

Impact of sample preparation methods for characterizing the geochemistry of soils and sediments by portable X-ray fluorescence

Kathleen Goff¹ | Randall J. Schaetzl²  | Somsubhra Chakraborty³ |
David C. Weindorf⁴  | Chase Kasmerchak⁵ | E. Arthur Bettis III¹

¹Department of Earth and Environmental Sciences, University of Iowa, 115 Trowbridge Hall, Iowa City, IA 52242

²Department of Geography, Environment, and Spatial Sciences, 673 Auditorium Rd., Michigan State University, East Lansing, Michigan 48823, USA

³Agricultural and Food Engineering Department, Indian Institute of Technology Kharagpur, Kharagpur, India 721302

⁴Department of Plant and Soil Science, Texas Tech University, Box 42122, Lubbock, TX 79409

⁵Department of Geography, University of Wisconsin, 550 N. Park Street, Madison, WI 53706

Correspondence

Randall J. Schaetzl, Michigan State University, East Lansing, MI.
Email: soils@msu.edu

Abstract

We examined the impact of three different sample preparation methods on bulk soil geochemistry data obtained from a hand-held, portable X-ray fluorescence (pXRF) spectrometer. We generated data from a soil core recovered from the surface, downward into unaltered loess, and into a buried soil at a site in eastern Iowa. Samples were scanned (i) directly from field-moist soil cores; (ii) after drying, grinding, and being loosely massed in plastic cups; and (iii) as pressed-powder pellets. Data derived using these methods were compared with data obtained from a standard benchtop X-ray fluorescence (XRF) unit. Generally, the results indicated that data from pressed powder pellets often provide the best correlation to benchtop XRF data, although the results were sometimes element or compound specific. Calcium oxide, Fe₂O₃, and K₂O generally provided the strongest correlations between pXRF- and XRF-reported values; SiO₂ data were more problematic. Field-moist pXRF scans generally underestimated element concentrations, but the correlations between pXRF and benchtop XRF measurements were greatly improved after applying pXRF-derived calibration standards. In summary, although element/compound data provided by pXRF showed significant relationships to benchtop XRF data, the results are improved with proper sample preparation (i.e., drying, grinding, pressing) and usually by calibrating the pXRF data against known standards.

1 | INTRODUCTION

X-ray fluorescence (XRF) spectroscopy is an analytical technique that is used to determine the elemental composition of a sample or material using high-energy, short-wavelength (X-ray) radiation. The X-ray tube in the instrument excites elements, which then irradiate and emit X-rays. When bombarded with X-ray radiation, different elements can be identified

by the characteristic fluorescent energy that they emit; this is referred to as “X-ray fluorescence.” X-ray fluorescence offers a rapid and generally cost-efficient way to generate multielement analytical data.

Researchers are increasingly using hand-held portable X-ray fluorescence (pXRF) instruments in the field and laboratory (Chakraborty et al., 2019; Stockmann, Cattle, Minasny, & McBratney, 2016), with soils and Quaternary sediments being common targets for such analyses (e.g., Jacobs & Davis, 2018; Mancini, Weindorf, & Chakraborty, 2019; Silva et al., 2018). Numerous studies have demonstrated that pXRF measurements correlate well with data obtained using

Abbreviations: pXRF, portable X-ray fluorescence; XRF, X-ray fluorescence.

conventional methods, such as bench-top XRF (Hunt & Speakman, 2015), or from various acid digestion (Schneider et al., 2016) or wet chemistry techniques (Sarala, 2016), followed by analysis of the extracts using inductively coupled plasma spectrometry (Booth et al., 2017; Lubos, Dreibrodt, & Bahr, 2016). Many studies have not only shown that pXRF instruments are capable of generating robust, accurate, and repeatable data but have also found them to be applicable to a wide array of environmental applications (e.g., Frahm and Doonan, 2013; Gunicheva, Aisueva, & Afonin, 1995; Kalnicky & Singhvi, 2001; Weindorf, Bakr, & Zhu, 2014, 2015; Arnoldussen & van Os, 2015; Sharma, Weindorf, Wang, & Chakraborty, 2015; Connors, Somers, & Day, 2016; Frahm et al., 2016; Booth et al., 2017; Duda et al., 2017). Thus, pXRF analyses continue to grow in popularity among soil scientists, ecologists, toxicologists, and geochemists as well as among public sector professionals (Horta et al., 2015).

As with any new method, researchers are actively attempting to determine its overall accuracy and to identify its main sources of error. Unfortunately, there exists no universally agreed-upon protocol for pXRF sample preparation, specifically for analyses of soils and/or finely ground geological (rock) samples. The USEPA Method 6200 (USEPA, 2007) is a widely cited method for analysis of soils and sediments, complete with suggested sample preparation procedures. Natural Resources Conservation Service protocols for using pXRF for elemental analysis on soils also report specifics on instrument calibration, standardization, and mode selection but provide only minimal instructions for sample preparation. Nonetheless, the Soil Survey Staff (2014) has observed that the results from soil analyses are more reproducible if the sample has been air dried, homogenized, and finely ground (<75 μm). By comparison, the Soil Science Society of America method for pXRF analysis of soils advocates drying and grinding to pass a 2-mm sieve (Weindorf & Chakraborty, 2016), a method that would parallel common soil preparation for particle size analysis as well as many other chemical extractions and microplate assays. The present study addresses this issue by evaluating the effects of different sample preparation techniques on pXRF data (Silva et al., 2018; Zhu & Weindorf, 2009).

For soil investigations, some studies have obtained data by placing the instrument directly onto a field-moist core or profile face (e.g., Ribeiro, Silva, Silva, & Guilherma, 2017; Stockmann et al., 2016; Silva et al., 2018). Samples returned to the laboratory are also sometimes scanned while they are field moist, although at this point most researchers dry, disaggregate, and/or sieve the samples before treatment or measurement. Moisture in the sample causes fluorescence attenuation, usually leading to underestimation of elemental data (Ge, Lai, & Lin, 2005; Kalnicky & Singhvi, 2001; Sahraoui & Hachicha, 2017). However, moisture levels of <20% generally cause minimal error in elemental determinations (USEPA, 2007). Some studies have compared scans of soil profile faces

Core ideas

- Handheld XRF data are highly useful in soils research.
- Method of preparation affects pXRF data quality.
- Accuracy of pXRF data may be element-specific.
- pXRF data accuracy can be improved by calibrating to known standards.
- For most applications, pressed powder pellets provide the most accurate pXRF data.

with samples analyzed in the laboratory (e.g., Schneider et al., 2016). For example, Stockmann et al. (2016) calculated geochemical weathering indices using elemental data obtained with pXRF to assess the relative degree of pedogenesis between three soils in Australia. Although the geochemical weathering index values calculated by Stockmann et al. (2016) varied greatly between field-moist vs dried samples, the depth trends showed similar patterns. Work by Hseu, Chen, Tsai, and Jien (2016) showed that pXRF measurements taken from field-moist samples for Cr were much higher than those obtained by soil digestion in HNO_3 and HCl (aqua regia). The authors attributed this difference to the resistance of Cr-bearing chromite minerals to the digestion reagents.

Although the accuracy of pXRF measurements from field-moist samples continues to be explored, most researchers conduct their analyses in a laboratory setting rather than on soil or rock samples *in situ*. Laboratory preparations typically involve combinations of drying, sieving, and grinding before placing the samples in containers for pXRF analysis (e.g., Duda et al., 2017; Frahm et al., 2016). The instrument is then placed in contact with the powdered sample; sometimes plastic film, such as Prolene thin film, is used to cover the sample before scanning (Lubos et al., 2016). Other researchers have physically compacted each sample in a standard-sized container, forming a pressed-powder pellet, prior to analysis. Regardless of pretreatment, many researchers acquire data from several scans and then use mean data in subsequent interpretations (Chakraborty et al., 2019).

Although different sample preparation techniques are being used within the pXRF community, few studies have examined the efficacy of various sample pretreatments on the overall accuracy of the data. The objective of this study was to examine the effects of three different preparation methods on pXRF data from three soil samples: (i) field-moist soils, (ii) dried and ground powders, and (iii) pressed pellets. Data generated using these preparation methods were compared with using traditional bench-top XRF data to determine the effects of sample pretreatment on final data accuracy. We hypothesized that data obtained from dried or ground samples and pressed powder pellets would be superior to data obtained from

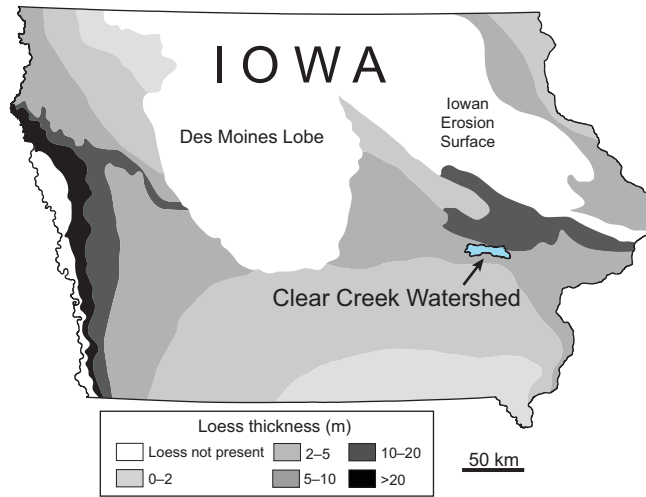


FIGURE 1 Map of Iowa showing loess thicknesses and the outline of the Clear Creek watershed; landform regions after Prior (1991), loess thickness after Bettis, Muhs, Roberts, & Wintle (2003)

field-moist samples because they provide for uniform and repeatable conditions of moisture and density.

2 | MATERIALS AND METHODS

2.1 | Study area and soils

Samples from Clear Creek, a tributary of the Iowa River in eastern Iowa (Figure 1), were selected for study. The watershed is a part of a Critical Zone Observatory for Intensively Managed Landscapes and is broadly representative of loess-mantled watersheds of the upper Midwest regarding climate, soil type, and land use. Eastern Iowa's modern landscape is a result of Quaternary glaciations, interglacial weathering and landscape dissection, and last-glacial loess accumulation (Anders, Bettis, Grimley, Stumpf, & Kumar, 2018). The Clear Creek Watershed is located within the Southern Iowa Drift Plain (Prior, 1991) and represents a hilly, dissected landscape underlain by Pre-Illinoian tills, with a mantle of loess.

Prior to the Illinoian (marine isotope stage 6) glaciation, the region likely witnessed several glacial advances and retreats (Anders et al., 2018; Kemmis, Bettis, & Hallberg, 1992; Rovey & Kean, 1996). The Pre-Illinoian deposits in the study area belong to the Wolf Creek and underlying Alburnett Formations, both of which contain multiple till units. The two formations are distinguished from one another through physical and mineralogical characteristics, primarily the clay mineralogy of the unaltered tills (Kemmis et al., 1992). The Wolf Creek Formation is the uppermost till unit at or near the surface in the study area.

The intensively farmed Clear Creek watershed spans ~ 270 km², with the predominant crop rotation history being

corn–soybean (cash grain) agriculture. The watershed is part of the Natural Resources Conservation Service's Major Land Resource Area 108C (Illinois and Iowa Deep Loess and Drift, West-Central Part). The dominant soil types here are Mollisols with minor areas of Alfisols, all formed within a humid-continental climate (udic soil moisture and mesic soil temperature regimes). The Köppen–Geiger climate type is Dfa: hot summer, humid continental (Peel, Finlayson, & McMahon, 2007). The loess-derived soils here are highly productive due to good soil structure, favorable available water contents derived from their silt loam textures, and high organic matter contents (Jones & Handreck, 1967; Schaetzl, Krist, & Miller, 2012).

Data for this study came from a core recovered from the Old Scotch pioneer cemetery near Conroy, Iowa, in the headwaters of the Clear Creek watershed. At the site, a 7.6-cm-diameter core (5.0 m in length) was collected from a site on an upper shoulder slope. The soil is mapped within the Tama series (fine-silty, mixed, superactive, mesic Typic Argiudolls) and is currently under turfgrass cover. Best-available information indicates that this site has been a designated cemetery since 1874. Because only 12 gravestones exist here, we assumed that there has been limited disturbance and likely no agricultural activity since that time. In essence, this site represents presettlement conditions and has been minimally disturbed by human activity.

2.2 | Geochemical characterization

The three different pXRF preparation methods (field-moist condition, dried and ground to a powder, and pressed pellets) were compared to evaluate their efficacy for accurately determining soil/sediment geochemistry and weathering zones for the cores: (Figure 2). For comparison, a Bruker S-8 Tiger benchtop (wavelength dispersive) XRF unit was used as a comparative standard to establish the bulk chemical composition of the samples. Samples analyzed on the benchtop XRF had been initially removed from the scraped surfaces of the cores, oven dried at 50°C for 12 h, and ground to a fine powder using a corundum mortar and pestle. Subsamples of ~ 0.2 – 0.5 g were further ground to pass a 75- μ m sieve, pressed into pellets, and made into homogeneous glass disks by fusion of the sample and a lithium tetraborate/lithium metaborate mixture (SGS Canada, 2016). Lithium metaborate is often mixed with lithium tetraborate to produce fusion fluxes of various ratios, each with different pH levels and XRF sample preparation applications. For example, a granular X-ray flux mixture of 35.3% lithium tetraborate and 64.7% lithium metaborate has universal application for aluminosilicates and is more suitable to solid sample preparation for materials such as mineral sands. Its significantly higher melting point compared with pure lithium metaborate is also beneficial to the

Methods of Analysis

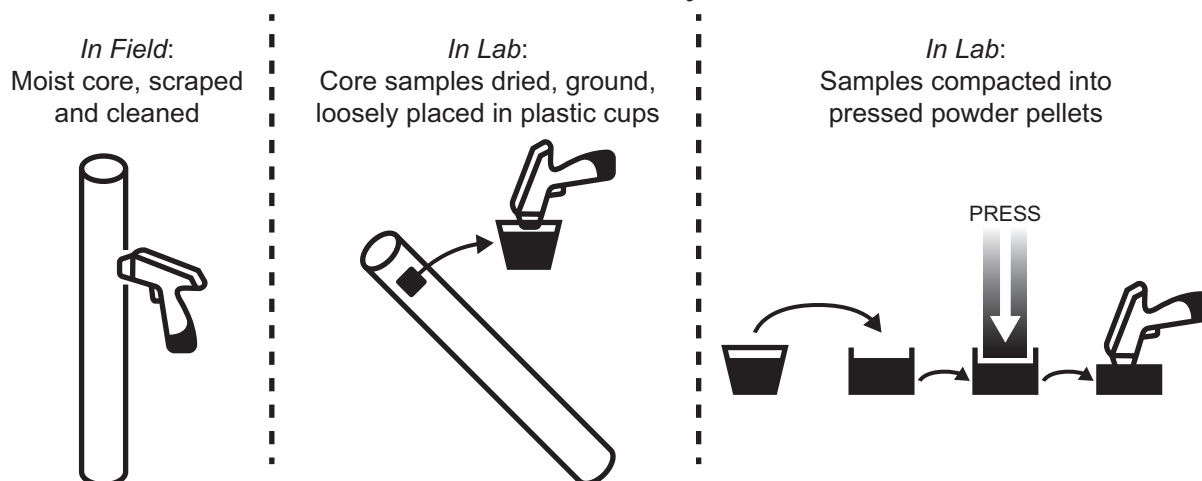


FIGURE 2 Schematic diagram of the field and laboratory methods used in this study

longevity and durability of the fusion apparatus. The XRF analyses were conducted for seven major elements (Si, Al, Zr, K, Ca, Ti, Fe, and Mn) at SGS Canada Inc., in Mississauga, Ontario. Detection limits vary by element. The detection limit from this method for all analytes is $>0.01\%$ of oxide constituent. Quality control was achieved using SiO_2 blanks, duplicates, and certified reference materials (SGS Canada, 2016). We then evaluated measurements from the three pXRF sample treatments against data obtained with the wavelength dispersive XRF.

The pXRF analyses were performed in Geochem Mode using an Olympus DELTA Professional pXRF unit, which has a 4W Ta/Au anode (preapplication) X-ray tube as the method of excitation source, a silicon drift detector, and an accelerometer and barometer for atmosphere pressure correction of light elements. The pXRF unit was operated on line at 110 VAC, without special filters, with a dwell time of 30 s beam-1, under normal atmosphere conditions. Instrument resolution was 150 eV per channel with a pulse density of 100,000 cps. Resulting waveforms were processed with the proprietary Olympus X-act Count Digital Pulse Processor and integrated software (Olympus Corporation, 2017). Each time the pXRF was initialized, a 316 alloy coin was used for factory calibration based upon Compton normalization. Detection limits for pXRF analyses vary by element (Table 1).

Initial scanning was completed by placing the pXRF device directly on the moist core at ≤ 10 -cm intervals after any outer sediment material had been scraped away and the exterior area flattened with a knife. If a horizon break occurred near the sample site/interval, the sample increment was lessened so that no sample was taken from different horizon types. The remainder of the analyses were conducted on dried samples recovered from the cleaned core (Figure 2). In the labora-

TABLE 1 Detection limits of the Olympus portable X-ray fluorescence (pXRF) spectrometer for the seven elements reported in this study

Analyzed element	Detection limit
Ti	10 ppm
Si	1.0%
Al	1.0%
Mn	10 ppm
K	50 ppm
Fe	10 ppm
Ca	50 ppm

tory, samples of ~ 100 g were removed from the core and ground using a Flayler mechanical grinder and ceramic mortar and pestle. Subsamples of ~ 20 g were then powdered using a corundum mortar and pestle, placed in 2.5-cm-diameter plastic cups with at least 2 cm of material in the cup, covered with a thin ($3.0 \mu\text{m}$) mylar film (Chemplex Industries SpectroCup Series 1400; Chemplex Spectromembrane Thin-Films), and lightly tamped by hand to achieve a level surface before being analyzed with the pXRF. All pXRF analyses of ground samples were performed with the analyzer housed in a DELTA portable workstation. The pXRF analyses also were conducted on pucks formed by compressing the sediment in 0.4×3 cm stainless steel cups using a stainless steel hydraulic press (model 25-011, Specac) at 25 tons of pressure per square inch, hereafter termed “pressed powder pellets.” Four replicate scans were conducted on each sample for each of the three methods; all data reported are mean elemental data. The pXRF data were converted to oxide values by using standard conversion factors for SiO_2 , Al_2O_3 , K_2O , CaO , TiO_2 , Fe_2O_3 , and MnO and are reported on a percentage

or milligram per kilogram basis. Four soil standard reference materials from the National Institute of Standards and Technology (<https://www.nist.gov/srm>; AGV-2, BIR-1, BCR-2, JA-1) were examined to develop linear calibration curves for selected elements or oxides using the Lucas-Tooth Calibration Method (Adams & Allen, 1998). The samples were loose powders packed in plastic cups beneath a thin film of Prolene. The average value of each standard, based on five analyses, was then compared with the known values reported by Jochum et al. (2005). An in-house standard of Peoria loess, which was geochemically similar to the core materials, was used as a fifth standard. It had been analyzed 55 times throughout the pXRF scanning procedure outlined above and had previously been analyzed by a benchtop XRF to constrain the elemental concentrations. This standard is commonly used by the University of Iowa Quaternary Materials Laboratory. Details on coefficients of variation are provided in Goff (2017).

Select soil samples (pressed pellets) were subjected to X-ray diffraction for mineralogical analysis using a Rigaku Ultima III powder diffractometer (Rigaku Corp.) equipped with Cu K α radiation ($\lambda = 1.54059 \text{ \AA}$) and a scintillation detector. The data were collected in parallel beam geometry using continuous mode from 3 to 80° 2 θ , step width of 0.02°, and collection time of 0.6 s per step. Data analysis was performed using MDI Jade v9.1.1 software, featuring whole-pattern fitting and Rietveld refinement.

The analyses and study design described herein were intended to examine the effects of in situ pXRF scans, data from which can be affected by preexisting soil water contents vs dried and ground samples from the same core. Inherent soil heterogeneity due to Fe/Mn concretions and secondary CaCO₃ deposits can also be problematic for in situ soil data using pXRF technologies.

3 | RESULTS AND DISCUSSION

3.1 | Core description and stratigraphy

The Old Scotch cemetery core had a 109-cm-thick Molisol formed in 410 cm of Peoria loess overlying a welded Farmdale/Sangamon Geosol (Figure 3). Standard soil and traditional weathering zone terminology were used to describe the cores (Soil Survey Staff, 1993) (Table 2). As expected, X-ray diffraction analysis confirmed the assumed mineralogy of the core. Quartz was dominant at 42.2%, with substantive quantities of muscovite (6.6%), dolomite (5.8%), and Fe/Mg/Al/Si hydroxides (5.8%) (Figure 4). Figure 4 also shows XRF data expressed on an elemental basis, which is useful in establishing comparisons to pXRF data reported as various oxides.

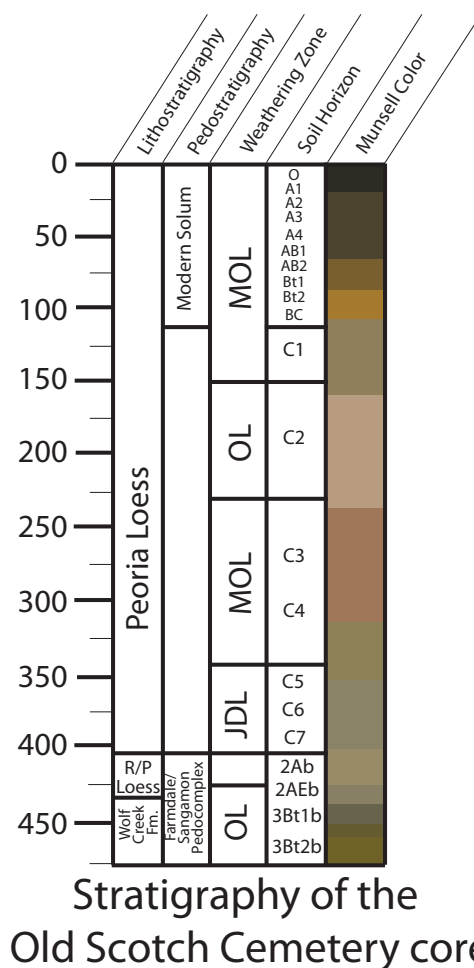


FIGURE 3 Lithostratigraphic, pedostratigraphic, and soil horizon sequences of cores collected in the Clear Creek watershed, Iowa. Note the different vertical axis scales

3.2 | Impacts of sample preparation methods on portable X-ray fluorescence data

In general and as expected, the data derived from the pXRF and the benchtop XRF were often quite different; SiO₂ and Fe₂O₃ data were especially problematic (Table 3). By using three different methods of sample preparation (i.e., moist core, dried and ground powder, and a pressed powder pellet), we sought to understand which method yields the most accurate pXRF results relative to data from the more traditional benchtop XRF instrument. We assumed that benchtop XRF data most accurately characterize the overall bulk chemical composition of the soils. Benchtop XRF data may still suffer from overlapping fluorescence energies of different elements and thus could limit data interpretability. Furthermore, “light” elemental detection remains challenging given their weak fluorescent energies and atmospheric attenuation issues. However, other laboratory approaches also suffer from inherent challenges. The effectiveness of routine acid digestions such as aqua regia are still questioned as to

TABLE 2 Standard terminology used to describe Quaternary material weathering zones^a

First symbol	Second symbol	Modifier
O: Oxidized	U: unleached, primary carbonates present	M: mottled, with 20–50% contrasting mottles
D: Deoxidized	L: leached, no carbonates present	
U: Unoxidized	L2: leached but some secondary carbonates present	
R: Reduced	J: jointed	

^aAfter Hallberg, Fenton, & Miller, 1978.

Phase ID (6)	Source	I/Ic	Wt%	#L	PC
■ Quartz - SiO ₂	PDF#04-016-2085	4.32(0%)	42.2 (0.9)	68	(101)=1.084
■ Rutile - TiO ₂	PDF#04-005-6161	3.37(0%)	0.4 (0.1)	15	<None>
■ Muscovite - (K,Na)Al ₂ (Si,Al) ₄ O ₁₀ (OH) ₂	PDF#00-034-0175	0.36(5%)	6.6 (0.5)	51	(002)=1.180
■ Tridymite - SiO ₂	PDF#04-012-1133	1.58(0%)	6.3 (0.2)	1224	<None>
■ Magnesium Iron Aluminum Silicate Hydroxide - (Mg _{11.06} Fe _{0.94})...	PDF#04-075-8292	0.82(5%)	5.8 (0.4)	198	(001)=0.991
■ Dolomite - CaMg(CO ₃) ₂	PDF#04-015-9838	2.33(0%)	5.8 (0.2)	44	<None>
□ Others + Amorphous			32.9 (0.5)		

XRF(Wt%): Fe=0.3%, Ti=0.2%, Ca=1.3%, K=0.3%, Si=39.8%, Al=2.2%, Mg=2.1%, Na=0.2%, O=52.7%, C=0.8%, H=0.1%

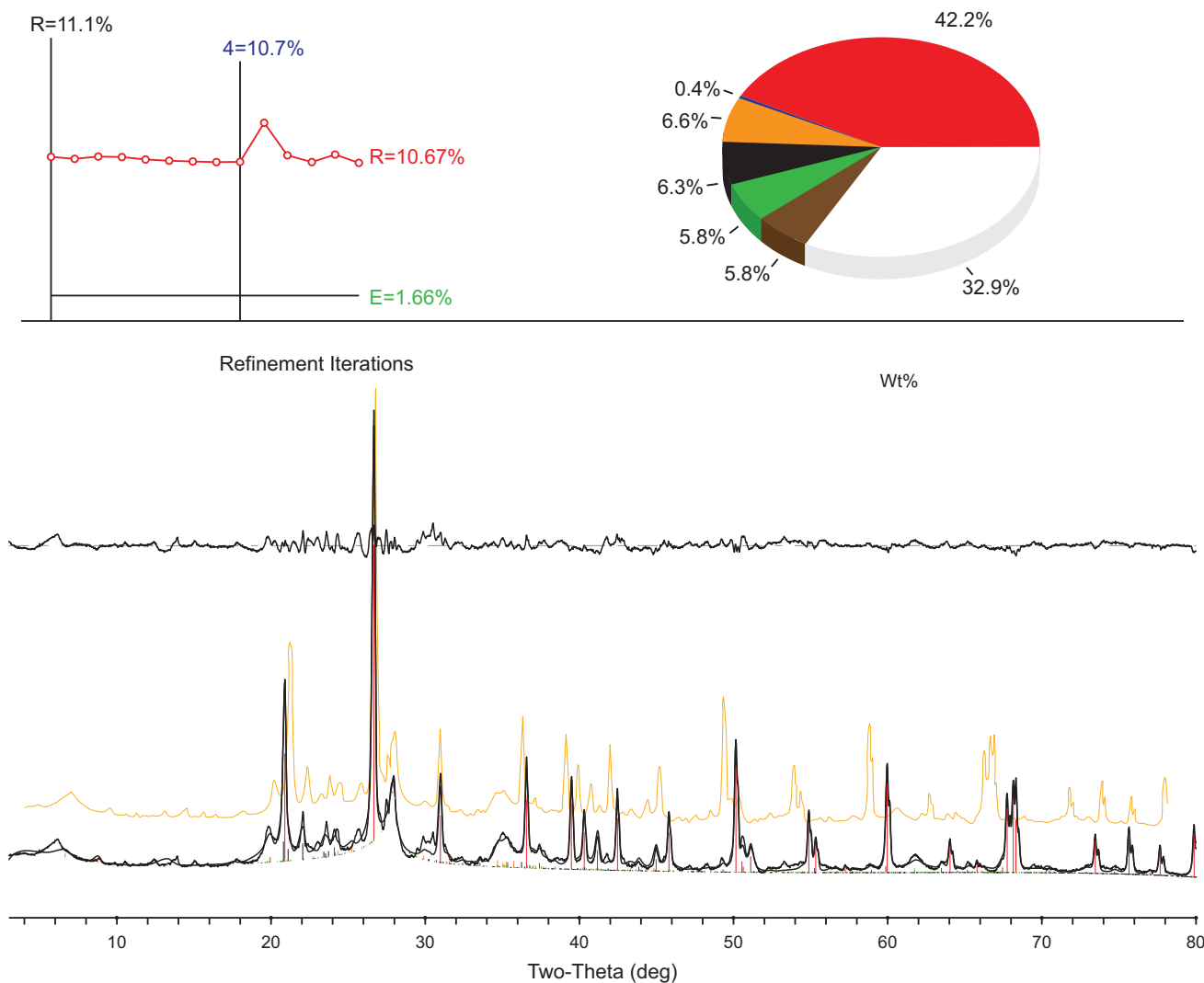


FIGURE 4 X-ray diffractogram from the Old Scotch Core (a sample from 364 cm depth) showing the mineralogy and elemental concentration of bulk soil as a pressed powder

TABLE 3 Elemental contents for an in-house standard of Peoria Loess, as determined by benchtop X-ray fluorescence (XRF) and portable X-ray fluorescence (pXRF)

Compound	Benchtop XRF	pXRF
		(average of 55 runs)
– wt% –		
Al ₂ O ₃	8.71	8.13
SiO ₂	70.30	52.24
K ₂ O	1.76	1.40
CaO	3.69	4.04
TiO ₂	0.66	0.74
Fe ₂ O ₃	2.96	3.80
MnO	0.07	0.07

whether complete matrix dissolution occurs. Digestion by hydrofluoric acid (preferable for complete matrix dissolution) is extremely hazardous and requires special Teflon-coated vessels for handling.

To that end, pXRF data from three different pretreatments (wet core, dried and ground powder, and pressed powder pellets) were compared with benchtop XRF data. Example data from the Old Scotch core are shown in Figure 5. Generally, CaO, TiO₂, and MnO data from the pXRF correlate best with benchtop XRF data, and for these compounds the correlations were strongest when using the pressed powder method of sample preparation. Nonetheless, many of the data are element specific, and thus the optimal sample preparation method is not always the same for the seven elements/compounds we report on in Figure 5. For example, data obtained with no preparation (i.e., from the wet core) appear to be most accurate for Al₂O₃ and Fe₂O₃ (and, to a lesser extent, MnO), whereas TiO₂ data are optimized by using pressed powders (Figure 5). The pXRF instrument also routinely overestimated contents of Fe₂O₃ and Al₂O₃ and generally underestimated contents of CaO and K₂O (Figure 5). Several researchers have reported a tendency for pXRF to overestimate Fe concentrations (e.g., Koch et al., 2017), a

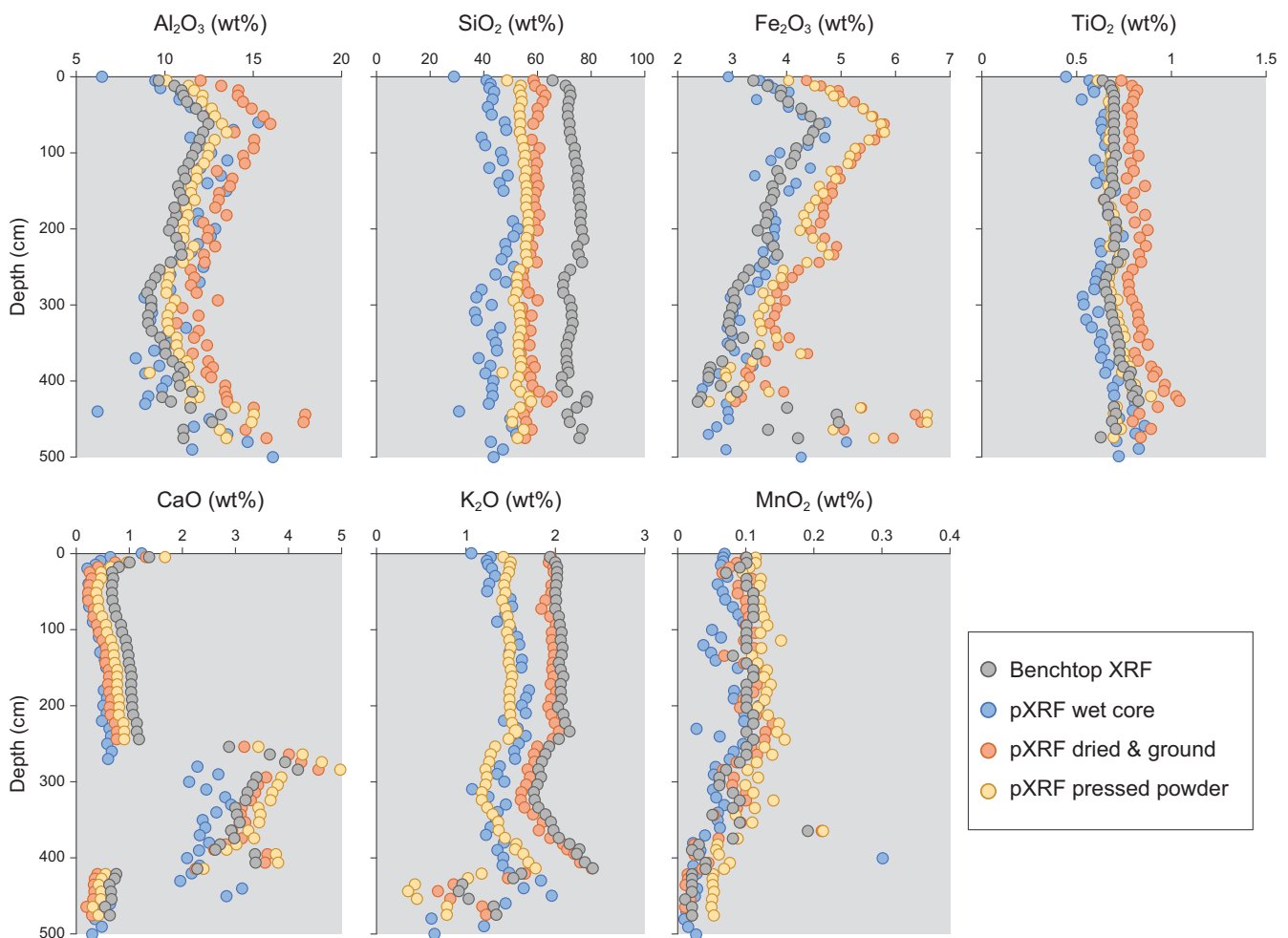


FIGURE 5 Depth plots of energy dispersive portable X-ray fluorescence (pXRF) and benchtop (wavelength dispersive) X-ray fluorescence (XRF) data for the Old Scotch core in the Clear Creek watershed, Iowa, for seven different oxides. The plots clearly illustrate the effects of sample preparation techniques on the XRF data

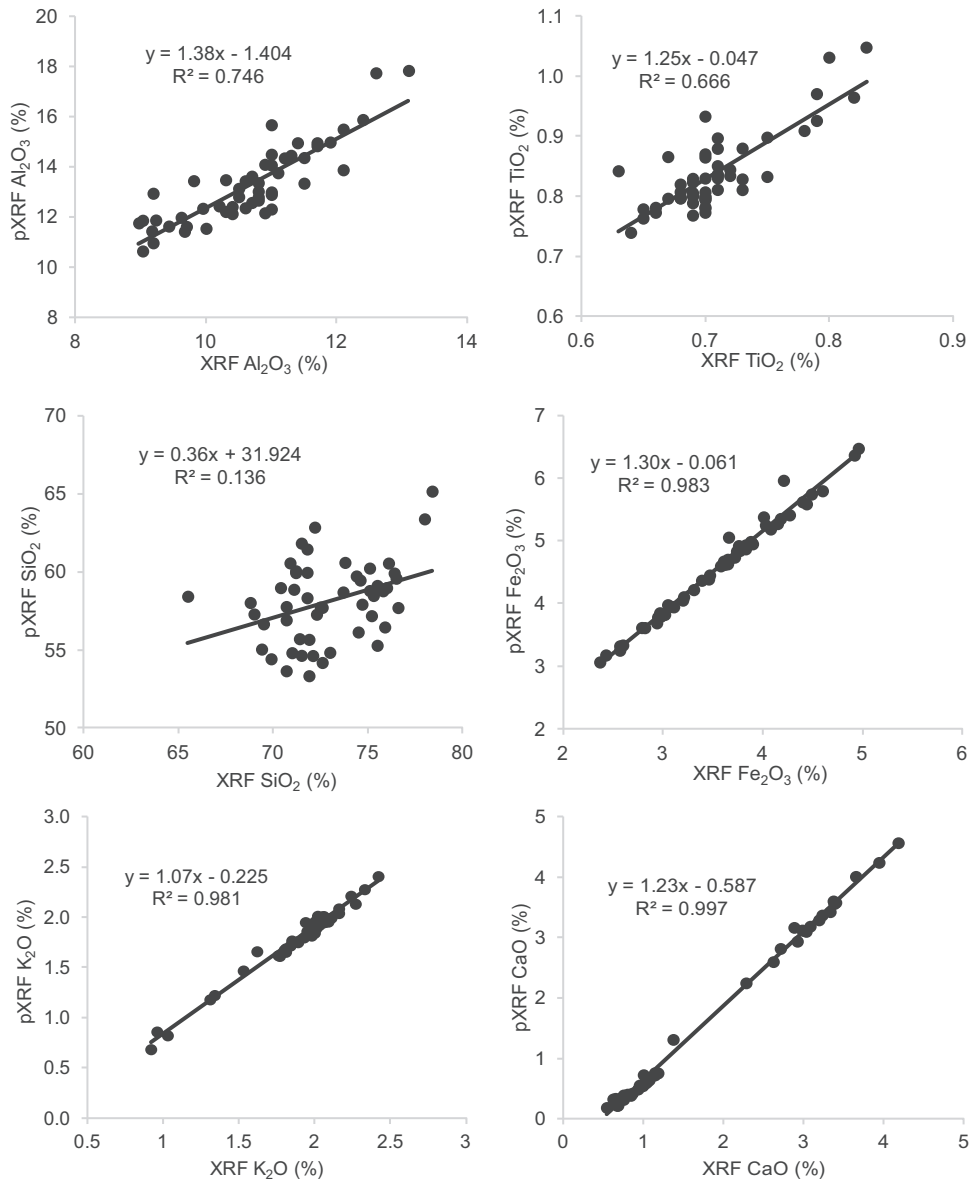


FIGURE 6 Scatterplots comparing selected oxide concentrations for samples from the Old Scotch core, Iowa, using energy dispersive portable X-ray fluorescence (pXRF) data on pressed pellets and benchtop (wavelength dispersive) X-ray fluorescence (XRF)

trend observed in the present study on all but the wet core samples (Figure 5). Gallhofer & Lottermoser (2018) offered an explanation of such predictive errors, noting that a high number of closely spaced K-lines (used for transitional metals such as Fe) and L-lines occurs in the low-energy region, causing spectral interferences. However, moisture is known to cause fluorescence attenuation, and thus it is likely that attenuation compensated for the overestimation of Fe in the present study, allowing the moist pXRF readings for Fe to align more closely with those of the benchtop XRF. Generally, the accuracy of the data for most elements increased using the pressed powder pellet pretreatment method relative to benchtop XRF

(K and Fe are the primary exceptions). Thus, these data will be used as the pXRF component from this point forward.

Correlations of (pressed powder) pXRF vs benchtop XRF data indicate that the highest R^2 values were obtained for CaO (0.997), Fe_2O_3 (0.983), and K_2O (0.981); analyses for Al_2O_3 (0.746), TiO_2 (0.666), and SiO_2 (0.136) yielded lower correlations (Figure 6). The Si data were relatively more problematic for this instrument than were data for other elements. Low correlation values for SiO_2 (and, to a lesser extent, Al_2O_3) probably reflect uneven attenuation of their low-frequency X-rays during pXRF analysis, whereas the slightly lower correlation values for TiO_2 might reflect uneven distribution

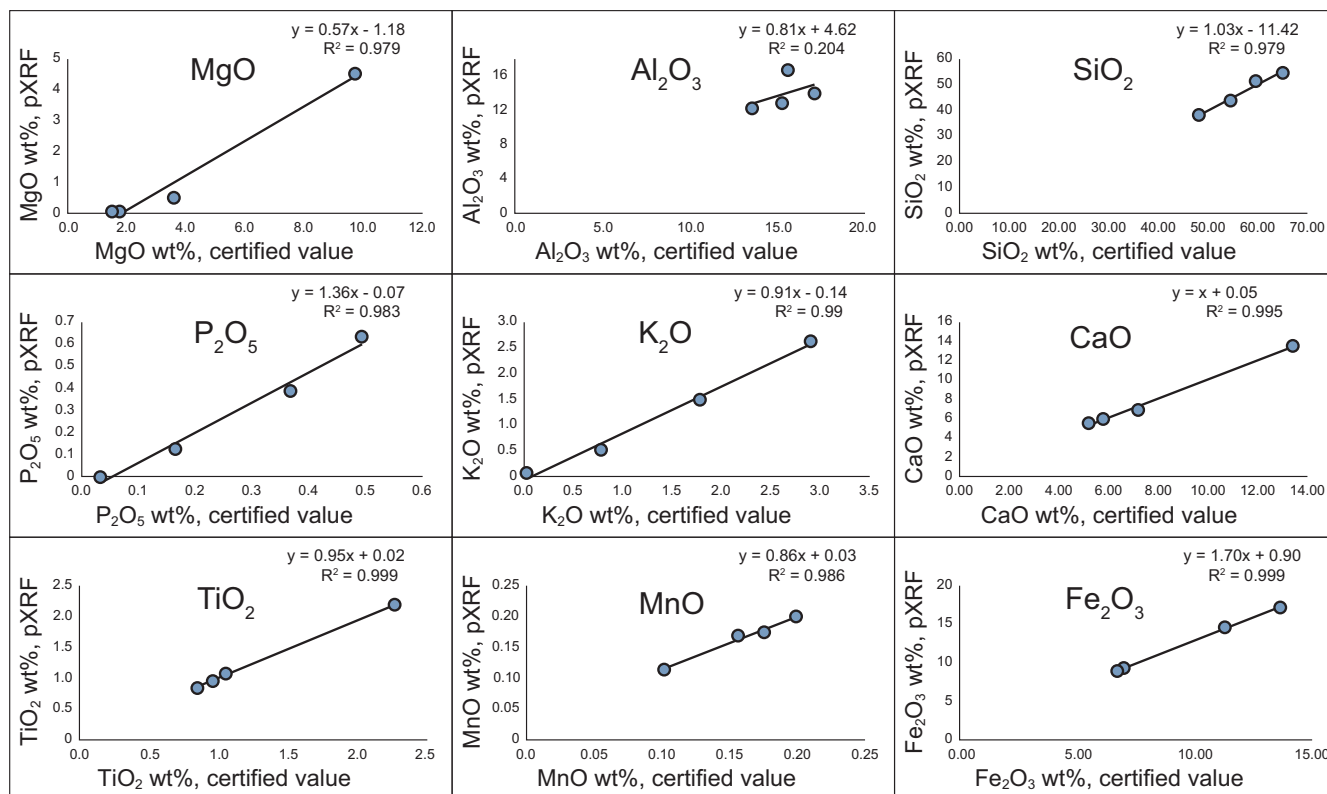


FIGURE 7 Calibrations developed for correcting energy dispersive portable X-ray fluorescence data, on a compound-by-compound basis, using data from this study and four National Institute of Standards and Technology standards as well as an internal Peoria Loess standard

of Fe-Ti oxides in the samples because of their overall lower concentrations.

3.3 | Calibration functions

Linear calibrations were developed for elements that appeared to vary consistently between benchtop XRF and pXRF analyses using four National Institute of Standards and Technology standards and the in-house Peoria Loess standard (Figure 7). The linear regressions, using weight % or mg kg⁻¹ of an oxide obtained by the pXRF vs the certified weight% or mg kg⁻¹ in the National Institute of Standards and Technology standards, were then used to correct (calibrate) the pXRF data. These calibrations, based on the standards shown in Figure 7, are for major oxides: CaO, MnO, MgO, Fe₂O₃, P₂O₅, K₂O, and TiO₂. They produced well-correlated calibrations. Except for SiO₂, the correlation coefficients are >0.7, with most being >0.9.

Table 4 illustrates the improvements in correlation between the uncalibrated vs calibrated pXRF data of the samples that were achieved by applying the calibration equations (Figure 7). Although most of the data were improved by using the calibration functions, data for some elements were only slightly improved or even slightly worsened (e.g., MnO and

Al₂O₃). Despite producing substantial improvement in R^2 values for SiO₂ as a result of pXRF correction, the concordance between benchtop XRF and calibrated pXRF SiO₂ data still appeared to be moderate at best ($R^2 = 0.60$). Figure 8 shows graphically the changes in the data for four elements obtained by applying the calibrations in Figure 7 to the raw pXRF data. Further improvements in the calibrations may be possible by using known standards that are closer in composition to the materials being analyzed.

3.4 | Benchtop X-ray fluorescence/portable X-ray fluorescence comparisons

Results indicate that the overall accuracy of the Olympus pXRF data is very good but somewhat element dependent. For example, the comparatively poor performance (precalibration) of some elements (e.g., Si, Ti, Al) (Figure 6) may create problems for determining weathering ratios, many of which are dependent on Al or Si oxide contents and often use Ti as an indicator of the contents of the slowly weatherable mineral tourmaline (Buggle, Glaser, Hambach, Gerasimenko, & Markovic, 2011; Schaeztl, 1992). Likely, the contents of low-energy light elements such as Mg, Al, and Si are more difficult to determine accurately because the X-rays emitted

TABLE 4 Linear regression equations comparing calibrated and raw portable X-ray fluorescence (pXRF) data to benchtop X-ray fluorescence (XRF) data, using data from the Old Scotch core pressed pellet samples

Oxide	Equation	R^2	Equation	R^2
	Calibrated pXRF data		Raw pXRF data	
SiO ₂	$y = 0.60x + 9.64$	0.60	$y = 0.35x + 31.92$	0.13
TiO ₂	$y = 0.97x + 0.02$	0.72	$y = 1.25x - 0.04$	0.66
Al ₂ O ₃	$y = 1.06x + 0.19$	0.72	$y = 1.37x - 1.40$	0.74
MnO	$y = 0.89x + 0.03$	0.90	$y = 1.07x - 0.004$	0.91
K ₂ O	$y = 0.94x - 0.47$	0.98	$y = 1.06x - 0.22$	0.98
Fe ₂ O ₃	$y = 1.47x + 0.92$	0.98	$y = 1.30x - 0.06$	0.98
CaO	$y = 1.28x - 0.47$	0.99	$y = 0.88x - 0.41$	0.99

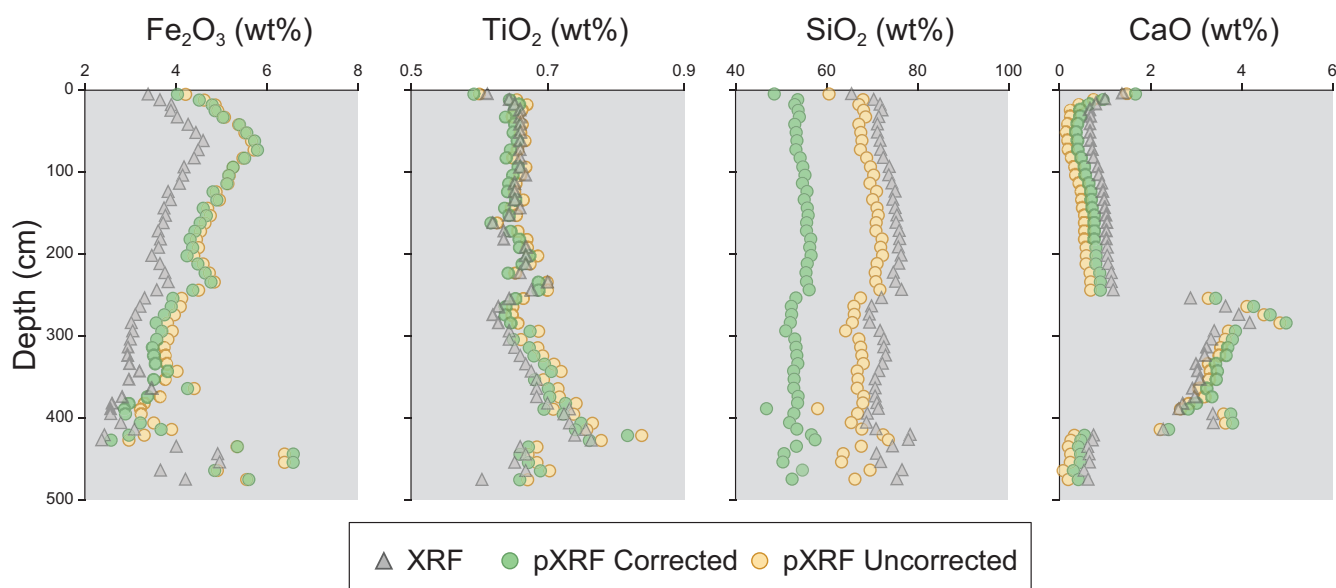


FIGURE 8 Depth plots showing agreement between calibrated and raw portable X-ray fluorescence data vs benchtop X-ray fluorescence data for Fe₂O₃, TiO₂, SiO₂, and CaO values for the Old Scotch core, Iowa

during excitation via analysis mechanisms are more easily attenuated by the atmosphere. As a result, these elements have lower R^2 values and poorer calibrations due to the low-energy condition and the inability of the current pXRF technology to properly correct for this issue (Table 4). Data from elements like Si and Fe typically differed more substantially from data determined by the benchtop XRF than did data from elements such as Ti and Mn (Figure 5).

As shown by Ryan et al. (2017) and as reproduced here (Figure 8; Table 4), the accuracy of raw pXRF data can be improved for most oxides by using calibrations. Such linear calibrations should ideally have a slope of 1.0 and an intercept at the origin. The calibrations established in this study differ significantly from these values, likely reflecting the inaccuracy that resulted from the internal calibration technique used by the Olympus instrument as well as issues related to X-ray attenuation, fluorescence, and interference. Thus, many pXRF data may have good correlations but are offset by XRF data

derived from benchtop instruments (Figure 5). Improvements in these calibrations could be achieved by using an increased number of standards and standards with a higher variability in composition. Particularly concerning is the fact that applying calibrations to known standards did not improve the Si data (Figure 8).

Conceptually, differences in reported pXRF elemental values for the three different sample preparations are to be expected. The intensity of characteristic fluorescence decreases as the moisture content of the soil increases due to the stronger X-ray absorption by soil water than by air in soil pores (Weindorf & Chakraborty, 2016). Therefore, dried, ground, and sieved soil samples should theoretically provide increased homogeneity by averaging out the influence of microscale inclusions and similar substances, such as Fe/Mn concretions, organic agglomerates laden with bound elements, or small carbonate concretions. However, compression of dried/ground powders may also artificially inflate

pXRF elemental readings by accentuating the number of atoms per unit area that are in contact with the X-ray beam. Indeed, the average bulk density of the pressed powder pellets was significantly higher (2.56 g cm^{-3}) than the average bulk density of the cores (1.69 g cm^{-3}). The “elegant” solution would be a dried/ground powder that could be compressed to a bulk density approaching field conditions. However, doing so would require field testing of bulk density, negating the benefit of using a rapid, field-portable method.

Future research should focus on assessing the ideal balance among sample bulk density, bulk and trace mineralogy, sample moisture conditions, and instrument parameterizations such as scanning (dwell) time. Another approach to be investigated involves comparisons between benchtop XRF data with raw fluorescence energies directly, circumventing the factory calibration based in Compton normalization. Despite these possible limitations, pXRF remains a powerful tool for rapid, in situ analysis of soils and ground geologic sediments, with more applications being rapidly developed.

4 | CONCLUSIONS


In this study, soil/sediment samples from cores taken in loess soils in eastern Iowa were evaluated by pXRF spectrometry using three different pretreatments: (i) field-moist conditions in the core (no pretreatment), (ii) dried/ground powder, and (iii) pressed-powder pellets. Results from the pXRF were compared with benchtop XRF data. The pXRF data from pressed powder pellets performed best for certain elements and oxides (e.g., CaO, TiO_2 , and MnO) and generally provided the strongest correlations between pXRF and XRF reported values. Data correlations for some other elements, especially SiO_2 and Al_2O_3 , were less robust. Scanning of field-moist samples consistently underestimated the concentrations of certain elements and oxides (e.g., SiO_2 and K_2O), which we attributed to fluorescence attenuation. Therefore, for the best results, soil samples should be dried, ground, sieved, and, in some cases, pressed into dense pellets before analysis via pXRF spectrometry.

Application of calibrations, developed from standard materials, to adjust the pXRF data resulted in considerable improvements, leading to data that more closely align with benchtop XRF data. More work is needed to simultaneously consider the influence of moisture, sample bulk density, pXRF operational parameterization (e.g., dwell time), and correction of reported pXRF data with local calibration samples. Those limitations notwithstanding, pXRF remains a powerful technique for rapid elemental analysis of soils, with new applications constantly emerging.

ACKNOWLEDGMENTS

This work was funded by NSF-EAR award #1331906 (Critical Zone Observatory for Intensively Managed Landscapes). The authors thank the B.L. Allen Endowment in Pedology at Texas Tech University for its help in conducting this research.

ORCID

Randall J. Schaetzl 

<https://orcid.org/0000-0002-6070-1365>

David C. Weindorf 

<https://orcid.org/0000-0002-3814-825X>

REFERENCES

- Adams, M. J., & Allen, J. R. (1998). Variable selection and multivariate calibration models for X-ray fluorescence spectrometry. *Journal of Analytical Atomic Spectrometry*, *13*, 119–124.
- Anders, A. M., Bettis, E. A. III, Grimley, D. A., Stumpf, A. J., & Kumar, P. (2018). Impacts of Quaternary history on critical zone structure and processes: Examples and a conceptual model from the intensively managed landscapes critical zone observatory. *Frontiers in Earth Science*, *6*, 1–16. <https://doi.org/10.3389/feart.2018.00024>.
- Arnoldussen, S., & van Os, B. J. H. (2015). The potential of lacquer-peel soil profiles for palaeo-geochemical analysis using XRF analysis. *Catena*, *128*, 16–30.
- Bettis, E. A. III, Muhs, D. R., Roberts, H. M., & Wintle, A. G. (2003). Last glacial loess in the conterminous USA. *Quaternary Science Reviews*, *22*, 1907–1946.
- Booth, A. D., Vandeginste, V., Pike, D., Abbey, R., Clark, C. A., Green, C. M., & Howland, N. (2017). Geochemical insight during archaeological geophysical exploration through in situ X-ray fluorescence spectrometry. *Archaeological Prospection*, *24*, 361–372.
- Buggle, B., Glaser, B., Hambach, U., Gerasimenko, N., & Markovic, S. (2011). An evaluation of geochemical weathering indices in loess-paleosol studies. *Quaternary International*, *240*, 12–21.
- Chakraborty, S., Li, B., Weindorf, D. C., Deb, S., Acree, A., De, P., & Panda, P. (2019). Use of portable X-ray fluorescence spectrometry for classifying soils from different land use land cover systems in India. *Geoderma*, *338*, 5–13.
- Connors, B., Somers, A., & Day, D. (2016). Application of handheld laser-induced breakdown spectroscopy (LIBS) to geochemical analysis. *Applied Spectroscopy*, *70*, 810–815.
- Duda, B. M., Weindorf, D. C., Chakraborty, S., Li, B., Man, T., Paulette, L., & Deb, S. (2017). Soil characterization across catenas via advanced proximal sensors. *Geoderma*, *298*, 78–91.
- Frahm, E., & Doonan, R. C. P. (2013). The technological versus methodological revolution of portable XRF in archaeology. *Journal of Archaeological Science*, *40*, 1425–1434.
- Frahm, E., Monnier, G. F., Jelinski, N. A., Fleming, E. P., Barber, B. L., & Lambon, J. B. (2016). Chemical soil surveys at the Bremer Site (Dakota County, Minnesota, USA): Measuring phosphorous content of sediment by portable XRF and ICP-OES. *Journal of Archaeological Science*, *75*, 115–138.
- Gallhofer, D., & Lottermoser, B. G. (2018). The influence of spectral interferences on critical element determination with portable

- X-ray fluorescence (pXRF). *Minerals*, 8(8), 320. <https://doi.org/10.3390/min8080320>.
- Ge, L., Lai, W., & Lin, Y. (2005). Influence of and correction for moisture in rocks, soils and sediments on in situ XRF analysis. *X-Ray Spectrometry*, 34, 28–34.
- Goff, K. R. (2017). Geochemical analysis of weathering zones from Clear Creek Watershed: Implications for modeling Quaternary landscape evolution (Master's thesis). Retrieved from University of Iowa <https://ir.uiowa.edu/etd/5481/>.
- Gunicheva, T. N., Aisueva, T. S., & Afonin, V. P. (1995). Non-destructive x-ray fluorescence analysis of soils and friable marine sediments. *X-ray Spectrometry*, 24, 187–192.
- Hallberg, G. R., Fenton, T. E., & Miller, G. A. (1978). Standard weathering zone terminology for the description of Quaternary sediments in Iowa. In G. R. Hallberg (Ed.), *Standard procedures for evaluation of Quaternary materials in Iowa* (Technical Information Series No 8, pp. 75–109). Iowa City, Iowa: Iowa Geological Survey.
- Horta, A., Malone, B., Stockmann, U., Minasny, B., Bishop, T. F. A., McBratney, A. B., ... Pozza, L. (2015). Potential of integrated field spectroscopy and spatial analysis for enhanced assessment of soil contamination: A prospective review. *Geoderma*, 241–242, 180–209.
- Hseu, Z.-Y., Chen, Z.-S., Tsai, C.-C., & Jien, S.-H. (2016). Portable X-ray fluorescence (pXRF) for determining Cr and Ni contents of serpentine soils in the field. In A. Hartemink & B. Minasny (Eds.), *Digital soil morphometrics* (pp. 37–50). New York: Springer.
- Hunt, A. M. W., & Speakman, R. J. (2015). Portable XRF analysis of archaeological sediments and ceramics. *Journal of Archaeological Science*, 53, 626–638.
- Jacobs, P. M., & Davis, A. T. (2018). Mineralogical and geochemical evidence of weathering in a middle to late Pleistocene paleosol sequence in the Driftless area of Wisconsin. *Quaternary Research*, 89, 756–768.
- Jochum, K. P., Nohl, U., Herwig, K., Lammel, E., Stoll, B., & Hofmann, A. W. (2005). GeoReM: A new geochemical database for reference materials and isotopic standards. *Geostandards and Geoanalytical Research*, 29, 333–338.
- Jones, L. H. P., & Handreck, K. A. (1967). Silica in soils, plants, and animals. *Advances in Agronomy*, 19, 107–149.
- Kalnicky, D., & Singhvi, R. (2001). Field portable XRF analysis of environmental samples. *Journal of Hazardous Materials*, 83, 93–122.
- Kemmis, T. J., Bettis, E. A. III, & Hallberg, G. R. (1992). *Quaternary geology of Conklin Quarry*. Des Moines, IA: Iowa Department of Natural Resources, Energy and Geological Resources Division.
- Koch, J., Chakraborty, S., Li, B., Moore-Kucera, J., Van Deventer, P., Daniell, A., ... Weindorf, D. C. (2017). Proximal sensor analysis of mine tailings in South Africa: An exploratory study. *Journal of Geochemical Exploration*, 181, 45–57.
- Lubos, C., Dreibrodt, S., & Bahr, A. (2016). Analysing spatio-temporal patterns of archaeological soils and sediments by comparing pXRF and different ICP-OES extraction methods. *Journal of Archaeological Science: Reports*, 9, 44–53.
- Mancini, M., Weindorf, D. C., & Chakraborty, S. (2019). Tracing tropical soil parent material analysis via portable X-ray fluorescence (pXRF) spectrometry in Brazilian Cerrado. *Geoderma*, 337, 718–728.
- Olympus Corporation. (2017). XRF and XRD Analyzers DELTA Premium. Tokyo, Japan: Olympus Corporation.
- Peel, M. C., Finlayson, B. L., & McMahon, T. A. (2007). Updated world map of the Köppen-Geiger climate classification. *European Geosciences Union*, 4, 439–473.
- Prior, J. C. (1991). *Landforms of Iowa*. Iowa City, IA: University of Iowa Press.
- Ribeiro, B. T., Silva, S. H. G., Silva, E. A., & Guilherma, L. R. G. (2017). Portable X-ray fluorescence (pXRF) applications in tropical soil science. *Ciência e Agrotecnologia*, 41, 245–254.
- Rovey, C. W. II, & Kean, W. F. (1996). Pre-Illinoian glacial stratigraphy in north-central Missouri. *Quaternary Research*, 45, 17–29.
- Ryan, J. G., Shervais, J. W., Li, Y., Reagan, M.K., Li, H. Y., Heaton, D., ... Petronotis, K. (2017). Application of a handheld X-ray fluorescence spectrometer for real-time, high-density quantitative analysis of drilled igneous rocks and sediments during IODP Expedition 352. *Chemical Geology*, 451, 55–66.
- Sahraoui, H., & Hachicha, M. (2017). Effect of soil moisture on trace elements concentrations. *Journal of Fundamental and Applied Sciences*, 9, 468–484.
- Sarala, P. (2016). Comparison of different portable XRF methods for determining till geochemistry. *Geochemistry: Exploration, Environment, Analysis*, 16, 181–192.
- Schaetzl, R. J. (1992). Texture, mineralogy and lamellae development in sandy soils in Michigan. *Soil Science Society of America Journal*, 56, 1538–1545.
- Schaetzl, R. J., Krist, F. J., Jr., & Miller, B. A. (2012). A taxonomically based, ordinal estimate of soil productivity for landscape-scale analyses. *Soil Science*, 177, 288–299.
- Schneider, A. R., Cancès, B., Breton, C., Ponthieu, M., Morvan, X., Conreux, A., & Marin, B. (2016). Comparison of field portable XRF and aqua regia/ICPAES soil analysis and evaluation of soil moisture influence on FPXRF results. *Journal of Soils and Sediments*, 16, 438–448.
- Sharma, A., Weindorf, D. C., Wang, D. D., & Chakraborty, S. (2015). Characterizing soils via portable X-ray fluorescence spectrometer: 4. Cation exchange capacity (CEC). *Geoderma*, 239, 130–134.
- Silva, S. H. G., Hartemink, A. E., Texeira, A. F. D., Inda, A. V., Guilherme, L. R. G., & Curi, N. (2018). Soil weathering analysis using a portable X-ray fluorescence (PXRF) spectrometer in an Inceptisol from the Brazilian Cerrado. *Applied Clay Science*, 162, 27–37.
- SGS Canada Inc. (2016). Sample preparation and XRF procedure. Mississauga, Ontario, Canada: SGS Canada.
- Soil Survey Division Staff. (1993). *Soil survey manual* (USDA Handbook #18). Washington, DC: US Government Printing Office.
- Soil Survey Staff. (2014). Kellogg soil survey laboratory methods manual (Version 5.0, Soil survey investigations report no. 42). Lincoln, NE: USDA-NRCS.
- Stockmann, U., Cattle, S. R., Minasny, B., & McBratney, A. B. (2016). Utilizing portable X-ray fluorescence spectrometry for in-field investigation of pedogenesis. *Catena*, 139, 220–231.
- US Environmental Protection Agency. (2007). Method 6200 – Field portable X-ray fluorescence spectrometry for the determination of elemental concentrations in soil and sediment. Retrieved from: <https://www.epa.gov/sites/production/files/2015-12/documents/6200.pdf> (verified 31 Jul. 2019).
- Weindorf, D. C., Bakr, N., & Zhu, Y. (2014). Advances in portable X-ray fluorescence (PXRF) for environmental, pedological, and agronomic applications. *Advances in Agronomy*, 128, 1–45.

- Weindorf, D. C., & Chakraborty, S. (2016). Portable X-ray fluorescence spectrometry analysis of soils. *Methods of Soil Analysis, 1*, 1–8. <https://doi.org/10.2136/methods-soil.2015.0033>.
- Weindorf, D. C., Chakraborty, S., Abdalsatar, A., Aldabaa, A., Paulette, L., Corti, G., ... Person, T. (2015). Lithologic discontinuity assessment in soils via portable X-ray fluorescence spectrometry and visible near-infrared diffuse reflectance spectroscopy. *Soil Science Society of America Journal, 79*, 1704–1716.
- Zhu, Y., & Weindorf, D. C. (2009). Determination of soil calcium using field portable X-ray fluorescence. *Soil Science, 174*, 151–155.

How to cite this article: Goff K, Schaetzl RJ, Chakraborty S, Weindorf DC, Kasmerchak C, Bettis EA III. Impact of sample preparation methods for characterizing the geochemistry of soils and sediments by portable X-ray fluorescence. *Soil Sci. Soc. Am. J.* 2020;84:131–143. <https://doi.org/10.1002/saj2.20004>