



UNIVERSITÀ POLITECNICA DELLE MARCHE
Repository ISTITUZIONALE

Lithologic Discontinuity Assessment in Soils via Portable X-ray Fluorescence Spectrometry and Visible Near-Infrared Diffuse Reflectance Spectroscopy

This is the peer reviewed version of the following article:

Original

Lithologic Discontinuity Assessment in Soils via Portable X-ray Fluorescence Spectrometry and Visible Near-Infrared Diffuse Reflectance Spectroscopy / Weindorf, David C.; Chakraborty, Somsubhra; Abdalsatar, Abdalsamad; Aldabaa, Ali; Paulette, Laura; Corti, Giuseppe; Cocco, Stefania; Michéli, Erika; Wang, Dandan; Li, Bin; Man, Titus; Sharma, Aakriti; Person, Taylor. - In: SOIL SCIENCE SOCIETY OF AMERICA JOURNAL. - ISSN 0361-5995. - STAMPA. - 79:0(2015), pp. 1704-1716.

[10.2136/sssaj2015.04.0160]

Availability:

This version is available at: 11566/228455 since: 2022-06-03T17:40:39Z

Publisher:

Published

DOI:10.2136/sssaj2015.04.0160

Terms of use:

The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. The use of copyrighted works requires the consent of the rights' holder (author or publisher). Works made available under a Creative Commons license or a Publisher's custom-made license can be used according to the terms and conditions contained therein. See editor's website for further information and terms and conditions.

This item was downloaded from IRIS Università Politecnica delle Marche (<https://iris.univpm.it>). When citing, please refer to the published version.

(Article begins on next page)

1 **Title: Lithologic discontinuity assessment in soils via portable X-ray fluorescence (PXRF)**
2 **spectrometry and visible near infrared diffuse reflectance spectroscopy (VisNIR DRS)**

3 **Authors:** David C. Weindorf^{1*}, Somsubhra Chakraborty², Abdalsamad Abdalsatar Ali Aldabaa³,
4 Laura Paulette⁴, Giuseppe Corti⁵, Stefania Cocco⁵, Erika Michéli⁶, Dandan Wang⁷, Bin Li⁸, Titus
5 Man⁹, Aakriti Sharma¹, Taylor Person¹

6 ¹Department of Plant and Soil Science, Texas Tech University, Lubbock, TX, USA

7 ²Uttar Banga Krishi Viswavidyalaya University, Cooch Behar, India

8 ³Desert Research Center, Cairo, Egypt

9 ⁴Universitatea de Științe Agricole și Medicină Veterinară, Cluj-Napoca, Romania

10 ⁵Facoltà di Agraria, Università Politecnica Delle Marche, Ancona, Italy

11 ⁶Szent István University, Gödöllő, Hungary

12 ⁷Nanjing University of Information Science & Technology, Nanjing, China

13 ⁸Louisiana State University, Baton Rouge, LA, USA

14 ⁹Babeș-Bolyai University, Cluj-Napoca, Romania

15 ***Corresponding Author:**

16 David C. Weindorf, PhD, PG

17 Associate Professor and BL Allen Endowed Chair of Pedology

18 Associate Dean for Research

19 Texas Tech University

20 Department of Plant and Soil Sciences

21 Box 42122

22 Lubbock, TX 79409 USA

23 David.weindorf@ttu.edu

24

25 Key words: Lithologic discontinuity, pedology, proximal sensors, VisNIR DRS, PXRF, parent
26 material

27

28

ABSTRACT

29 Lithologic discontinuity identification can be arduous and erroneous in instances where distinct
30 morphological differences between parent materials are absent. Often, investigators must wait for
31 laboratory data to help differentiate parent materials via physicochemical properties. This paper
32 uses visible near infrared diffuse reflectance spectroscopy (VisNIR DRS) and portable X-ray
33 fluorescence (PXRF) spectrometry for establishing parent material differentia more quickly. Ten
34 pedons containing 135 samples were scanned *in situ* in the USA, Italy, and Hungary,
35 morphologically described by trained pedologists, then sampled for standard laboratory
36 characterization. Compared to laboratory data and/or morphologically described discontinuities,
37 PXRF data were associated with large, abrupt changes in standardized PXRF differences of
38 elements (DEs), noted in data plots as DE maxima and minima; areas of likely discontinuity.
39 Standardized VisNIR DRS calculated differences (CDs) in reflectance spectra (350-2500 nm) were
40 also associated with discontinuities based upon CD reflectance maxima and minima. Notably
41 within both types of data plots, lithologic discontinuities were not well captured by the proximal
42 sensors when CD or DE values fell in the data plot mid-section (e.g., not at maxima or minima
43 within the data plots). Across the pedons evaluated, PXRF was more useful for detecting
44 discontinuities than VisNIR DRS. Summarily, PXRF showed good alignment with
45 morphologically established discontinuities in eight out of ten pedons while VisNIR DRS showed

46 good alignment in only five pedons. Both PXRF and VisNIR DRS provided useful information
47 for lithologic discontinuity recognition, especially in soils with nondescript morphology.

48 INTRODUCTION

49 Lithologic discontinuities (LDs) are defined as a zone within the pedo-stratigraphic column
50 representing a change in lithology, sediment type, or parent material (Soil Science Society of
51 America, 2014). The formation of LDs can be by geologic depositional processes prior to
52 pedogenesis, depositional upbuilding (e.g., new sediment addition) during soil formation,
53 weathering and vertical or lateral translocations, or bioturbation (Phillips and Lorz, 2008; Schaetzl
54 and Thompson, 2015). In some cases, LDs are marked by changes in soil texture, coarse fragment
55 content, soil organic carbon, or other physicochemical parameters (Schaetzl, 1998). If the
56 aforementioned features are present, morphological establishment of the LDs is relatively
57 straightforward to the trained pedologist. However, many instances exist where LDs are
58 nondescript and cannot be easily surmised. In fact, many pedologists concede that LDs are often
59 difficult to recognize in the field due to a lack of clear morphological expression (e.g., Price et al.,
60 1975; Soil Survey Staff, 1993). For example, in northeastern Wisconsin and the Upper Peninsula
61 of Michigan, Schaetzl and Luehmann (2013) noted that pedoturbation could effectively mix loess
62 with underlying sandy glacial sediment in zones up to 50 cm thick. This underlies the fact that
63 many LDs have boundaries which are not abrupt. Thus, pedologists are left to field-identify
64 suspected LDs using data they can obtain from the soil profile, collect samples, and await the
65 results of physicochemical laboratory analyses in support of their suppositions. Given the depth
66 and breadth of experience of most pedologists, their field conclusions on soil physicochemical
67 properties, soil profile pedogenesis, and suspected LDs are remarkably accurate; yet at times even
68 such talented professionals find themselves in need of confirmatory laboratory analyses. Such

69 laboratory data typically involves the skeletal, immobile fraction of soils. Grain size analysis may
70 be evaluated independently (e.g., sand, silt, clay) or as ratios of sand/silt, coarse sand/fine gravel
71 fractions, quartz/feldspar ratios, and elemental composition or mineralogy (Foss and Rust, 1968;
72 Raad and Protz, 1971; Schaetzl, 1998; Price et al., 1975; Habecker et al., 1990). While these
73 techniques are generally effective, they require laboratory analysis; lacking the ability to provide
74 pedologists with the necessary data while evaluating pedons in the field. However, the advent of
75 field portable, proximal sensors [e.g., portable X-ray fluorescence (PXRF) spectrometry and
76 visible near infrared diffuse reflectance spectroscopy (VisNIR DRS)] offer new means of
77 investigation *in situ* and provide field soil scientists with quantitative data on-site (McLaren et al.,
78 2012; Hartemink and Minasny, 2014). Importantly, these approaches offer advantages over
79 traditional laboratory analyses such as non-destructiveness, alacrity, and low operating cost.

80 Portable X-ray fluorescence utilizes fluorescent emission spectra given off by elements
81 bombarded with low power X-rays (10-40 kV). The wavelength (energy) of the emitted spectra
82 are characteristic of unique elements present in a sample, whereas emission intensity gives an
83 indication of elemental abundance. Conversely, VisNIR DRS involves the use of reflected light in
84 the 350-2,500 nm range. Reflectance spectra are parsed into discreet intervals (e.g., 2 to 10 nm) to
85 construct reflectance profiles which are then statistically compared to other quantitative soil
86 parameter data. Various soil parameters are uniquely associated with combinations of specific
87 reflectance spectra (Chakraborty et al., 2010). Comprehensive overviews of PXRF, VisNIR DRS,
88 and their potential synthesis in soil analyses have been offered by Weindorf et al. (2014) and Horta
89 et al. (2015).

90 Previously, PXRF and VisNIR DRS have been independently used to successfully predict a
91 wide range of soil physicochemical properties, including organic carbon (Morgan et al., 2009;

92 Chakraborty et al., 2013), gypsum content (Weindorf et al., 2009; Weindorf et al., 2013a), salinity
93 (Swanhart et al., 2014), pH (Sharma et al., 2014), texture (Zhu et al., 2011), cation exchange
94 capacity (Sharma et al., 2015), diagnostic subsurface horizons/features (Weindorf et al., 2012a),
95 moisture (Zhu et al., 2010), and organic/inorganic pollutants (Weindorf et al., 2013b; Chakraborty
96 et al., 2010; Weindorf et al., 2012b; Paulette et al., 2015). Most importantly, Weindorf et al.
97 (2012c) showed that PXRF could be used for enhanced soil horizonation whereby horizons could
98 be differentiated using elemental data from PXRF in soil profiles where morphological differentia
99 were unremarkable. Applied to the present study, VisNIR DRS models have another advantage in
100 that they should be able to better detect irregular decreases in organic carbon content with depth;
101 an established approach for recognizing buried soils and potential discontinuities.

102 Although each of these techniques has successfully predicted soil physicochemical properties
103 independently, the latest research has investigated the synthesis of data from these two approaches
104 for enhanced predictive model performance. For example, a fused PXRF/VisNIR DRS approach
105 was used to provide optimized predictive models of soil salinity in playas of West Texas, USA
106 (Aldabaa et al., 2015), total carbon and total nitrogen in soils (Wang et al., 2015), and hydrocarbon
107 quantification in contaminated soils (Chakraborty et al., 2015). In all three studies, performance
108 of the fused PXRF/VisNIR DRS predictive models outperformed the models which utilized only
109 a singular proximal sensor.

110 Given the success of VisNIR DRS and PXRF at predicting numerous soil physicochemical
111 properties, evaluation of their use for field identification of LDs in soils appears timely. If proven
112 successful, it would offer pedologists a rapid, quantifiable means of determining LDs *in situ*,
113 especially in nondescript soils where no morphological differences present themselves and in
114 instances where mixing between two parent materials produces a gradual or diffuse boundary

115 between materials. As such, the objective of this research was to compare soil LDs established by
116 traditional morphological field description with physicochemical data produced through standard
117 laboratory characterization to that of proximally sensed PXRF and VisNIR DRS data. Our goal
118 was to relate the datasets to determine the effectiveness of PXRF/VisNIR DRS in establishing LD
119 boundaries. We hypothesize that both PXRF and VisNIR DRS will successfully differentiate
120 parent materials *in situ* allowing for LD identification.

121 **MATERIALS AND METHODS**

122 ***General Occurrence and Features***

123 In an effort to test the effectiveness of this approach on a wide variety of LDs, samples of 10
124 pedons were collected in West Texas (TX), USA (n=5), Italy (IT)(n=2), and Hungary (HU)(n=3).
125 Collectively, the pedons consisted of 135 samples collected at fixed depths. [The coordinates of
126 samples from 10 locations and their taxonomic classification are given in Table 1.](#)

127 In Texas, sampling was conducted in Cochran and Terry counties in major land resource area
128 (MLRA) 77C: Southern High Plains – Southern Part. The area is found on an expansive level
129 plateau characterized by an ustic moisture regime (405-560 mm of precipitation) which borders
130 on aridic, with a thermic temperature regime (13-17°C) (Soil Survey Staff, 2006). Soils of the area
131 are largely derived from aeolian deposits of the Blackwater Draw Formation of Pleistocene age,
132 with some alluvium and lacustrine sediments associated with shallow playas and ephemeral
133 streams (Soil Survey Staff, 2006).

134 In Italy, soils were sampled in two different sites: Valleremita and Gallignano. The former
135 developed on layers of detritus known as grèzes litées, which formed during the last glaciation
136 (Würm) by slopes accumulated of layers of well-sorted angular stones originated by frost

137 shattering and displaced by snowmelt. Along the central part of Apennines chain, large areas are
138 covered by this type of layered deposits made of shattered limestone fragments of different
139 dimensions immersed in a silty matrix. The soil moisture regime is udic (945 mm of precipitation)
140 and the temperature regime is mesic (12.6°C)(Soil Survey Staff, 2010). Gallignano soils developed
141 from finely-ground marine sediments that consisted of lithologic units with pelitic-arenaceous or
142 arenaceous-pelitic composition, all containing carbonates. The soil is characterized by an ustic
143 moisture regime (780 mm) that borders on udic, and a mesic temperature regime (13.6°C)(Soil
144 Survey Staff, 2010).

145 In Hungary, all sampled soils were located in North-Central Hungary and developed from
146 pleistocene loess. The composition of the loess varies in the Carpathian Basin according to the
147 major distance sources and local sources of the aeolian sediments (Horvath, 2001). Pedon HU-2
148 was located close to the pediment of the Matra Hills, which served as the local source of fine
149 particles from weathered andesitic material (Horvath et al., 2005). Pedons HU-4 and HU-5 were
150 influenced by coarser sandy local sources of older Tertiary deposits eroded to the surface
151 (Stefanovits, 1962). Profile HU-2 developed in a stable plateau position under natural grass
152 vegetation. Pedons HU-4 and HU-5 experienced more erosion and translocations of surface
153 materials during the late Pleistocene and the Holocene. The natural vegetation in the Holocene was
154 forest. The annual precipitation of the sites is between 450-550 mm, the moisture and temperature
155 regimes being ustic and mesic respectively (Michéli et al., 2006).

156 Pedons from Texas, USA were collected utilizing a hydraulic probe (Giddings Probe). Pedons
157 from Italy were collected from exposed road cuts or erosional escarpments. In Hungary, pedons
158 were sampled from soil pits opened with a backhoe. At each location, the evaluated area (of both
159 the excavation walls and cores) was scraped clean with a knife, then scanned with proximal sensors

160 at 10 cm increments (e.g., 0-10 cm, 10-20 cm, and so on) *in situ* in a manner consistent with
161 Weindorf et al. (2012c). Texas, USA field scanning included both PXRF and VisNIR DRS, while
162 Italy and Hungary field scanning only used PXRF due to logistical limitations relative to
163 international transportation of equipment. After scanning, morphological field evaluation
164 (Schoeneberger et al., 2002) was used to determine the suspected depth of LDs. Field notes were
165 made and profiles were photographed (Fig. 1). Soils were sampled at 10 cm increments to coincide
166 with the aforementioned proximal scanning depths, thus avoiding any bias associated with
167 morphologically established LD boundaries. Samples were sealed in plastic bags and sent to the
168 Texas Tech University pedology laboratory for further characterization. Samples collected in Italy
169 and Hungary were dried and crushed prior to shipment to Texas Tech University.

170 ***Soil Characterization***

171 In the laboratory, all dried samples were ground to pass a 2 mm sieve, then subjected to
172 standard soil characterization. Particle-size analysis was accomplished via hydrometer with clay
173 readings at 1440 min using a model 152-H hydrometer per Gee and Bauder (1986) with sand
174 determined gravimetrically after wet sieving at 53 μm . Soil pH and electrical conductivity (EC_p)
175 were determined via saturated paste after 24 h equilibration using an Accumet XL20
176 pH/conductivity meter (Salinity Laboratory Staff, 1954; Soil Survey Staff, 2004)(Fisher Scientific,
177 Pittsburgh, PA, USA). Soil organic matter (SOM) was determined per Nelson and Sommers (1996)
178 after 8 h of ashing at 400°C to minimize dehydroxilation of mineral soil. Percent calcium carbonate
179 was determined on TX pedon samples via a pressure calcimeter (Sherrod et al., 2002). Pedons
180 from Italy and Hungary were subjected to total C total N analyses using Dumas method high
181 temperature combustion on a LECO TruSpec CN analyzer (St. Joseph, MI)(Soil Survey Staff,
182 2014a).

183 *Portable X-ray Fluorescence Spectrometry*

184 Each sample was subjected to PXRF scanning with a DP-6000 Delta Premium® PXRF
185 (Olympus, Waltham, MA, USA) with deference to USEPA Method 6200 (USEPA, 2007). The
186 instrument features an Rh X-ray tube operated at 10-40 KV with an integrated large area silicon
187 drift detector (165 eV). Before scanning, the instrument was calibrated with a ‘316’ alloy
188 calibration clip tightly fitted over the aperture. Scanning was conducted in Soil Mode (3 beam)
189 which is capable of detecting the following suite of elements: V, Cr, Fe, Co, Ni, Cu, Zn, Hg, As,
190 Se, Pb, Rb, Sr, Zr, Mo, Ag, Cd, Sn, Sb, Ti, Mn, P, S, Cl, K, and Ca; each sample was then scanned
191 a second time using Geochem Mode (2 beam) to measure Mg. Scanning in Soil and Geochem
192 Modes was conducted at 30 s per beam. Geochem and Soil Mode scans were both done in duplicate
193 with the spectrometer repositioned between each scan. Data were then averaged between scans to
194 obtain a mean of elemental data for each soil sample evaluated. The performance of the PXRF was
195 checked via scanning NIST certified soil samples; results for one of those (NIST 2710a – Montana
196 I Soil) follows: *PXRF reported*/NIST certified [**recovery**] K 24,376/21,700 mg kg⁻¹ [**1.12**]; Ca
197 8,998/9,640 mg kg⁻¹ [**0.93**]; Ti 3,415/3,110 mg kg⁻¹ [**1.10**]; Mn 2189/2140 mg kg⁻¹ [**1.02**]; Fe
198 47,055/43,200 mg kg⁻¹ [**1.09**]; Cu 3346/3420 mg kg⁻¹ [**0.98**]; Zn 4236/4180 mg kg⁻¹ [**1.01**]; As
199 1538/1540 mg kg⁻¹ [**1.00**]; Sr 259/255 mg kg⁻¹ [**1.02**]; Ba 691/792 mg kg⁻¹ [**0.87**]; Pb 5476/5520
200 mg kg⁻¹ [**0.99**]. Given that Weindorf et al. (2012c) reported PXRF scans conducted under field,
201 laboratory, or monolith conditions achieved almost the same results and the influence of moisture
202 <20% on PXRF data is nominal (Melquiades et al., 2011; Piorek, 1998), only field moist scans
203 were used for this study. All field-moist samples evaluated as part of this study were, in fact, quite
204 dry.

205 *Visible Near Infrared Diffuse Reflectance Spectroscopy and Spectral Pretreatment*

206 All soil samples were scanned using a PSR-3500[®] portable VisNIR DRS spectroradiometer
207 (Spectral Evolution, Lawrence, MA, USA) with a spectral range of 350 to 2500 nm. The
208 spectroradiometer had a 2-nm sampling interval and a spectral resolution of 3.5, 10, and 7-nm
209 from 350 to 1000 nm, 1500 nm, and 2100 nm, respectively. Scanning was accomplished using a
210 contact probe with a 5W built-in light source. Samples were dried, ground and scanned at room
211 temperature in the laboratory, evenly distributed in an opaque polypropylene sample holder and
212 scanned from the top with the contact probe connected to the PSR-3500[®] with a metal-clad fiber
213 optic cable. Full contact with the sample was guaranteed to avoid outside interference. Each sample
214 was scanned four times, rotating the sample 90° between scans. The four scans were then used to
215 obtain an average spectral curve. Each individual scan was an average of 10 internal scans over
216 1.5 seconds. White referencing of the detector (after each sample) was accomplished using a 12.7
217 cm x 12.7 cm NIST traceable radiance calibration panel. This prevents fluctuating downwelling
218 irradiance from saturating the detector.

219 Raw reflectance spectra were processed using R version 2.11.0 (R Development Core Team,
220 2008) with custom R routines following Chakraborty et al. (2015). These routines involved: 1) a
221 parabolic spline to correct for “gaps” between detectors, 2) averaging replicate spectra, and 3)
222 fitting a weighted (inverse measurement variance) smoothing spline to each spectra with direct
223 extraction of smoothed reflectance at 10 nm intervals. The present study used Savitzky–Golay first
224 derivative spectra with a first-order polynomial across a ten band window for subsequent spectral
225 analysis. Mathematical pretreatment of spectra reduced model error with pretreatment
226 transformation implemented in the Unscrambler[®]X 10.3 software (CAMO Software Inc.,
227 Woodbridge, NJ).

228 *Development of Hypothetical Discontinuity Indices*

229 A soil horizon is a layer of soil or soil material approximately parallel to the land surface and
230 differing from adjacent genetically related layers in physical, chemical, and biological properties
231 or characteristics such as color, structure, texture, consistency, kinds and number of organisms
232 present, or degree of acidity or alkalinity (Soil Science Society of America, 2014). The
233 differentiation of soil horizons is critical for the understanding and classification of soil since
234 horizon formation is a function of a variety of physical, chemical, geological, and biological
235 processes associated with the landscape and climate over long time periods (Schaetzl and
236 Thompson, 2015; Soil Survey Staff, 1999; Soil Survey Staff, 1993). The process of field
237 horizonation is, to some extent, a subjective approximation of soil features by field soil scientists.
238 Soil scientists use all tools available to differentiate soil horizons and establish minimal within-
239 horizon variability, considering a variety of soil properties simultaneously. As such, significant
240 variations in soil properties should occur between horizons in a given pedon. Obviously, the most
241 important part of horizonation is the identification of differences between soil horizons (i.e., what
242 makes a given horizon sufficiently different from adjacent horizons above or below justifying its
243 differentiation as a unique horizon?). As such, for purposes of this research, three different
244 discontinuity indices (differences in laboratory analyses, PXRF-determined elements, and
245 VisNIR-determined spectra) were used as quantitative metrics for differentiating one soil horizon
246 from another.

247 In this study, we followed the general methodology set forth by Weindorf et al. (2012c), here
248 summarized as follows. Principal component analysis (PCA) was used to establish the degree of
249 horizon differentiation using data collected from scanning layers and various other soil variables
250 as the key components of the data matrix. Essentially, orthogonal transformation was utilized in
251 PCA to change a set of observations of possibly correlated variables into linearly uncorrelated

252 variables known as principal components. Jolliffe (1986) notes that doing so diminishes the chance
253 that correlated variables are continually considered in variance calculations. This procedure results
254 in the establishment of new coordinates, termed loadings, to represent the principal component
255 dataset variances.

256 In the present study, pH, EC, fractions of sand, silt, and clay, and SOM, were determined for
257 each depth of each pedon; the data from such analyses was then used for PCA. For each evaluated
258 depth, the principal components of laboratory analysis results were extracted in the matrix of
259 correlation utilizing a minimum retained eigenvalue of 1, 25 maximum iterations, and a
260 convergence level of 0.001, again following Weindorf et al. (2012c). The differences of laboratory
261 analysis (DLAs) between soil layers were established via PCA per Eq. 1 (Weindorf et al., 2012c):

$$262 \quad DLA_n = \sqrt{\sum_{i=1}^F (L_{i(n-1)} - L_{in})^2} \quad [1]$$

263 where, DLA_n represents the difference of laboratory analyses of layer n to the above layer $n-1$;
264 F is the total number of significant principal components obtained in PCA; $L_{i(n-1)}$ and L_{in} are the
265 PC scores of layer n and the above layer $n-1$ on principal component i , respectively.

266 As Weindorf et al. (2012c) note, since scaling of variables directly impacts PCA, the original
267 laboratory data can be standardized into the same scale for each pedon as divided by the averages
268 of the variables prior to PCA. Because the original soil property data were placed into the same
269 scale and the principal components routinely accounted for 90% of the variances observed, the
270 differences between data points of the principal components represents the variability of the
271 original dataset. As such, when any soil variable is considered, the calculated difference increases
272 accordingly.

273 As mentioned previously, a range of soil features are generally used by field surveyors during
274 the process of horizon description, including soil color, texture, and structure, which are essentially
275 affected by the physical and chemical composition of the soil. For example, besides SOM and
276 water content, Fe and Mn are the primary coloring agents for many soils. Several soil variables
277 including pH, silt/clay fraction, SOM, oxides and hydroxides, and microorganisms are documented
278 as factors influencing the content and behavior of trace elements (Kabata-Pendias and Pendias,
279 2001). While elemental variability has not traditionally been used for horizon differentiation, it
280 represents quantifiable chemical differences within the soil and a viable parameter for unique
281 horizon recognition. Portable X-ray fluorescence scanning provides quantifiable data on a large
282 number of macro and trace elements. Thus, the abundance of a single element or several elements
283 within a given pedon can be considered jointly with other factors when assigning horizon
284 boundaries. As such, differences of elements (DEs), as determined by PXRF, between horizons
285 were calculated via Eq. 2 (Weindorf et al., 2012c):

$$286 \quad DE_n = \sqrt{\sum_{i=1}^F (L_{i(n-1)} - L_{in})^2} \quad [2]$$

287 where, DE_n is the difference of elemental contents of the layer n to the above layer $n-1$.
288 Likewise, changes in elemental abundance within the pedon cause an increase in the DEs between
289 soil layers. Considering both the elemental precision level of the PXRF and the elemental ranges
290 found by PXRF within the profiles, the contents of fifteen elements (K, Ca, Ti, V, Cr, Mn, Fe, Ni,
291 Cu, Zn, Rb, Sr, Zr, Ba, and Pb) were selected for PCA in this study, but only elements with a
292 measured quantity more than 10 times greater than their reported PXRF errors were selected for
293 use.

294 Finally, in the same manner, the calculated differences (CDs) of VisNIR DRS reflectance
295 values between soil layers were established via PCA per Eq. 3 (adapted from Weindorf et al.,
296 2012c):

$$297 \quad \text{VisNIRdifferences}_n = \sqrt{\sum_{i=1}^F (L_{i(n-1)} - L_{in})^2} \quad [3]$$

298 Equations 2 and 3 are fundamentally the same as Eq. 1, except the PXRF readings of elemental
299 contents and VisNIR DRS reflectance values were used as the matrix for PCA in Eqs. 2 and 3,
300 respectively. Notably, since SOM is a key factor in horizon differentiation, we only considered a
301 subset (1700-2500nm) of the total VisNIR DRS range which has been proven as the most
302 informative region for SOM (Sudduth and Hummel, 1993). All statistical analyses were executed
303 in XL Stat 2014 (Addinsoft, Paris, France).

304 **RESULTS AND DISCUSSION**

305 *Field and Laboratory Assessment*

306 Results of our laboratory analyses are presented as supplementary information in Table 2-
307 Supp. Analyses of some samples from Italy and Hungary were not possible due to limited sample
308 quantity available after shipment.

309 *Texas*

310 Most of the Texas soils had sandy soil textures, often sandy loam. Site TX-1 consisted of
311 shallow playa lacustrine sediments with sandy aeolian sediments overlying, thus establishing the
312 lithologic discontinuity. Laboratory data shows a doubling of SOM % at a depth of 30-40 cm (1.00
313 %) vs. the overlying horizon at 0.50 %. Similarly, clay content increases from 22 to 35 % at that
314 boundary causing soil texture to shift from sandy clay loam soil to sandy clay soil. However, an

315 even more pronounced shift in soil properties was observed at a depth of 60-70 cm whereby clay
316 content increased dramatically (42 %) relative to the overlying horizon (28 %); textural class of
317 the former is clay soil while the latter is sandy clay loam soil. Such laboratory data align well with
318 field morphological evidence of a discontinuity, only one of which was noted *in situ* at 55 cm
319 (Table 2-Supp).

320 By contrast, field investigation identified two possible discontinuities at site TX-2 (at depths
321 of 33 and 77 cm). The soil was mapped as an Amarillo fine sandy loam, which is often buried to
322 various thicknesses by soil material that has eroded by wind from the adjacent dunes mantled by
323 Drake soils (Aridic Calcustepts). Laboratory data supports the two suspected discontinuities
324 owing to a doubling of SOM % (0.20 to 0.51 %) at 33 cm, and abrupt reduction at 77 cm (0.52 to
325 0.18 %). Similarly, at these same depths, clay content is changed from 17 to 28 % and 36 to 23 %,
326 respectively.

327 Site TX-3 consisted of Quaternary alluvial sandy loam soil in a shallow draw covered by
328 aeolian influence from Midessa (Aridic Calcustept) and Posey (Calcic Paleustalf) sandy loam
329 soil in surrounding upland positions (Soil Survey Staff, 2015). While similar taxonomically, Drake
330 and Midessa soils differ in their calcium carbonate equivalent in calcic horizons, the former having
331 <40 % (Soil Survey Staff, 2015). *In situ* evaluation of the pedon suggested a discontinuity at 90
332 cm. Laboratory data detected physicochemical differences at the same depth, but also a smaller
333 possible discontinuity at 50 cm reflected by a sudden doubling of SOM % (0.15 to 0.34%), and
334 modest increases in electrical conductivity and clay contents relative to overlying horizons all of
335 which showed steady decreases. However, laboratory data show the lower discontinuity boundary
336 would be more aptly placed at 100 cm, where differences in SOM and clay %, are more apparent.
337 It is fair to note that many of the parameters evaluated as part of this study have the ability to

338 translocate within a given soil profile (e.g., clay, SOM, salts, CaCO₃). However, such translocation
339 tends to decrease rapidly with depth in areas under moisture-limited semi-arid climates.

340 Site TX-4 was in a low topographic position with sand and sandy loam soil, but with surficial
341 inputs from soil material derived from Tokio (Calcic Haplustalf) sandy loam soil in somewhat
342 higher topographic positions (Soil Survey Staff, 2015). Similar to TX-3, the depth of the
343 discontinuity noted *in situ* could be adjusted downward by ~15 cm to correspond with laboratory
344 data. An *in situ* discontinuity depth of 35 cm was proposed, but laboratory data show pronounced,
345 abrupt differences in physicochemical properties at 50 cm, where SOM % doubles, CaCO₃ %
346 doubles, clay increases 10 %, and texture shifts from loamy sand to sandy clay loam soil. Notably,
347 some translocated materials within a given soil profile may be deposited above or below the actual
348 discontinuity owing to differential hydraulic conductivity affected by shifting soil texture or other
349 factors. For example, Weindorf et al. (2010) discussed the impact of hydraulic discontinuity on
350 the formation of placic horizons in Louisiana. Thus, the location of the actual discontinuity must
351 be considered carefully in the context of accumulations or physicochemical differentia which may
352 occur either slightly above or below the actual LD.

353 Site TX-5 was similar to TX-3 featuring aeolian deposits of sandy loam soil with inputs from
354 nearby Midessa and Tokio soils. Here, the laboratory data support discontinuity establishment in
355 the same location as the *in situ* morphological assessment (52 cm)(Table 2-Supp). At this depth,
356 SOM % increases by 1.5 fold, clay content doubles, and increases in salinity and CaCO₃ are
357 observed relative to overlying horizons. While many of these features may initially be considered
358 part of normal subsoil pedogenesis through illuvial processes, the compelling parameter is SOM
359 %. Subsoil increases in SOM alone may lead evaluators to consider this as a buried soil. However,
360 when considered simultaneously with other physicochemical factors showing pronounced

361 differences, lithologic discontinuity recognition is reasonable, possibly in conjunction with being
362 buried.

363 *Italy*

364 Pedon IT-2 (Valleremita) occurred on a very steep, forested hillslope (~55%), and featured
365 multiple discontinuities as colluvium from differential sources. Morphological field description
366 indicated discontinuities at 61, 86, 116, and 143 cm. Laboratory data were variable across horizons,
367 with some trends noted, though not as obviously as some other pedons. Specifically, there was a
368 trend of decreasing SOM % from the surface (18.12 %) to a depth of 90-100 cm (0.66%); a
369 boundary which likely coincides with the second suspected discontinuity at 86 cm. Following on,
370 SOM % increases again to a depth of 130-140 cm (2.46%); coinciding with the fourth suspected
371 discontinuity. Less profound differences were observed at 61 cm with sand and silt contents
372 increasing 3-4 % while clay content decreased by 7%. Few remarkable changes were detected in
373 the laboratory data at 116 cm, suggesting that the field notation of such may be errant (a suggestion
374 later refuted by proximally sensed data).

375 *In situ*, Pedon IT-3 (Gallignano) was suspected of having a discontinuity at 41 cm as colluvium
376 over residuum. However, laboratory data not only discounted this suspected discontinuity, they
377 identify a likely alternate deeper in the profile. While no remarkable differences in laboratory data
378 were noted at 41 cm, laboratory data indicate a clear shift at 110-120 cm where, relative to the
379 overlying horizon, the texture shifts from loam to sandy loam soil, sand content increases 21 %,
380 silt content decreases 15 %, and SOM % dips to 0.25 % (the lowest in the entire profile) before
381 increasing again with the next lowest horizon. This one single depth (110-120 cm) also represents
382 the highest salinity ($352 \mu\text{S m}^{-1}$) of any depth below 30 cm.

383 *Hungary*

384 Three pedons were evaluated in Hungary, each showing differential expression of possible
385 discontinuities. *In situ*, Pedon HU-2 showed a strong calcic horizon at 100 cm; an area where a
386 suspected discontinuity occurred. However, high levels of CaCO₃ accumulation may also be due
387 to normal pedogenesis, casting doubt upon this initial supposition. Laboratory data clearly show a
388 doubling of carbon (1.3 to 2.9%) at the 100 cm boundary. Also, clay content decreases ~4%
389 relative to the overlying horizon; a modest decrease but one which also changes soil textural class
390 from silty clay loam to silt loam soil. Interestingly, at the 110-120 cm depth, SOM % reaches a
391 minimum of 0.58 %, before steadily increasing below that with depth. Thus, the increase in SOM
392 % deep in the profile gives an indication that a discontinuity in this area may be warranted as
393 opposed to simple pedogenic carbonate accumulation.

394 *In situ* evaluation of Pedon HU-4 indicated two possible discontinuities: 90 cm and 146 cm
395 (loess over lacustrine sediments). Both suspected discontinuities were clearly observable in the
396 laboratory data. Relative to the overlying horizon, the SOM doubles (0.32 to 0.60 %), and electrical
397 conductivity triples (107 to 382 $\mu\text{S m}^{-1}$) at 90 cm. At 140-150 cm, sand content decreases by 22
398 %, silt content increases by 16 %, and carbon content goes from 2.35 to 4.07 % relative to the
399 overlying horizon. A third discontinuity was clearly evident in the laboratory data, though elusive
400 during field description. At 110-120 cm, soil texture was silt loam, and carbon was 6.30 %. Both
401 overlying and underlying horizons were sandy loam soil while carbon content was 0.34 % above
402 and 3.89 % below.

403 Pedon HU-5 showed evidence of a discontinuity at 80 cm *in situ*. Though debatable as to the
404 exact depth at which the discontinuity starts, laboratory data clearly shows a dramatic shift in
405 physicochemical properties from 80 to 110 cm. Except for the surface horizon (likely impacted by

406 soil pit spoil), the upper part of the profile is acidic (4.1-4.8) and shows a steady increase in clay
407 content from sandy loam (14 % clay) soil, to sandy clay loam (23-31 % clay) soil, to clay (40 %
408 clay) soil with depth. But at 90 cm, clay content begins to decrease, silt content begins to increase,
409 and carbon levels increase by as much as 20 fold. While the silt content can be linked to calcic
410 horizon formation, this does not explain the rapid decrease in sand content (68 % in the upper part
411 of the profile lowering to 22 % by 100 cm). At 80-90 cm, SOM % is also the highest of any horizon
412 (0.91 %) in this profile except for the surface horizon. As such, discontinuity status in this profile
413 is likely.

414 *Proximal Sensor Approaches*

415 In discussing the ability of PXRF and VisNIR DRS to elucidate differences in profile parent
416 material origin, the 10 evaluated pedons were qualitatively grouped into classes of good, fair, and
417 poor for both PXRF and VisNIR DRS. Notably, these classes were comparing the field-determined
418 LDs with PXRF and VisNIR data. Often, laboratory characterization data was useful in helping to
419 explain why PXRF and VisNIR data plots performed the way they did in Figs. 2, 3, and 4. “Good”
420 matches between the datasets indicated that proximal sensor data aligned well with field-described
421 LDs; that is, plot maxima and minima generally occurred within ~5 cm of the field-described
422 discontinuity with most discontinuities within a given pedon meeting this criterion. “Fair” matches
423 between the datasets indicated that proximal sensor data somewhat aligned with field-described
424 LDs. For example, the datasets identified LDs at approximately the same depths, but proximal
425 sensor data suggested that a given LD might be more appropriate placed 10-20 cm higher or lower
426 than field-described LDs. Furthermore, “fair” matches could contain a mix of multiple LD plot
427 alignments, some of which were “good” while others were “poor.” “Poor” matches between the
428 datasets indicated almost no relation between field-described LDs and proximal sensor data. Often,

429 this was expressed as nondescript plots with no maxima or minima, or plots where field described
430 LDs were >20-30cm from proximal sensor maxima/minima. In some instances, laboratory data
431 and/or field suspected discontinuities aligned with PXRF and VisNIR DRS predictive plots. But
432 in other instances, wide discrepancy was found. Weindorf et al. (2012c; 2014) outlined the
433 rationale for such differences with regard to PXRF as follows: 1) PXRF data aligns well with
434 traditional morphological horizons, 2) PXRF reveals more horizons than traditional morphological
435 descriptions due to differences in elemental concentrations imperceptible to the human eye, and/or
436 3) PXRF reveals fewer horizons than morphological descriptions based on differences
437 undetectable to the PXRF (e.g., differences in soil structure, rooting, bulk density, soil organic
438 carbon). Although VisNIR DRS should reasonably be able to detect differences in organic carbon
439 (Morgan et al., 2009)(and by extension perhaps even differences in rooting density), soil
440 characteristics such as bulk density, soil structure, and consistence likely remain elusive to these
441 two proximal sensors. However, those characteristics seldom form the sole basis for lithologic
442 discontinuity designation. Nonetheless, the authors do not advocate the sole use of proximal
443 sensors for LD establishment. Rather, we suggest that such sensors can provide useful quantitative
444 elemental and spectral data that can be used to complement traditional morphological description,
445 especially in instances where the boundaries of LDs are morphologically nondescript.

446 ***PXRF Assessment***

447 With regard to PXRF analysis of discontinuity assessment, eight pedons qualitatively showed
448 good alignment with laboratory and/or field established continuities; two pedons were fair. In most
449 instances, PXRF discontinuities were marked by either maximum or minimum DE values
450 evaluated on a pedon by pedon basis (Fig. 2). In some cases, these maximum and minimum values

451 were helpful in adjusting the depth of the laboratory/field determined discontinuity where clear
452 trends were observed.

453 Pedons TX-1 and TX-2 showed fair alignment while TX-3, TX-4, and TX-5 showed good
454 alignment. In TX-1, the field suspected discontinuity at 55 cm was non-detectable by PXRF; these
455 results were supported by laboratory data. However, laboratory data point to a discontinuity at 60-
456 70 cm, and at 70 cm, PXRF DEs reach a minimum, suggesting a possible discontinuity. At TX-2,
457 a field suspected discontinuity at 33 cm aligns well with a PXRF DE maximum and laboratory
458 data. However, the second field suspected discontinuity at 77 cm was not well represented by
459 PXRF DEs. Here, the DE trend line is moving steadily downward, but not near a maximum or
460 minimum value. As such the PXRF DE minimum is not achieved until 90 cm; a considerable
461 departure from laboratory/field data. However, laboratory data align well with the PXRF DE
462 minimum at 90 cm, showing maximum sand content, minimum clay content, and minimum subsoil
463 soil organic matter are found at this same depth (Fig. 3), suggesting that the field identified
464 discontinuity might be more aptly lowered from 77 to 90 cm. The remaining Texas pedons showed
465 strong alignment between PXRF and laboratory/field discontinuity location. At TX-3, a minimum
466 PXRF DE was found at 90 cm; very near the field and laboratory suspected discontinuity. PXRF
467 provides some support to evaluating a possible second discontinuity at ~60 cm where laboratory
468 data shows some indications of a discontinuity and PXRF DEs are maximized. At TX-4, the PXRF
469 DE minimum at 30 cm aligns well with field discontinuity suspected at 35 cm, and a laboratory-
470 suspected discontinuity at 50 cm is reflected strongly by a PXRF DE maximum at that same depth.
471 Finally, a PXRF minimum DE at 52 cm in TX-5 aligns well with both laboratory and field data in
472 support of a discontinuity at that depth.

473 Of all the pedons evaluated, Pedon IT-2 was the most complex, with four different field-
474 suspected discontinuities. Somewhat surprisingly, PXRF did an excellent job at noting these;
475 showing wide swings in DE maxima and minima accordingly. Field suspected discontinuities were
476 set at 61, 86, 116, and 143 cm. At 60-70 cm, PXRF DEs were minimum but by 80-90 cm, they
477 had shifted to maximum, aligning perfectly with both field and laboratory data. At 116 cm,
478 laboratory data was marginal in supporting a field suspected discontinuity, but PXRF reached a
479 DE minimum in perfect unison with the field depth. For the lowest discontinuity, laboratory data
480 suggested that moving the depth slightly higher in the profile may be appropriate. However, a
481 PXRF DE minimum suggests that the field assessment was accurate and should be left unchanged.
482 For Pedon IT-3, PXRF data indicates that the suspected field discontinuity at 41 cm should be
483 moved slightly higher in the profile as a DE maximum is achieved at ~25 cm. Though not noted
484 in the field, a suspected laboratory-identified discontinuity at ~110-120 cm is well supported by a
485 PXRF DE minimum achieved at that same depth. Here, both laboratory and PXRF were
486 compelling in identifying something different in the soil substrate which was not visually
487 detectable.

488 All three Hungarian pedons showed good alignment between PXRF and laboratory/field data.
489 Pedon HU-2 had a field suspected discontinuity at 100 cm. However, laboratory data suggested
490 that it is more appropriately moved deeper to 110-120 cm (noted by green dashed line in Fig. 3).
491 A PXRF DE minimum was reached at ~115 cm, a depth at which maximum silt, minimum clay,
492 and near minimum subsoil soil organic matter levels were achieved (Fig. 3). Pedon HU-4 had field
493 suspected discontinuities at 90 and 146 cm. The former was well captured by a PXRF DE
494 minimum, while the latter was not well captured by PXRF; the DE trend line was still decreasing
495 at that depth. While not evident in the field, laboratory data shows a possible discontinuity at 110-

496 120 cm; a depth clearly captured by a PXRF DE maximum at ~110 cm. Finally, pedon HU-5 shows
497 a maximum PXRF DE at ~83 cm, clearly reflective of both laboratory and field discontinuity
498 placement at 80 cm. Here, the clay reaches a maximum and subsoil soil organic matter is near its
499 maximum as well; both decline sharply below this depth.

500 The plots shown in Fig. 3 lead to an important question: should morphological or laboratory-
501 based data take precedence in assigning a discontinuity in soils? While both are important, the
502 physicochemical laboratory-based data are often elevated in stature owing to their quantitative
503 limits rather than qualitative measures employed by morphological description. If nothing else,
504 this research has illustrated instances where laboratory and morphological data do not precisely
505 align in establishing discontinuities. However, PXRF has repeatedly shown a propensity to reflect
506 quantitative differences in soil physicochemical properties as illustrated by laboratory
507 characterization data.

508 *VisNIR DRS Assessment*

509 For VisNIR DRS analysis of discontinuity assessment, five pedons qualitatively showed good
510 alignment with laboratory and/or field established discontinuities; three pedons were fair, and two
511 were poor. Similar to PXRF DE differential, VisNIR DRS identified discontinuities were marked
512 by either maxima or minima in calculated spectral differences (Fig. 3). Recall that VisNIR DRS is
513 especially sensitive to organic carbon within soils; thus, deference will be paid to how calculated
514 differences (CDs) align with SOM.

515 Texas pedons were among the weakest in showing VisNIR DRS indicated discontinuities with
516 one good, two fair, and two poor results. Pedon TX-1 showed a decreased CD at the suspected
517 field discontinuity (55 cm) qualifying it for fair matching, but it did not align well with maximum

518 and minimum CDs in the pedon. Even worse, TX-2 field suspected discontinuities occurred on
519 actively sloped CDs; again not reflective of CD maxima and minima. Pedon TX-3 was the best of
520 the Texas pedons, with a CD minimum at ~85-95 cm, aligning nicely with field-identified
521 discontinuity at 90 cm. Pedon TX-4 had a near minimum CD at 35 cm, but VisNIR DRS data show
522 that it might be more appropriately placed slightly deeper at ~45 cm. At this same depth, a PXRF
523 DE maximum further supports the idea of abrupt changes in soil properties at this depth. A possible
524 discontinuity in Pedon TX-5 was among the worst identified by VisNIR DRS. While PXRF was
525 highly capable of noting changes in the profile at 55 cm, VisNIR DRS showed a broad, low CD
526 spread with no remarkable spikes at that depth. A large CD peak was noted at ~100 cm, likely
527 reflecting the ~5-10% increase in CaCO₃ present at the depth relative to underlying and overlying
528 horizons which should logically affect spectral reflectance as a feature of color. However, other
529 laboratory data were unremarkable at this depth and the increase in CaCO₃ is likely simply
530 pedogenic.

531 Italian pedons were among the best characterized by VisNIR DRS. Pedon IT-2 had clear and
532 compelling CD maxima and minima at each of the field identified discontinuities. Similarly pedon
533 IT-3 reached a CD minimum at ~45 cm, aligning nicely with the field identified discontinuity.
534 Furthermore, a laboratory-suspected discontinuity at ~115 cm was well identified in the VisNIR
535 DRS data as a CD maximum.

536 Hungarian pedons were generally well described by VisNIR DRS with two pedons showing
537 good and one showing fair alignment with field identified discontinuities. For Pedon HU-2, a field
538 suspected discontinuity at 100 cm is clearly marked by a CD minimum in the VisNIR DRS data.
539 Pedon HU-4 was fair in its assessment, showing a clear CD minimum at one field discontinuity
540 (90 cm), but showing rather unremarkable CD features at the second field discontinuity (146 cm).

541 Somewhat surprisingly, one of the compelling features of the second discontinuity was a sharp
542 increase in organic carbon, yet VisNIR DRS seemed unable to capture this in the subsoil pedon
543 CD. Pedon HU-5 showed better alignment with a VisNIR DRS CD minimum aligning well with
544 a field described discontinuity at 80 cm.

545 *Application of VisNIR DRS and PXRF in Discontinuity Evaluation*

546 In conducting this research, PXRF was noted to be slightly better at discontinuity assessment
547 relative to VisNIR DRS (Table 3). Shifts in soil mineralogical composition are more likely adeptly
548 quantified as elemental differences rather than alterations in reflectance spectra. This is not to say
549 that reflectance spectra are useless in this regard; rather, both techniques can be used as
550 complimentary approaches. In some instances, VisNIR DRS will have capabilities to sense
551 differential levels of organic carbon in soils; a parameter imperceptible to PXRF directly. In other
552 instances, PXRF and VisNIR DRS can dualistically elucidate differences in a soil profile. For
553 example, in areas with a pronounced calcic horizon, PXRF will sense higher levels of calcium,
554 while VisNIR DRS will detect greater spectral reflectance owing to lighter soil color. What
555 remains to be interpreted by the analyst is whether such differences represent natural pedogenic
556 accumulations (e.g., illuviated clay, calcium carbonate, gypsum), or a true indicator of a lithologic
557 discontinuity. In fact, one important parameter to be considered is whether the soils being
558 evaluated should be classified as buried soils. Here, the irregular decrease in organic carbon with
559 depth (Soil Survey Staff, 2014b) should be considered more strongly than other factors; for
560 example, alluvial soils subject to flooding in low-lying areas.

561 One of the more important conclusions identified by the present study is the concept that
562 relative maxima and minima in either DEs or CDs of PXRF and/or VisNIR DRS data, respectively,
563 can be important indicators of possible changes in soil parent material. In some instances, these

564 depths are easily reflected by traditional morphological description or laboratory data, but in other
565 areas, they are less visually remarkable. In essence, the maxima and minima for the proximal
566 sensors presented herein provide analysts with ancillary information that can warrant more careful
567 evaluation of certain depths or boundaries within the soil, whether visually perceptible or not.

568 Summarily, we conclude that the data afforded by the use of PXRF and VisNIR DRS offer
569 pedologists unique insight into predicted differences between soil horizons; differences which may
570 be indicative of lithologic discontinuities. We do not advocate the strict use of proximal sensors in
571 the establishment of discontinuities, absent laboratory and morphological data. However, these
572 instruments provide pedologists with another data stream, quickly and easily acquired *in situ*,
573 which can help identify areas of lithologic discontinuity within a given pedon, whether visually
574 observable or not. Collectively, these proximal sensors can detect depth-changes in both organic
575 and inorganic soil constituents, many of which may align with changes in parent material. Hence,
576 the method may offer insight into the presence of discontinuities that may not normally have been
577 detected in the field.

578 CONCLUSIONS

579 This research evaluated the use of portable X-ray fluorescence (PXRF) spectrometry and
580 visible near infrared diffuse reflectance spectroscopy (VisNIR DRS) for identification of lithologic
581 discontinuities in soils. Ten pedons consisting of 135 sampled depths from three different countries
582 were scanned with both proximal sensors, and the data was then compared to both standard
583 laboratory-generated soil characterization data as well as morphological descriptive data noted *in*
584 *situ*. Results showed that large, abrupt changes in standardized PXRF differences of elements
585 (DEs) often successfully identified discontinuities (whether suggested by laboratory data and/or
586 morphological description) appearing in the data plots as DE maxima and minima. Similarly,

587 standardized VisNIR DRS calculated differences (CDs) in reflectance spectra (350-2500 nm)
588 identified discontinuities based upon CD reflectance maxima and minima. With both types of data
589 plots, discontinuities were not well captured by the proximal sensors when CD or DE values fell
590 in the data plot mid-section. Across the ten pedons evaluated, PXRF appeared to show slightly
591 better detection of discontinuities relative to VisNIR DRS. However, VisNIR DRS also showed
592 dexterity in identifying differences with certain pedons not well captured by PXRF. Summarily,
593 we recommend the integrated use of proximal sensors in conjunction with laboratory data and
594 morphological evaluation of lithologic discontinuities in soil profiles. The proximal data are
595 quickly and easily acquired *in situ* and can provide quantitative differentia in support of
596 discontinuity recognition both in instances where morphological and laboratory data indicate
597 differences, but also in instances where differences are morphologically nondescript.

598

ACKNOWLEDGEMENTS

599 The authors are grateful to Lubbock Soil Survey Staff (Craig Byrd, Kelly Attebury, Todd Carr,
600 Alain Basurco, Juan Saenz), Alberto Agnelli, Valeria Cardelli, Chien Lu Ping, Gary Michaelson,
601 Walker C. Weindorf, David Brockman, Trent Smith, and Taylor Marburger for their assistance in
602 field sampling and laboratory analysis. The authors gratefully acknowledge financial support of
603 the project from the BL Allen Endowment in Pedology at Texas Tech University.

604

605

REFERENCES

606 Aldabaa, A.A.A., D.C. Weindorf, S. Chakraborty, A. Sharma, and B. Li. 2015. Combination of
607 proximal and remote sensing methods for rapid soil salinity quantification. *Geoderma* 239-
608 240:34-46. doi: <http://dx.doi.org/10.1016/j.geoderma.2014.09.011>.

609 Chakraborty, S., D.C. Weindorf, C.L.S. Morgan, Y. Ge, J.M. Galbraith, B. Li, and C.S. Kahlon.
610 2010. Rapid identification of oil-contaminated soils using visible near-infrared diffuse
611 reflectance spectroscopy. *J. of Env. Qual.* 39:1378-1387. doi:10.2134/jeq2010.0183.

612 Chakraborty, S., D.C. Weindorf, N. Ali, B. Li, Y. Ge, J.L. Darilek. 2013. Spectral data mining for
613 rapid measurement of organic matter in unsieved moist compost. *Appl. Opt.* 52:B82–B92.

614 Chakraborty, S., D.C. Weindorf, B. Li, A.A.A. Aldabaa, and M.N. Ali. 2015. Development of a
615 hybrid proximal sensing method for rapid identification of petroleum contaminated soils.
616 *Science of the Total Environment* 514:399-408. doi: 10.1016/j.scitotenv.2015.01.087.

617 Chang, C., D.A. Laird, M.J. Mausbach, and C.R. Hurburgh. 2001. Near infrared reflectance
618 spectroscopy: Principal components regression analysis of soil properties. *Soil Sci. Soc. Am.*
619 *J.* 65:480–490.

620 Foss, J.E., and R.H. Rust. 1968. Soil genesis study of a lithologic discontinuity in glacial drift in
621 Western Wisconsin. *Soil Sci. Soc. Am. J.* 32(3):393-398.
622 doi:10.2136/sssaj1968.03615995003200030036x.

623 Gee, G.W., and J.W. Bauder. 1986. Particle-size analysis. p. 383–411. *In* A. Klute (ed.) *Methods*
624 *of soil analysis. Part 1. Physical and mineralogical methods.* 2nd ed. SSSA, Madison, WI.

625 Habecker, M.A., K. McSweeney, and F.W. Madison. 1990. Identification and genesis of fragipans
626 in Ochrepts of North Central Wisconsin. *Soil Sci. Soc. Am. J.* 54(1):139-146.
627 doi:10.2136/sssaj1990.03615995005400010022x.

628 Hartemink, A.E., and B. Minasny. 2014. Towards digital soil morphometrics. *Geoderma* 230-
629 231:305-317.

630 Horta, A., B. Malone, U. Stockmann, B. Minasny, T.F.A. Bishop, A.B. McBratney, R. Pallasser,
631 and L. Pozza. 2015. Potential of integrated field spectroscopy and spatial analysis for enhanced
632 assessment of soil contamination: A prospective review. *Geoderma* 241-242:180-209.
633 doi:10.1016/j.geoderma.2014.11.024.

634 Horváth, E. 2001. Marker horizons in the loesses of the Carpathian Basin. *Quaternary International*
635 76:157-163.

636 Horváth, Z., E. Michéli, A. Mindszenty, and J. Berényi-Üveges. 2005. Soft-sediment deformation
637 structures in Late Miocene–Pleistocene sediments on the pediment of the Mátra Hills.
638 *Tectonophysics* 410(1-4):81-95.

639 Jolliffe, I.T. 1986. *Principal component analysis*. Springer-Verlag, New York.

640 Kabata-Pendias, A., and H. Pendias. 2001. *Trace elements in soils and plants*. CRC Press, Boca
641 Raton, FL.

642 McLaren, T.I., C.N. Guppy, M.K. Tighe, N. Forster, P. Grave, L.M. Lisle, and J.W. Bennett. 2012.
643 Rapid, nondestructive total elemental analysis of vertisol soils using portable X-ray
644 fluorescence. *Soil Science Society of America Journal* 76:1436-1445.

645 Melquiades, F.L., R.O. Bastosa, G.E. V. Biasia, P.S. Parreirab, and C.R. Appoloni. 2011.
646 Granulometry and moisture influence for in situ soil analysis by portable EDXRF. *Proceedings*
647 *of the XXXIII Brazilian Workshop on Nuclear Physics* 1351:317-320.

648 Michéli, E., M. Fuchs, P. Hegymegi, and P. Stefanovits. 2006. Classification of the major soils of
649 Hungary and their correlation with the World Reference Base for Soil Resources (WRB) -
650 *Agrokémia és Talajtan* 55(1):19-328.

651 Morgan, C.L.S., T.H. Waiser, D.J. Brown, and C.T. Hallmark. 2009. Simulated in situ
652 characterization of soil organic and inorganic carbon with visible near-infrared diffuse
653 reflectance spectroscopy. *Geoderma* 151(3-4):249-256.

654 Nelson, D.W., and L.E. Sommers. 1996. Total carbon, organic carbon, and organic matter. *In* D.L.
655 Sparks (ed.), *Methods of soil analysis. Part 3.* SSSA Book Ser. 5. SSSA, Madison, WI. p. 961–
656 1010.

657 Paulette, L., T. Man, D.C. Weindorf, and T. Person. 2015. Rapid assessment of soil and
658 contaminant variability via portable X-ray fluorescence spectroscopy: Copșa Mică, Romania.
659 *Geoderma* 243-244:130-140. doi:10.1016/j.geoderma.2014.12.025.

660 Phillips, J.D., and C. Lorz. 2008. Origins and implications of soil layering. *Earth Science Reviews*
661 89:144-155.

662 Piorek, S. 1998. Determination of metals in soils by field-portable XRF spectrometry. *In* Lopez-
663 Avila, V. et al. (Eds.) *Current protocols in field analytical chemistry.* John Wiley and Sons,
664 New York. pp. 3B.1.1 – 3B.1.18.

665 Price, T.W., R.L. Blevins, R.I. Barnhisel, and H.H. Bailey. 1975. Lithologic discontinuities in
666 loessial soils of Southerwestern Kentucky. *Soil Sci. Soc. Am. J.* 39(1):94-98.
667 doi:10.2136/sssaj1975.03615995003900010026x.

668 R Development Core Team. 2008. R: A language and environment for statistical computing.
669 Available online with updates at: <http://www.cran.r-project.org>. R Foundation for Statistical
670 Computing, Vienna, Austria. (Verified 6 January 2014).

671 Raad, A.T., and R. Protz. 1971. A new method for the identification of sediment stratification in
672 soils of the Blue Springs basin. *Geoderma* 6:23-41.

673 Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. *Agric.*
674 *Handb.* 60. U.S. Gov. Print. Office, Washington, DC.

675 Schaetzl, R. 1998. Lithologic discontinuities in some soils on drumlins: Theory, detection, and
676 application. *Soil Sci.* 163(7):570-590.

677 Schaetzl, R., and M.D. Luehmann. 2013. Coarse-textured basal zones in thin loess deposits:
678 Products of sediment mixing and/or paleoenvironmental change? *Geoderma* 192:277-285.

679 Schaetzl, R., and M.L. Thompson. 2015. *Soils: Genesis and geomorphology*. 2nd Ed. Cambridge
680 University Press, Cambridge, MA. 778 pp.

681 Schoeneberger, P.J., D.A. Wysocki, E.C. Benham, and W.D. Broderson (ed.). 2002. Field book
682 for describing and sampling soils, Version 2.0. USDA-NRCS, National Soil Survey Center,
683 Lincoln, NE.

684 Sharma, A., D.C. Weindorf, T. Man, A. Aldabaa, and S. Chakraborty. 2014. Characterizing soils
685 via portable X-ray fluorescence spectrometer: 3. Soil reaction (pH). *Geoderma* 232-234:141-
686 147. doi: <http://dx.doi.org/10.1016/j.geoderma.2014.05.005>.

687 Sharma, A., D.C. Weindorf, D.D. Wang, and S. Chakraborty. 2015. Characterizing soils via
688 portable X-ray fluorescence spectrometer: 4. Cation exchange capacity (CEC). *Geoderma* 239-
689 240:130-134 doi: <http://dx.doi.org/10.1016/j.geoderma.2014.10.001>.

690 Sherrod, L.A., G. Dunn, G.A. Peterson, and R.L. Kolberg. 2002. Inorganic carbon analysis by
691 modified pressure-calcmeter method. *Soil Sci. Soc. Am. J.* 66(1):299-305.

692 Soil Science Society of America. 2014. Glossary of soil science terms. Available at
693 <https://www.soils.org/publications/soils-glossary> (verified 18 June 2014).

694 Soil Survey Staff. 1993. Soil survey manual. Soil Conservation Service. U.S. Department of
695 Agriculture Handbook 18. Available online at <http://www.nrcs.usda.gov> (verified 5 May,
696 2015).

697 Soil Survey Staff. 1999. Soil taxonomy: A basic system of soil classification for making and
698 interpreting soil surveys. 2nd edition. Natural Resources Conservation Service. U.S.
699 Department of Agriculture Handbook 436. Available online at <http://www.nrcs.usda.gov>
700 (verified 5 May, 2015).

701 Soil Survey Staff. 2004. Soil survey laboratory methods manual. USDA-NRCS. U.S. Gov. Print.
702 Off., Washington, DC.

703 Soil Survey Staff. 2006. Land resource regions and major land resource areas of the United States,
704 the Caribbean, and the Pacific Basin. USDA-NRCS Handbook 296. Available at
705 http://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/survey/?cid=nrcs142p2_053624
706 (verified 18 June 2014).

707 Soil Survey Staff. 2010. Keys to Soil Taxonomy, 11th Ed. USDA-NRCS. Lincoln, NE.

708 Soil Survey Staff. 2014a. Kellogg soil survey laboratory methods manual; Soil survey
709 investigations report No. 42, Version 5.0. USDA-NRCS. National Soil Survey Center, Lincoln,
710 NE.

711 Soil Survey Staff. 2014b. Illustrated guide to Soil Taxonomy. USDA-NRCS. National Soil Survey
712 Center, Lincoln, NE.

713 Soil Survey Staff. 2015. Official soil series descriptions. Available at
714 <https://soilseries.sc.egov.usda.gov/osdname.asp> (verified 17 Feb. 2015).

715 Stefanovits, P. 1963. The soils of Hungary. 2nd ed. (In Hungarian) Akadémiai Kiadó. Budapest.

716 Sudduth, K.A., and J.W. Hummel. 1993. Near-infrared spectrophotometry for soil property
717 sensing. In: DeShazer, J.A., Meyer, G.E. (ed.), Proceedings of SPIE Conference on Optics in
718 Agriculture and Forestry, 16-17 November, 1992 Boston, MA, USA, vol. 1836. SPIE,
719 Bellingham, WA, pp. 14-25.

720 Swanhart, S., D.C. Weindorf, S. Chakraborty, N. Bakr, Y. Zhu, C. Nelson, K. Shook, and A. Acree.
721 2014. Soil salinity measurement via portable X-ray fluorescence spectrometry. *Soil Science*
722 *179(9):417-423*. doi: 10.1097/SS.0000000000000088.

723 US Environmental Protection Agency. 2007. Method 6200: Field portable X-ray fluorescence
724 spectrometry for the determination of elemental concentrations in soil and sediment. Available
725 at http://www.epa.gov/osw/hazard/testmethods/sw846/online/6_series.htm (verified 3 Dec.
726 2013).

727 Wang, D.D., S. Chakraborty, D.C. Weindorf, B. Li, A. Sharma, S. Paul, and M. Nasim Ali. 2015.
728 Synthesized proximal sensing for soil characterization: Total carbon and total nitrogen.
729 *Geoderma* 243-244:157-167. doi: <http://dx.doi.org/10.1016/j.geoderma.2014.12.011>.

730 Weindorf, D.C., Y. Zhu, R. Ferrell, N. Rolong, T. Barnett, B. Allen, J. Herrero, and W. Hudnall.
731 2009. Evaluation of portable X-ray fluorescence for gypsum quantification in soils. *Soil Sci.*
732 *174(10):556-562*. doi:10.1097/SS.0b013e3181bbbd0b.

733 Weindorf, D.C., N. Bakr, Y. Zhu, B. Haggard, S. Johnson, and J. Daigle. 2010. Characterization
734 of placic horizons in ironstone soils of Louisiana, USA. *Pedosphere* 20(4): 409-418.

735 Weindorf, D.C., Y. Zhu, P. McDaniel, M. Valerio, L. Lynn, G. Michaelson, M. Clark, and C.L.
736 Ping. 2012a. Characterizing soils via portable X-ray fluorescence spectrometer: 2. Spodic and
737 Albic horizons. *Geoderma* 189-190:268-277. doi:10.1016/j.geoderma.2012.06.034.

738 Weindorf, D.C., Y. Zhu, S. Chakraborty, N. Bakr, and B. Huang. 2012b. Use of portable X-ray
739 fluorescence spectrometry for environmental quality assessment of peri-urban agriculture.
740 *Env. Mon. Assess.* 184:217-227. doi: 10.1007/s10661-011-1961-6.

741 Weindorf, D.C., Y. Zhu, B. Haggard, J. Lofton, S. Chakraborty, N. Bakr, W. Zhang, W.C.
742 Weindorf, and M. Legoria. 2012c. Enhanced pedon horizonation using portable X-ray
743 fluorescence spectroscopy. *Soil Sci. Soc. Am. J.* 76(2):522-531. doi:10.2136/sssaj2011.0174.

744 Weindorf, D.C., J. Herrero, C. Castañeda, N. Bakr, and S. Swanhart. 2013a. Direct soil gypsum
745 quantification via portable X-ray fluorescence spectrometry. *Soil Sci. Soc. Am. J.* 77:2071-
746 2077.

747 Weindorf, D.C., L. Paulette, and T. Man. 2013b. In situ assessment of metal contamination via
748 portable X-ray fluorescence spectroscopy: Zlatna, Romania. *Environmental Pollution* 182:92-
749 100. doi: 10.1016/j.envpol.2013.07.008.

750 Weindorf, D.C., N. Bakr, and Y. Zhu. 2014. Advances in portable X-Ray fluorescence (PXRF) for
751 environmental, pedological, and agronomic applications. *Advances in Agronomy* 128:1-45.
752 doi: <http://dx.doi.org/10.1016/B978-0-12-802139-2.00001-9>.

753 Zhu, Y., D.C. Weindorf, S. Chakraborty, B. Haggard, S. Johnson, and N. Bakr. 2010.
754 Characterizing surface soil water with field portable diffuse reflectance spectroscopy. *J. of*
755 *Hydrol.* 391:133-140 doi:10.1016/j.jhydrol.2010.07.014.

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

759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779

FIGURE CAPTIONS

Fig. 1. Photographs of sampled pedons in a) Texas (TX-5), b) Italy (IT-2), and c) Hungary (HU-4). Field-suspected lithologic discontinuities are marked with a dot. Depth measurements on tape measure are in cm.

Fig. 2. Differences of element (DEs) as determined by portable X-ray fluorescence (PXRF) spectrometry for 10 pedons suspected of having lithologic discontinuities in Texas, Italy, and Hungary. Field suspected discontinuity depths are noted with a dashed line bounded by a gray bar of ± 5 cm.

Fig. 3. Depth plots showing the differences of elements (DEs) as determined by portable X-ray fluorescence (PXRF) spectrometry against laboratory-determined characterization data (sand, silt, clay percentage and soil organic matter percentage) and morphologically established discontinuities (gray shaded boxes) for pedons TX-2 from Texas, USA, and HU-2 and HU-5 from Hungary. Pedon HU-5 is an example of good alignment between proximal data, field morphological assessment, and laboratory data, while Pedons TX-2 and HU-2 are examples of PXRF DE minima suggesting that the morphologically established discontinuity should likely be recognized ~ 15 cm deeper in the profile where PXRF data and laboratory data closely align.

Fig. 4. Calculated differences (CDs) of visible near infrared diffuse reflectance spectroscopy (VisNIR DRS) reflectance values between soil layers for 10 pedons suspected of having lithologic discontinuities in Texas, Italy, and Hungary. Field suspected discontinuity depths are noted with a dashed line bounded by a gray bar of ± 5 cm.