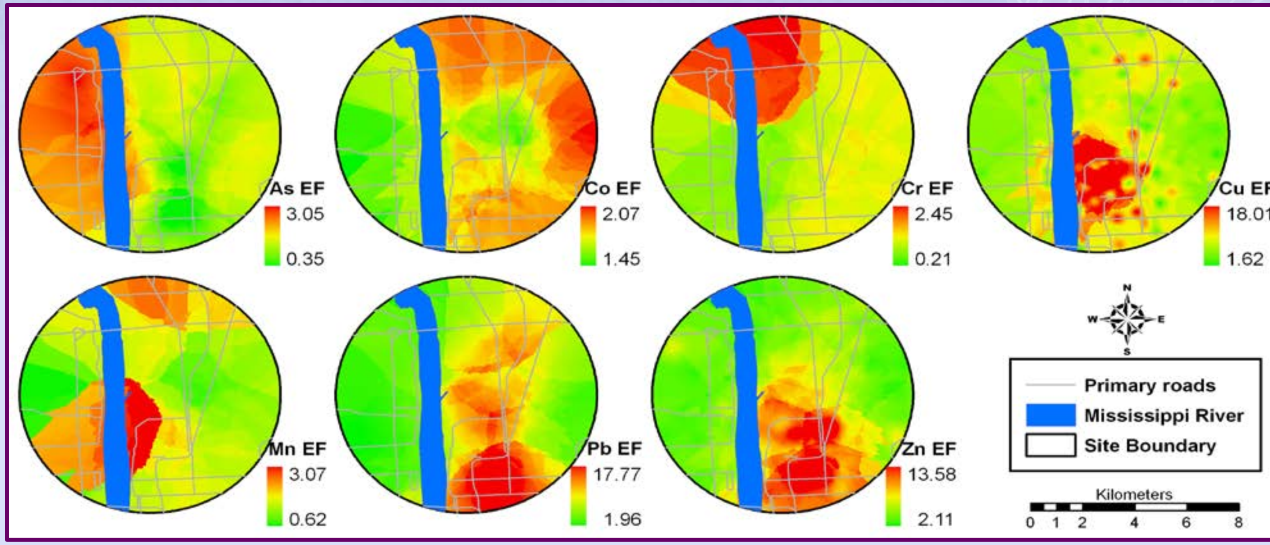
Spatial Variability of Heavy Metals in Peri-urban Agriculture



- Enrichment factors of various elements above geochemical background levels for two sites in Louisiana, USA

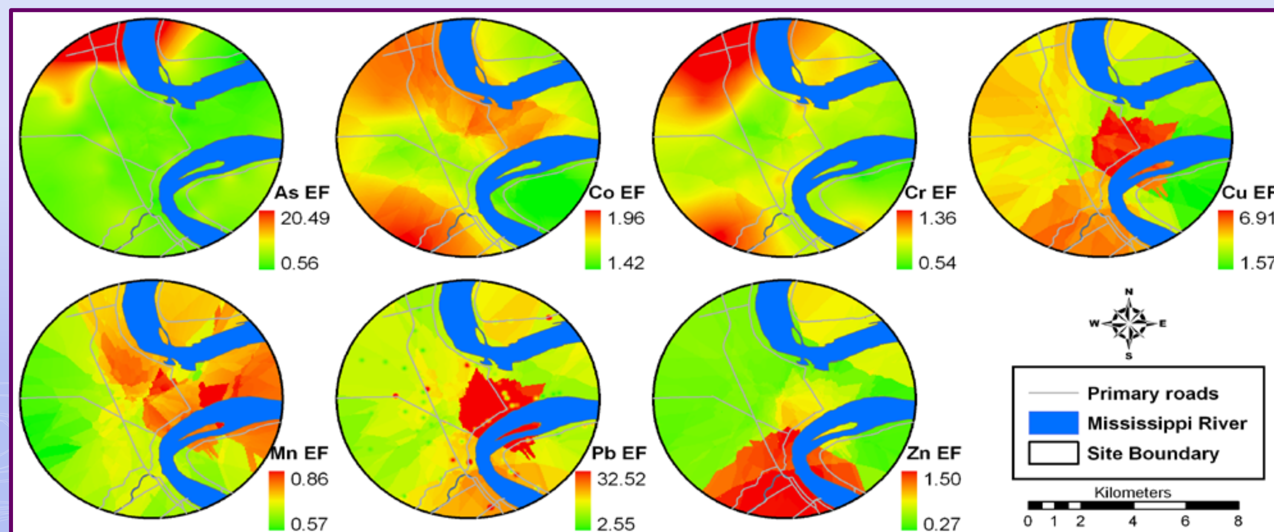
Spatial Variability of Heavy Metals in Peri-urban Agriculture

- Spatial variability of metals at BRS1 ➔



And

BRS2 ➔



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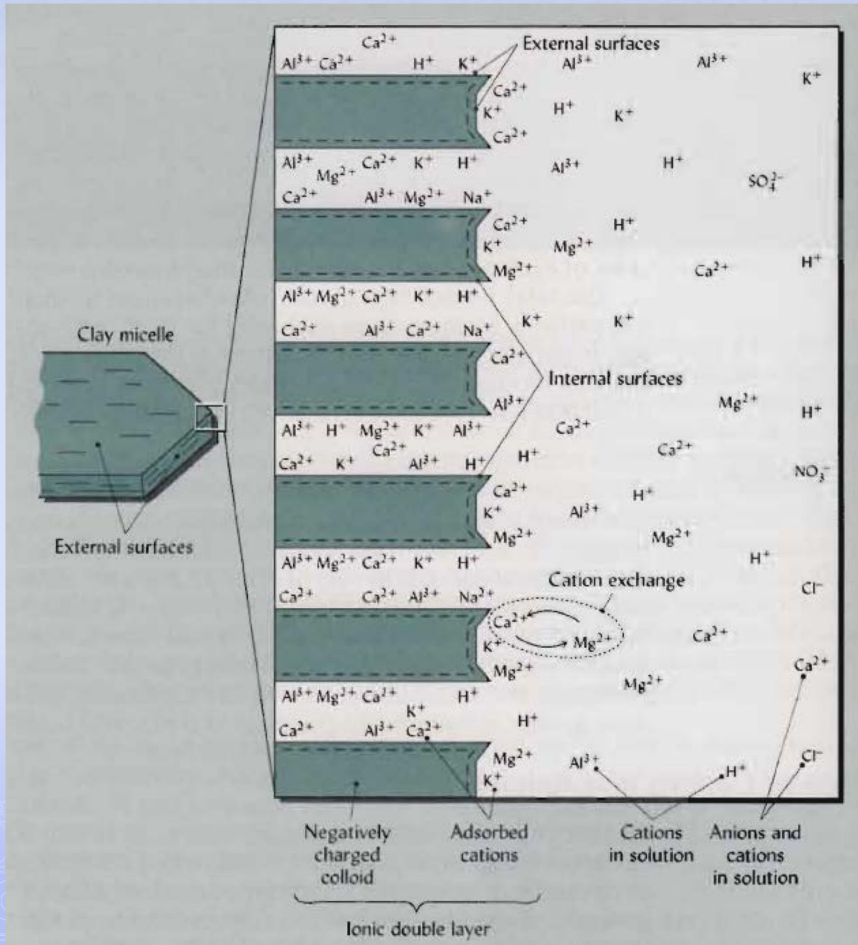
Spatial Variability of Heavy Metals in Peri-urban Agriculture

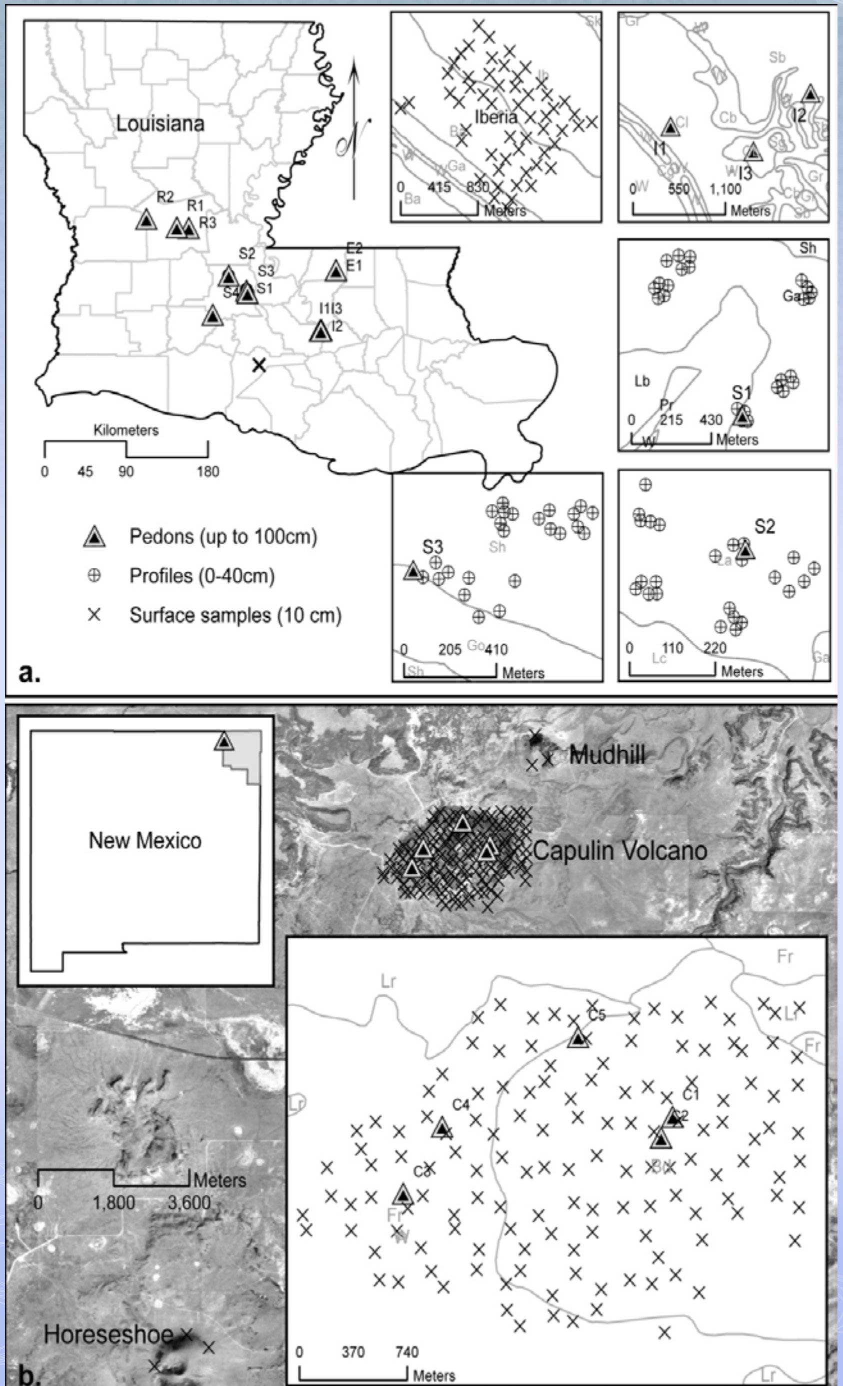
- Conclusions:
  - PXRF is able to accurately quantify elemental concentrations with significant correlations to ICP-AES
  - Coupled with GPS and GIS, spatial variability of elemental concentrations can be rapidly modeled on-site
- Further reading
  - Weindorf, D.C., Y. Zhu, S. Chakraborty, N. Bakr, and B. Huang. 2010. Use of portable x-ray fluorescence spectrometry for environmental quality assessment of peri-urban agriculture. Env. Mon. Assess. doi: 10.1007/s10661-011-1961-6.

Soil Texture Via PXRF



From Brady and Weil, 2002

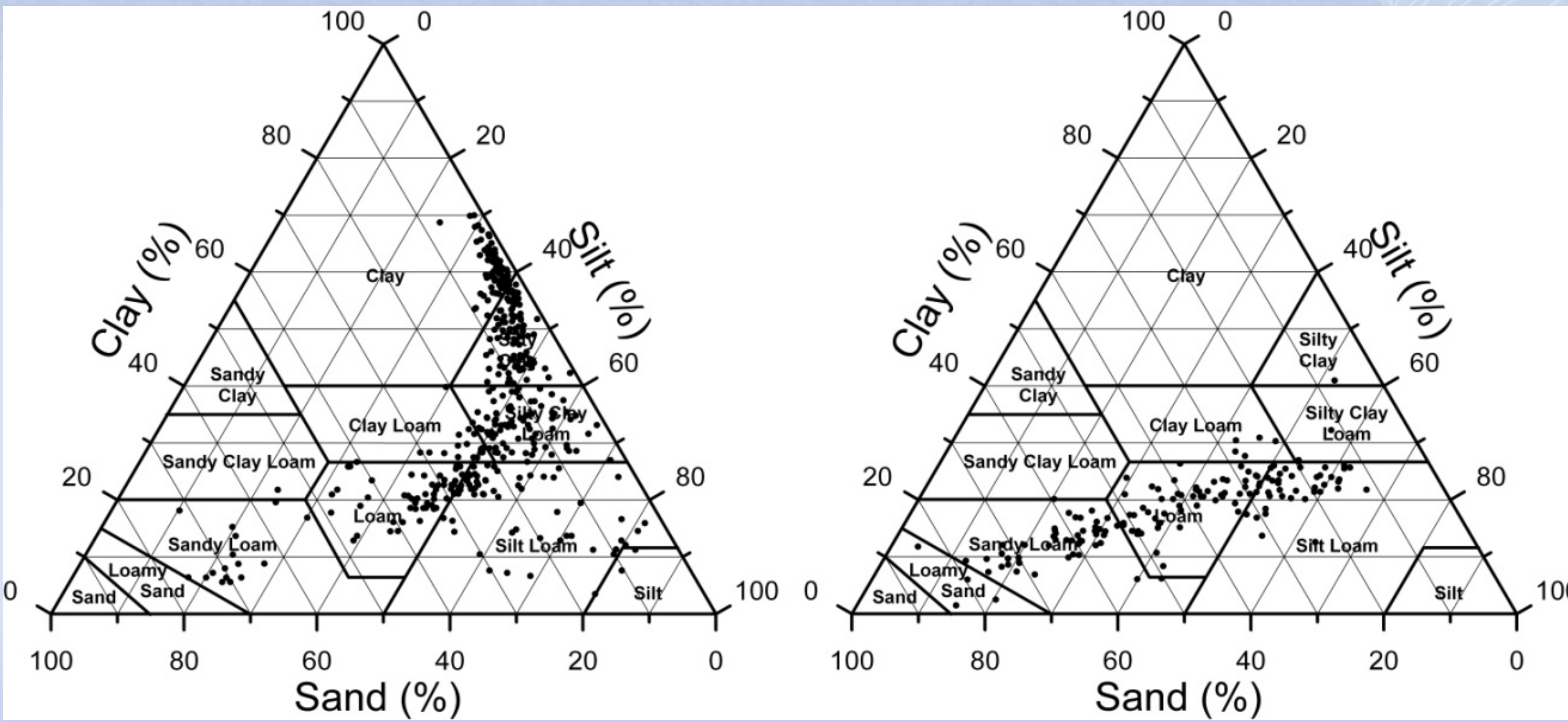
- Electrostatically charged clay particles are surrounded by a swarm of cations
  - Facilitates high cation exchange capacity, base saturation, buffering capacity, etc.
  - PXRF can be used to look at specific trace elements on exchange complex as an indicator of soil texture



Soil Texture Via PXRF

- 584 soil samples were collected
  - South central Louisiana
  - North eastern New Mexico
- Scanned under both field and laboratory conditions
  - I.e. field moist, air dry
- Compared to lab textural data
  - Pipette method
- Sample set split for modeling (66%), validation (33%)

Soil Texture Via PXRF



Louisiana New Mexico

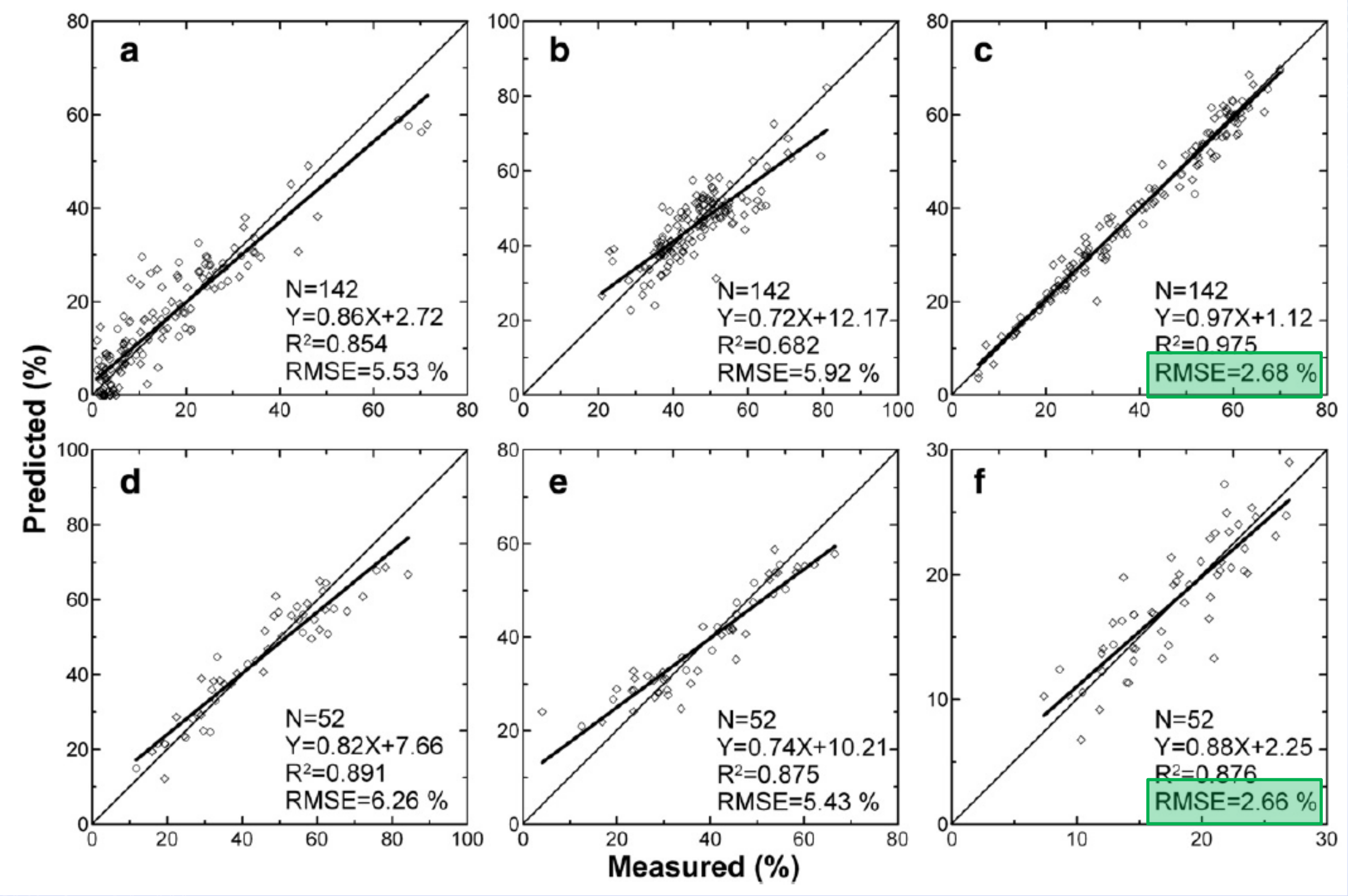
- Soil textures evaluated as part of this study

Soil Texture Via PXRF

	Sand	*Silt*	*Clay*	*K*	*Ca*	*Ti*	*Cr*	*Mn*	*Fe*	*Co*	*Cu*	*Zn*	*As*	*Rb*	*Sr*	*Zr*	*Ba*	*Pb*
Sand		**−0.97**	**−0.86**	**−0.45**	**0.88**	**0.74**	**0.53**	**0.66**	**0.85**	**0.78**	**0.81**	**0.41**	**−0.39**	**−0.93**	**0.87**	**−0.82**	**0.40**	**−0.56**
Silt	−0.19		**0.71**	**0.40**	**−0.82**	**−0.77**	**−0.60**	**−0.62**	**−0.88**	**−0.81**	**−0.81**	**−0.42**	**0.33**	**0.90**	**−0.88**	**0.81**	**−0.48**	**0.57**
Clay	−0.77	−0.47		**0.47**	**−0.83**	**−0.53**	**−0.29**	**−0.62**	**−0.61**	**−0.56**	**−0.63**	**−0.29**	**0.46**	**0.80**	**−0.67**	**0.66**	**−0.17**	**0.44**
K	−0.75	−0.11	0.75		**−0.49**	**0.03**	**0.03**	**−0.29**	**−0.21**	**−0.21**	**−0.26**	**−0.26**	**0.28**	**0.54**	**−0.28**	**0.54**	**0.27**	**0.10**
Ca	−0.37	0.37	0.09	0.18		**0.64**	**0.43**	**0.71**	**0.77**	**0.74**	**0.75**	**0.42**	**−0.43**	**−0.88**	**0.82**	**−0.80**	**0.34**	**−0.49**
Ti	−0.67	−0.28	0.78	0.71	0.01		**0.71**	**0.61**	**0.94**	**0.86**	**0.82**	**0.32**	**−0.19**	**−0.76**	**0.85**	**−0.66**	**0.73**	**−0.63**
Cr	−0.76	−0.29	0.87	0.74	0.15	0.74		**0.49**	**0.73**	**0.68**	**0.59**	**0.34**	**−0.15**	**−0.55**	**0.65**	**−0.52**	**0.67**	**−0.42**
Mn	−0.48	0.02	0.42	0.46	0.15	0.48	0.49		**0.66**	**0.64**	**0.62**	**0.55**	**−0.28**	**−0.70**	**0.70**	**−0.63**	**0.50**	**−0.27**
Fe	−0.79	−0.39	0.97	0.81	0.12	0.85	0.88	0.52		**0.93**	**0.87**	**0.46**	**−0.23**	**−0.88**	**0.93**	**−0.81**	**0.68**	**−0.64**
Co	−0.80	−0.34	0.94	0.80	0.14	0.83	0.87	0.47	0.97		**0.82**	**0.48**	**−0.17**	**−0.82**	**0.87**	**−0.77**	**0.64**	**−0.60**
Cu	−0.67	−0.30	0.79	0.65	0.18	0.68	0.74	0.43	0.81	0.82		**0.47**	**−0.25**	**−0.83**	**0.83**	**−0.79**	**0.51**	**−0.59**
Zn	−0.76	−0.32	0.89	0.73	0.19	0.68	0.83	0.45	0.88	0.87	0.78		**−0.11**	**−0.45**	**0.46**	**−0.56**	**0.32**	**−0.15**
As	−0.60	−0.13	0.63	0.63	0.11	0.68	0.58	0.46	0.71	0.68	0.54	0.58		**0.38**	**−0.27**	**0.38**	**0.06**	**−0.05**
Rb	−0.85	−0.24	0.91	0.90	0.19	0.74	0.86	0.44	0.92	0.91	0.76	0.91	0.65		**−0.89**	**0.90**	**−0.40**	**0.61**
Sr	−0.61	0.38	0.30	0.45	0.48	0.05	0.39	0.30	0.31	0.33	0.33	0.46	0.21	0.50		**−0.79**	**0.67**	**−0.57**
Zr	0.58	0.26	−0.69	−0.65	−0.12	−0.39	−0.62	−0.33	−0.67	−0.66	−0.56	−0.71	−0.44	−0.74	−0.40		**−0.32**	**0.54**
Ba	−0.83	−0.20	0.88	0.67	0.20	0.65	0.86	0.49	0.86	0.85	0.73	0.87	0.54	0.86	0.55	−0.67		**−0.32**
Pb	−0.47	−0.07	0.47	0.32	0.15	0.28	0.42	0.24	0.43	0.44	0.42	0.57	0.26	0.51	0.39	−0.39	0.51	

- Correlations between elements and soil textural fractions
  - Bold = New Mexico
  - Standard = Louisiana

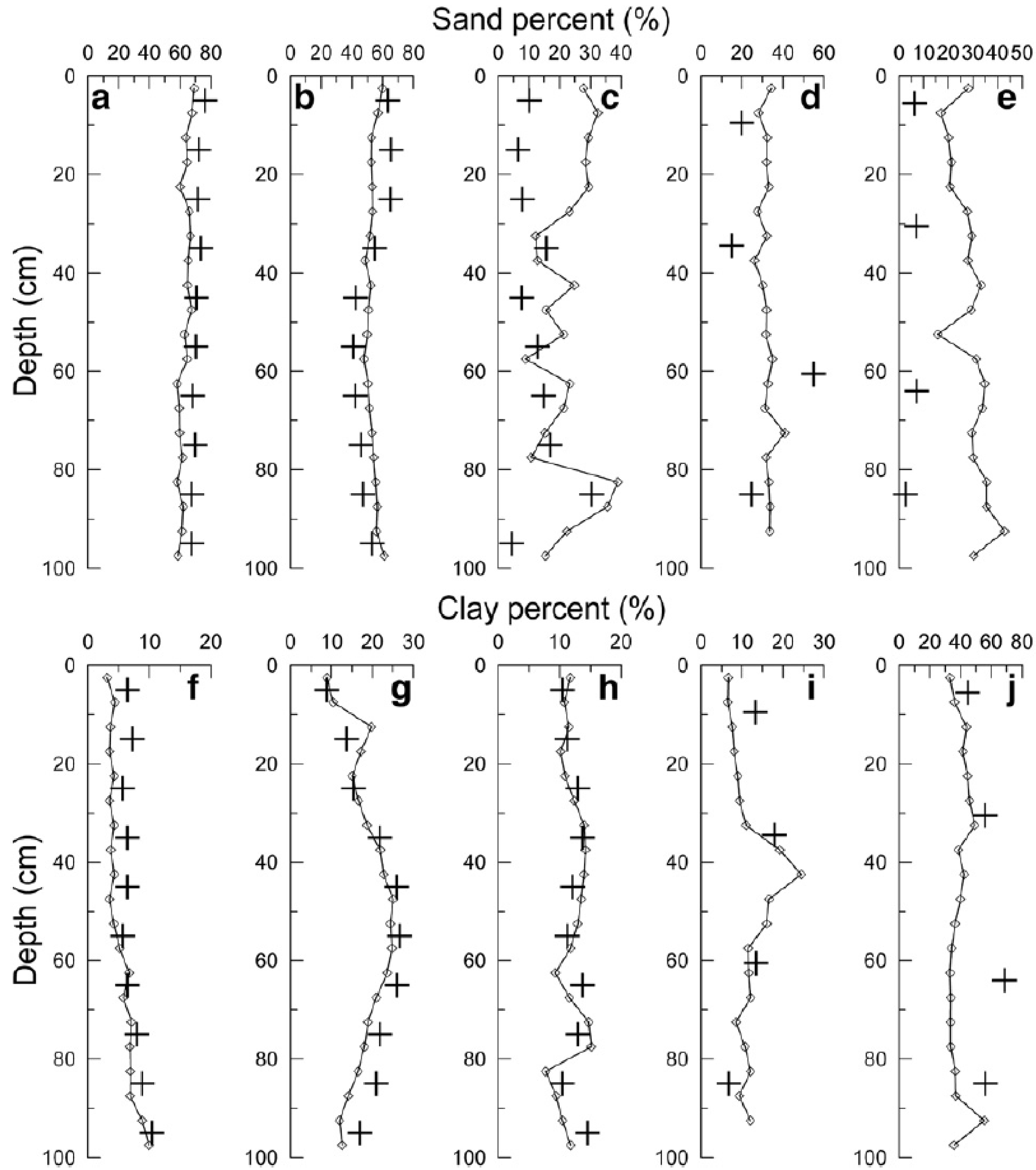
Soil Texture Via PXRF



- Validation of regression model sub-datasets
  - Louisiana sand, silt, clay (a, b, c)
  - New Mexico sand, silt, clay (d, e, f)

Soil Texture Via PXRF

- Lab measured (+) and PXRF predicted (◊) sand and clay contents for 5 pedons in Louisiana



Conclusions

- Clay and sand percentages can be quantitatively predicted using PXRF values for Fe & Rb as model variables
  - Offers in-situ, rapid approach
  - Regional models should be established
  - Lower clay RMSE values than other approaches
    - PXRF: Clay RMSE 2.68% (LA) and 2.66% (NM)
    - VisNIR DRS: Clay RMSE 4.1% (Waiser et al., 2007)
    - VisNIR DRS: Clay RMSE 7.9% (Viscarra Rossel et al., 2009)
    - EM34/EM38: Clay RMSE 4.6-6.7% (Triantafilis and Lesch, 2005)

Further Reading

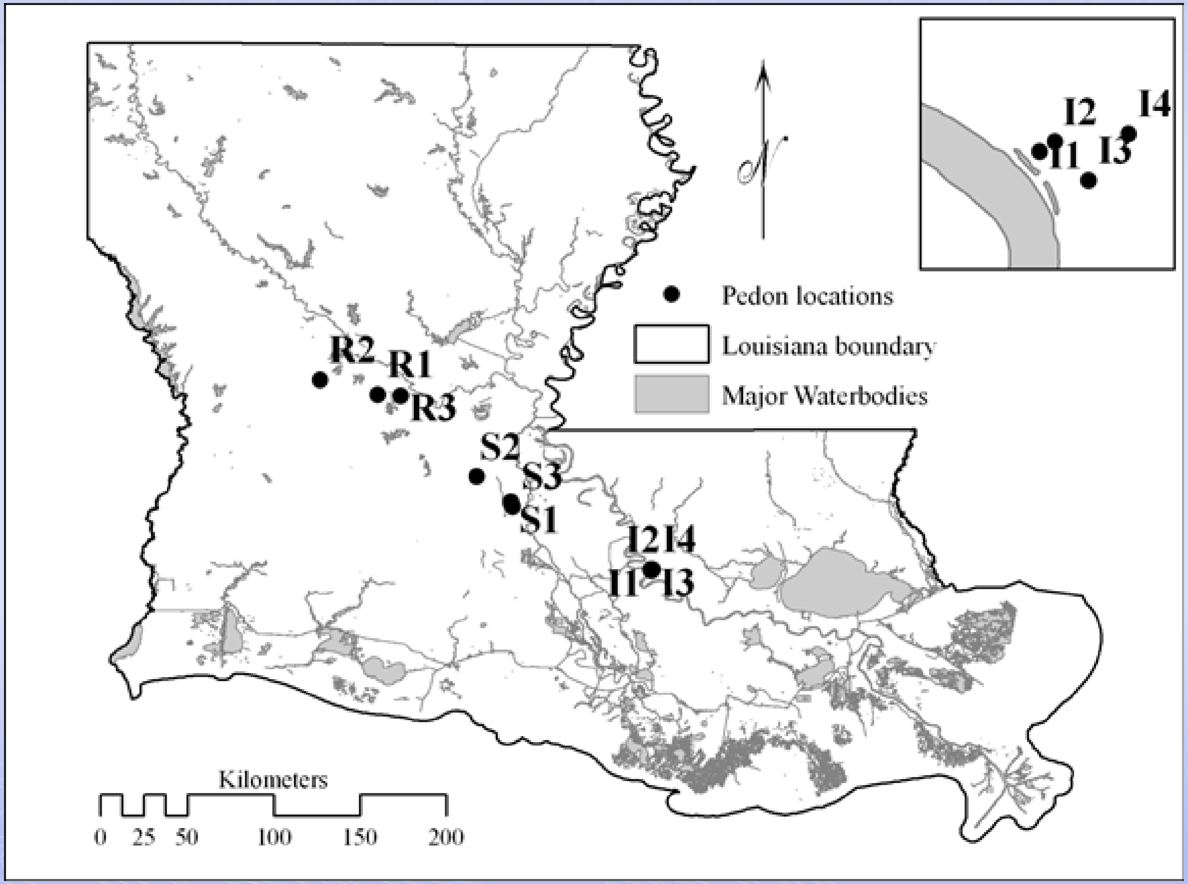
- Zhu, Y., D.C. Weindorf, and W. Zhang. 2011. Characterizing soils using a portable x-ray fluorescence spectrometer: 1. Soil texture. Geoderma 167-168:167-177. doi:10.1016/j.geoderma.2011.08.010.

Enhanced Pedon Horizonation Via PXRF

Soil pedon in Rapides Parish, LA; Weindorf.

- Soil horizons can be differentiated on any number of characteristics including elemental concentration
  - Have taxonomic and land use implications
- PXRF was used to discriminate soil horizons based on elemental differences (Ca, Mg, Fe, Mn, Cu, Zn)

Enhanced Pedon Horizonation Via PXRF



- 10 pedons in central Louisiana were morphologically described, scanned at discreet intervals (5 cm) with PXRF, and sampled for lab analysis

Enhanced Pedon Horizonation Via PXRF

- For elemental analysis, 15 elements (K, Ca, Ti, Cr, Mn, Fe, Co, Cu, Zn, As, Rb, Sr, Zr, Ba, and Pb) were selected for PCA in this study
  - Only elements with a measured quantity 10 times greater than their reported PXRF errors were used
- Eight soil variables including pH, EC, fractions of sand, silt, and clay, soil water content, bulk density, and porosity were considered as laboratory analyses for PCA

Enhanced Pedon Horizonation Via PXRF

- To quantitatively describe differences between horizons, 3 equations were established:
  - Difference in clay contents:

$$DC_n = \left| \frac{C_{n-1} - C_n}{C_{average}} \right|$$

  - DC_n is clay difference of the layer n to the above n-1 layer in a pedon; C_{n-1}, C_n, and $C_{average}$ are the clay content of the layer n, the clay content of the above layer n-1, and the average clay content of the pedon, respectively

Enhanced Pedon Horizonation Via PXRF

- Difference in lab analyses:

$$DLA_n = \sqrt{\sum_{i=1}^{F} (L_{i(n-1)} - L_{in})^2}$$

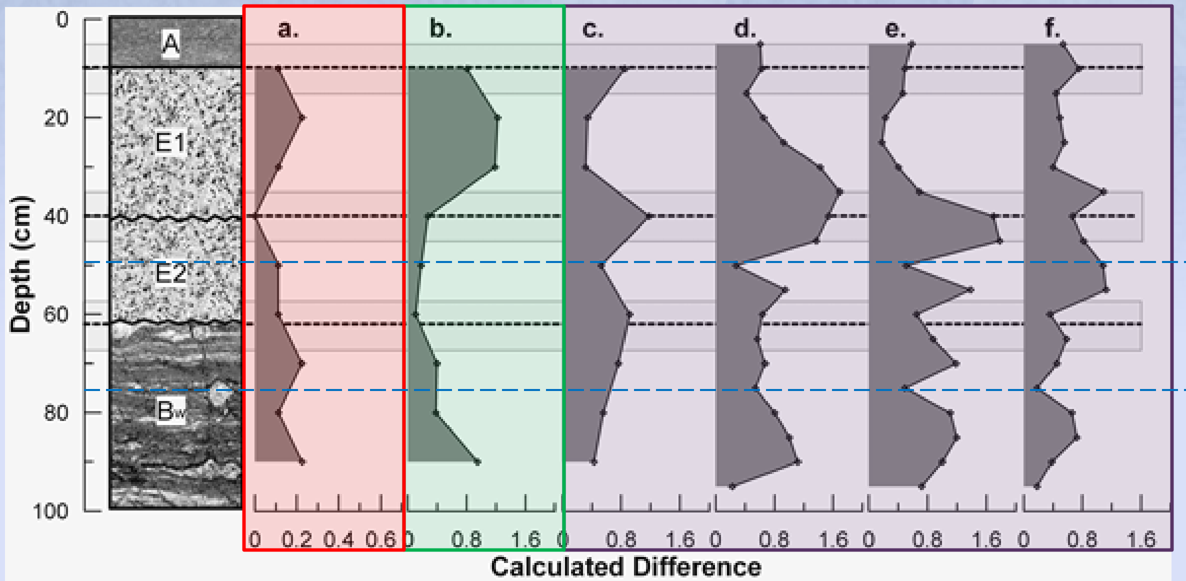
- DLA_n is the difference of laboratory analysis of layer n to the above layer n-1; F is the total number of significant principal components obtained in PCA; $L_{i(n-1)}$ and L_{in} are the loadings of layer n and the above layer n-1 on principal component i, respectively

- Difference in elements:

$$DE_n = \sqrt{\sum_{i=1}^{F} (L_{i(n-1)} - L_{in)})^2}$$

- DE_n is the difference of elemental contents of the layer n to the above layer n-1
- This equation is the same as DLA_n, except that the PXRF readings of elemental contents were used as the matrix for PCA here

Enhanced Pedon Horizonation Via PXRF



Elemental differences imperceptible via other means

- Field horizonation and calculated differences between layers for pedon R1 in Louisiana, USA (a. differences of clay; b. differences of laboratory analysis; c. elemental differences of PXRF readings on bulk density samples; d. elemental differences of PXRF readings under field conditions; e. elemental differences of PXRF readings on samples under laboratory conditions; and f. elemental differences of PXRF readings on monolith). The dotted lines are the boundaries of horizons according to field morphological description and the shaded areas are the ±5 cm buffer zone of the boundaries.

Enhanced Pedon Horizonation Via PXRF

- 3 key possibilities:
  1. PXRF data aligns nicely with morphological horizons (dramatic, clear shifts in mineralogy/texture, etc.)
  2. PXRF identifies fewer horizons than morphological description (Due to organic matter or structural changes in soil – imperceptible to PXRF)
  3. PXRF identifies more horizons than morphological description (Due to precipitation of Fe, Ca, etc. in the subsoil)
     - Example: multiple spodic, calcic, or gypsic horizons within a pedon

Enhanced Pedon Horizonation Via PXRF

- Soil horizons should not be horizonated strictly via PXRF elemental data
- Rather, it should be used as a tool for refining or enhancing morphologically established features
  - Key advantage: PXRF can be non-destructively applied to permanently mounted pedon monoliths
    - Could serve as a good historical baseline for evaluating temporal anthropogenic changes to soil quality

Further Reading

- Weindorf, D.C., Y. Zhu, B. Haggard, J. Lofton, S. Chakraborty, N. Bakr, W. Zhang, W.C. Weindorf, and M. Legoria. 2012. Enhanced pedon horizonation using portable x-ray fluorescence spectroscopy. Soil Sci. Soc. Am. Doi: 10.2136/sssaj2011.0174.

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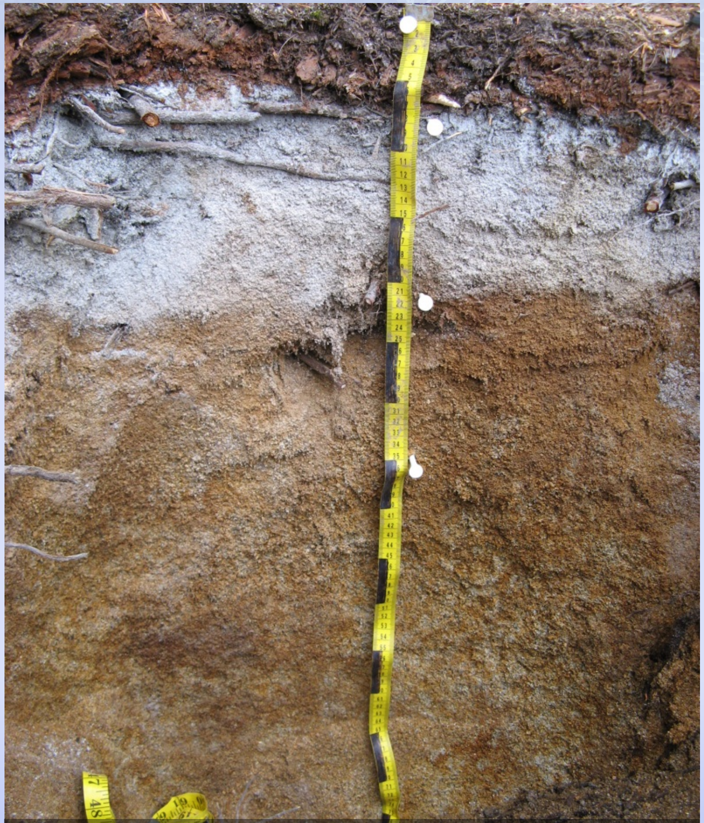
Current Work

- Differentiation of spodic, andic features via PXRF
  - Spodic/andic horizons are often characterized metallic complexes, which can appear quite ubiquitous within a given pedon
  - 11 pedons (Andic Spodosols, Andic Inceptisols) scanned in-situ in Idaho and Alaska (Fall 2011)
    - Paper under review (Geoderma)
    - Research supported by Olympus Innov-X



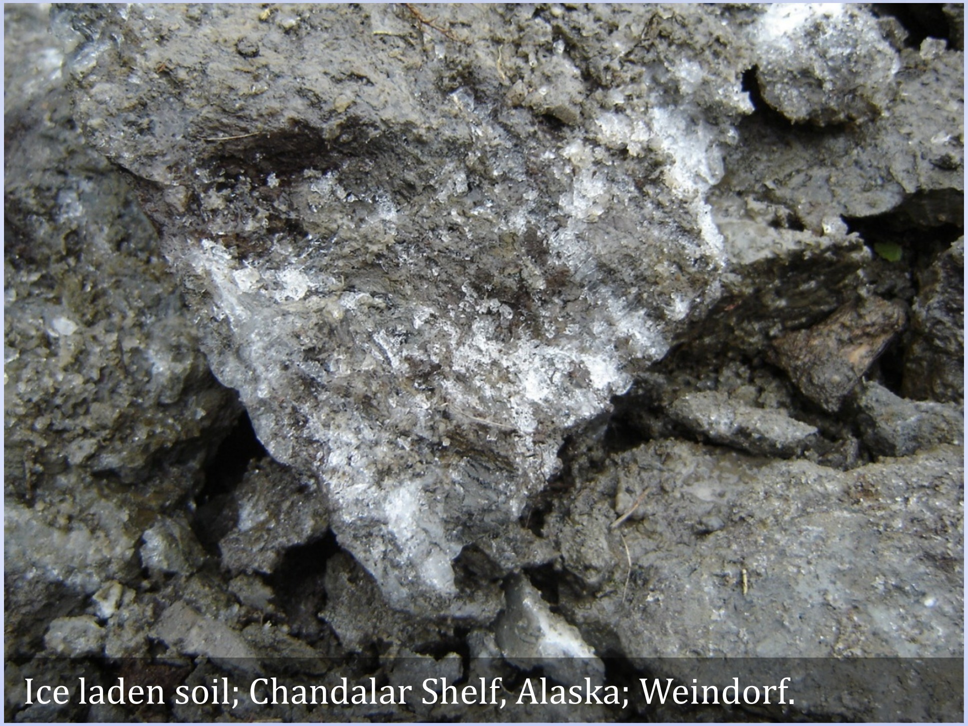
Sandy, mixed, frigid Aquic Haplorthod, near Priest Lake, Idaho; Weindorf.

Future Work – Summer 2012

- Assessment of soil salinity levels via quantification of Cl^-
- Potentially applicable to a wide range of salts (KCl, NaCl, etc.)

- Preliminary regression of soil saturated paste EC (0-45 dS m^{-1}) to Cl^- (0-15,300 ppm) yields R^2 of 0.91

Future Work – Summer 2012



Ice laden soil; Chandalar Shelf, Alaska; Weindorf.

- Evaluation of moisture effects on PXRF fluorescence denudation
  - Preliminary work, corrective models being developed in laboratory
  - Field samples will be scanned/collected in Alaska
    - Moisture effects studied both in liquid and solid (ice) form

Future Work – Fall 2012

- Spatiotemporal assessment of phytoremediation in areas of heavy metal contamination
  - Grant under review by Executive Agency for Higher Education, Research, Development and Innovation Funding (UEFISCDI) to assess heavy metals in Zlatna, Romania

Table 2

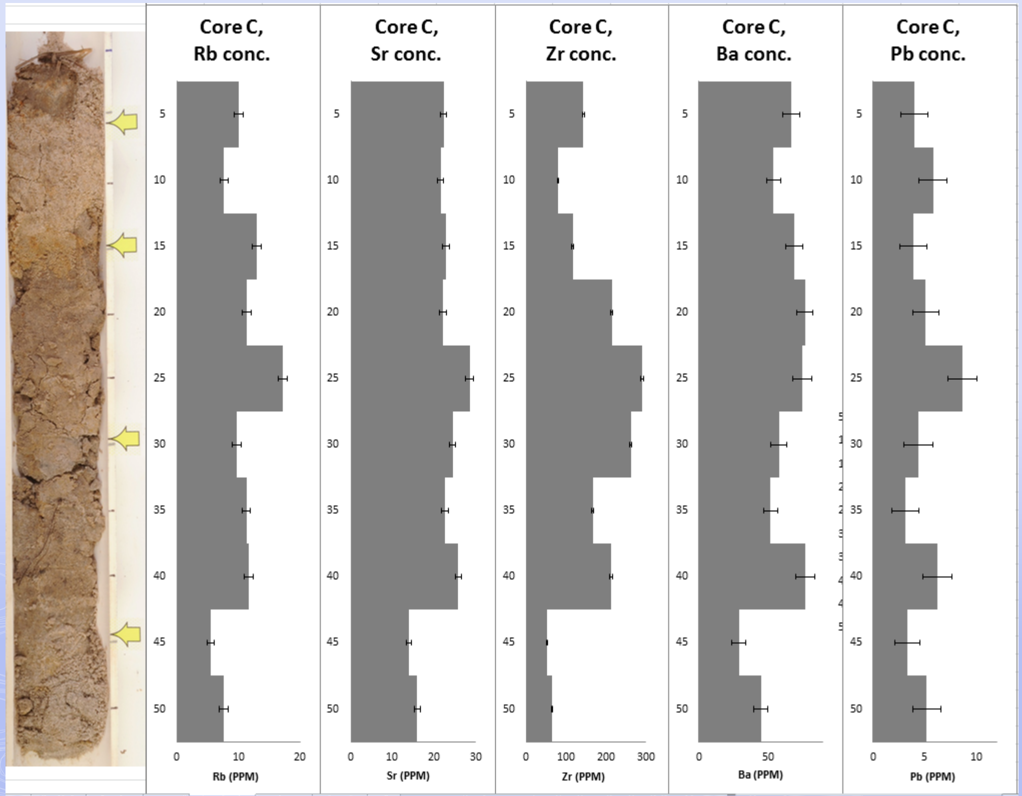
The number of plant species that are reported to have hyperaccumulation traits (metal concentration >1000 mg/kg dry weight) (Reeves, 2003)

Metals	Number of species
As	04
Cd	01
Co	34
Cu	34
Pb	14
Ni	>320
Se	20

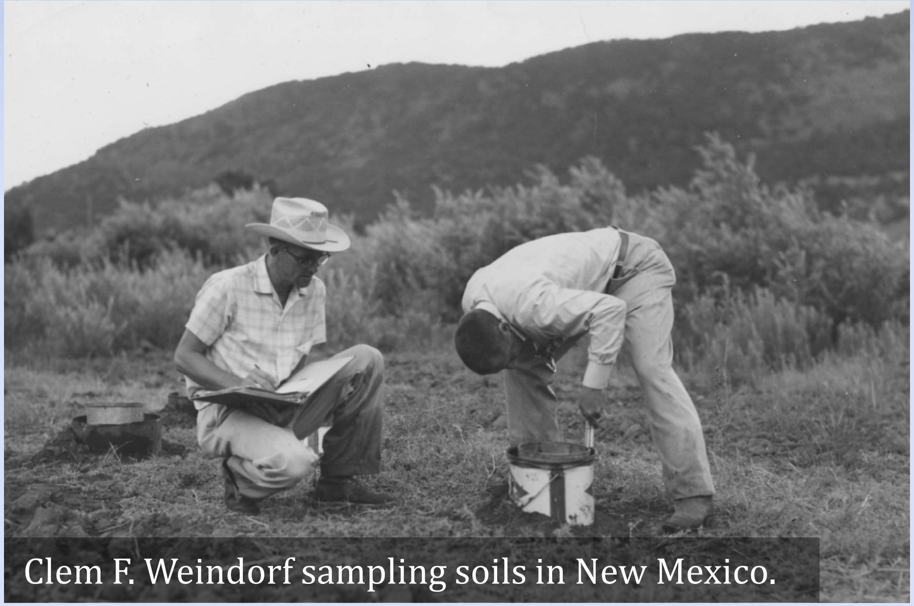
From Lone et al., 2008. DOI: 10.1631/jzus.B0710633

Future Work – Fall 2012

- Subaqueous soil cores
  - Will use PXRF to potentially differentiate depositional events
    - Sediment tracing
    - Storm surge documentation
- Spatial variability of Pb at Catahoula Lake, LA



Conclusions



Clem F. Weindorf sampling soils in New Mexico.

David C. Weindorf scanning soils with PXRF in China.

- Rapid advances in technology have given soil scientists new tools for quantification in the field
- PXRF produce quality, quantitative data in the field, in seconds

Conclusions

- Advantages of PXRF:
  - Rapid (60-90 seconds)
  - Portability – Analyses completed on-site
  - Non-destructive
  - Equipment is available for rental
  - Minimal to no consumables
  - Direct reporting of data

Questions/Comments?