Review article

Portable X-ray fluorescence for environmental assessment of soils: Not just a point and shoot method

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ABSTRACT

Portable XRF is a rapid, mobile, high throughput, and potentially cost effective instrumental analytical technique capable of elemental assessment. It is widely used for environmental assessment of soils in a variety of contexts such as agriculture and pollution both in-situ and ex-situ, to varying levels of success. Portable XRF performance for soil analysis is often validated against wet chemistry techniques but a range of factors may give rise to elementally dependent disparities affecting accuracy and precision assessments. These include heterogeneity, analysis times, instrument stability during analyses, protective thin films, incident X-rays, sample thickness, sample width, analyte interferences, detector resolution, power source fluctuations and instrumental drift. Light elements comprising water and organic matter (i.e. carbon, oxygen) also negatively affect measurements due to X-ray scattering and attenuation. The often-overlooked phenomenon of variability in both soil organic matter and water can also affect soil density (e.g. shrink-swell clays) and thus sample critical thickness which in turn affects the effective volume of sample analyzed. Compounding this, for elements having lower characteristic fluorescence energy, effective volumes of analyses are lower and thus measurements may not be representative of the whole sample. Understanding the effects and interplay between determined elemental concentrations and soil organic matter, water, and critical thickness together with the subtlety of theoretical effective volumes of analyses will help analysts mitigate potential problems and assess the applicability, advantages and limitations of PXRF for a given site. We demonstrate that with careful consideration of these factors and a systematic approach to analysis which we summarize and present, PXRF can provide highly accurate results.

1. Introduction

With miniaturization of integrated circuits and advancements in computing power, battery capacity and X-ray generation tubes, portable X-ray fluorescence (PXRF) devices have become a viable option for geochemical measurements (Bosco, 2013; Gałuszka et al., 2015; Sharma et al., 2015). X-ray fluorescence (XRF) is a total elemental analysis technique (Gałuszka et al., 2015; Hu et al., 2014; Lemière, 2018; Sharma et al., 2015; Tighe et al., 2018; Weindorf et al., 2014a). Electrons exist in atoms at discrete energy levels unique to each element (Potts and West, 2008). X-ray fluorescence occurs when a sample is illuminated by X-rays resulting in the ionization of its elements via the ejection of inner shell electrons. Subsequently, higher energy electrons transition to lower energy states and fill the voids in the inner electron shells yielding either X-ray fluorescence or auger electrons (Kikongi et al., 2017; Shackley, 2011). Auger electrons are generated when the X-ray fluorescence of an atom is re-absorbed by the outer electrons of the emitting element itself and this effect dominates for lighter elements

with lower atomic numbers (Z) (Kikongi et al., 2017). Due to the conservation of energy, the electrons undergoing transitions emit X-rays (fluorescence) unique to the atom. X-ray fluorescence instruments detect and relate this fluorescence to a sample's atomic makeup. The X-ray fluorescence method generates measurements based on the entire contents of the analyte and matrix dependent fluorescence egression volume (Ravansari and Lemke, 2018).

In soil science, it is necessary to quantify the geochemical composition of samples for purposes such as agricultural productivity, or pollution assessment and mitigation (Brown et al., 2016; Bugdalski et al., 2014; Dao et al., 2013; Goulding and Jaklevic, 1973; Gutierrez-Gines et al., 2013; Hu et al., 2014; McLaren et al., 2012; Parsons et al., 2013; Tighe et al., 2018; Weindorf et al., 2012a). The potential of PXRF to economically, rapidly and simultaneously generate multi-elemental data is attractive to users (Radu and Diamond, 2009; Rouillon et al., 2017; Shand and Wendler, 2014; Taylor et al., 2004). There is growing acceptance of PXRF as an analytical device for soil science (Gutierrez-Gines et al., 2013; McLaren et al., 2012; Ravansari and Lemke, 2018;

Rouillon et al., 2017; Tighe et al., 2018; Weindorf et al., 2012b), including for example, as a standardized United States Environmental Protection Agency analytical method (U.S. EPA) Method 6200 (ISO, 2013; USEPA, 2007b).

Portable XRF can produce soil elemental data rapidly and at a lower cost than that of traditional laboratory wet chemistry methods (Rouillon and Taylor, 2016; Taylor et al., 2004). Widely used alternatives to PXRF include inductively coupled plasma (ICP) and flame spectrometry based methods that require sample acquisition from the field, sample preparation and digestion in the lab. Collecting, transporting, preparing, and digesting samples for ICP or flame spectrometry based analyses is labor intensive and destructive. The mobility of PXRF in contrast to ICP or flame spectrometry instrumentation is a clear advantage and allows the instrument to be deployed in the field as a handheld device at the sampling spot (henceforth referred to as "in-situ"). Portable XRF is a non-destructive analytical method, and sample preparation costs associated with its use in the lab (henceforth referred to as "ex-situ") are less than the costs associated with digestion techniques. Authors have noted lower PXRF performance for measurements under in-situ conditions as compared to ex-situ or some digestion methods (e.g. aqua regia) (Hu et al., 2014). In general, poor accuracy or precision of the technique can be ascribed to inherent limitations of the equipment, but may also be due to sub-optimal considerations of sample processing, instrumental settings, calibration assumptions, or lack of attempts to quantify and isolate sources of measurement uncertainty (Ramsey and Ellison, 2019). Compiling and synthesizing these factors is critical to enable analysts to confidently apply PXRF to soils.

In this work, we review analytical considerations that contribute to variability in PXRF analysis. We aim to identify knowledge gaps and limitations relating to PXRF application to soil, focusing on analytical variability and sources of measurement error. In-situ and ex-situ applications are discussed in each section. Furthermore we define research needed to augment, improve and extend PXRF capability and utility. This review focuses in part on the effects of organic matter, water and X-ray energies on soil PXRF measurements which have not been previously reviewed together. Key findings are presented as a best practice stepwise approach to PXRF analysis.

2. Factors affecting soil PXRF measurements

Factors affecting soil PXRF measurements include organic matter, water content, heterogeneity, sample geometry, analysis film thickness, sample thickness, matrix interferences and detector resolution, X-ray energy and intensity, power source fluctuations and instrumental drift over time. These factors are elucidated in subsequent sections. A flowchart outlining factors that influence results when using PXRF on soils, and when they are most effectively considered, is provided in Fig. 1. Table 1 provides an overview of typical measurement performance for PXRF instrumentation. Measurements conducted on certified reference materials (CRM) generally compare well with certified values (average $R^2 \geq 0.96$). Comparisons between ex-situ measurements conducted via PXRF and ICP methods are less similar (average $R^2 \geq 0.72$) possibly due to the variability associated with potential incomplete digestion in addition to discrepancies between effective and representative volumes of analyses for the two methods (discussed further in subsequent sections). Comparisons drawn between in-situ PXRF and ex-situ ICP methods are even more dissimilar (average $R^2 \leq 0.59$) owing to the introduction of additional variability from uncontrolled environmental factors such as water, organic matter or heterogeneity (Hu et al., 2014; Ravansari and Lemke, 2018; Rouillon and Taylor, 2016). High coefficients of determination alone do not guarantee equality between comparative measurements. Considerations must also be given to the regression coefficients, slopes, intercepts and relative standard deviations (RSD) for assessment of measurement bias, uncertainty and general data quality (Table 2) (USEPA, 1998).

2.1. Organic matter

Soil organic matter (SOM) can vary from < 0.1% (e.g. desert) to over 90% (e.g. wetland) depending on pedogenic conditions (Coles, 2012; Schnitzer, 1982). Recent work has shown that organic matter can exert elementally dependent effects on PXRF measurements (Bacon et al., 2019; Ravansari and Lemke, 2018; Shuttleworth et al., 2014). Shuttleworth et al. (2014) found that in-situ PXRF lead (Pb) measurements calibrated internally via "soils" mode with a Niton XL3t 900 instrument, corrected for water dilution effects and carried out on peatland (organic rich) soils, consistently but non-significantly underestimated analyte concentrations when compared with laboratory based wet chemistry techniques. This was attributed to the scattering effects of water and low density/matrix effects of peat (organic matter) which reduced the apparent concentrations rendered by PXRF (Shuttleworth et al., 2014). Ravansari and Lemke (2018) developed elementally dependent correction coefficients for PXRF measurements accounting for deviations caused by organic matter which varied from as low as 0.76 to as high as 1.34 over a wide range of organic matter values (0% to 31%). This suggests organic matter should be quantified and accounted for during calibration, particularly when employing PXRF on organic rich soils (Fig. 1) or to improve accuracy, such as with assessments of contamination (Ravansari, 2016; Ravansari and Lemke, 2016; 2018). Further development of such correction procedures may improve data.

Portable XRF as yet cannot be used to directly analyze SOM (Ravansari and Lemke, 2018) since light elements in SOM (such as carbon) possess low energy fluorescence which is currently impossible to detect due to attenuation (Löwemark et al., 2011; Otaka et al., 2014). Nevertheless, soil organic matter is of critical importance (Reeves, 1997; Swift, 1996). Recently, SOM monitoring efforts have gained further importance internationally for benchmarking progress on regional, national and international treaties such as the United Nations' (UN) "4 per 1000 initiative" (ratified and in force as of November 2016 signed by 179 of the 197 UN member countries). The 4 per 1000 initiative aims to increase agricultural soil carbon by 0.4% per year thereby aiding global food security, reducing atmospheric carbon and mitigating climate change (4p (1000), 2018; UNFCCC, 2016; van Groenigen et al., 2017). Therefore, instrumental developments enabling parallel quantification of SOM during analyses will add to the instrument's utility and applicability (e.g. soil carbon monitoring efforts and/ or automatic integrated OM algorithmic correction procedures).

2.2. Water content

For ex-situ measurements, deviations caused by water content can be negated by air drying (Faithfull, 2003) or oven drying samples (ASTM, 2010; 2014), but this is not possible during in-situ assessment (Fig. 1). Water affects PXRF measurements by reducing apparent concentrations and poses particular issue for low Z elements possessing fluorescent energies below 5 KeV (Kalnicky and Singhvi, 2001). These effects have generally been regarded as minor when water content is below 20% and elements of interest have fluorescence energies higher than 5 KeV (Kalnicky and Singhvi, 2001; USEPA, 2007b). However, Parsons et al. (2013) showed that water may significantly affect soil PXRF measurements. For measurements conducted with a Niton XLt 700 PXRF instrument operated using factory calibrated 'soils' mode, deviations as great as 37% in soil arsenic (As) measurements occurred for a 20% gravimetric water content (Parsons et al., 2013). Ge et al. (2005) noted relative standard errors as great as 40% for iron (Fe) measurements conducted on ore samples containing 20% water content. Such deviations in measurement accuracy have been attributed to both dilution effects and higher scattering due to water content (Bastos et al., 2012; Ge et al., 2005; IAEA, 2005; Schneider et al., 2016; Shuttleworth et al., 2014; Tjallingii et al., 2007).

Shuttleworth et al. (2014) employed Eq. (1) to mitigate the dilution
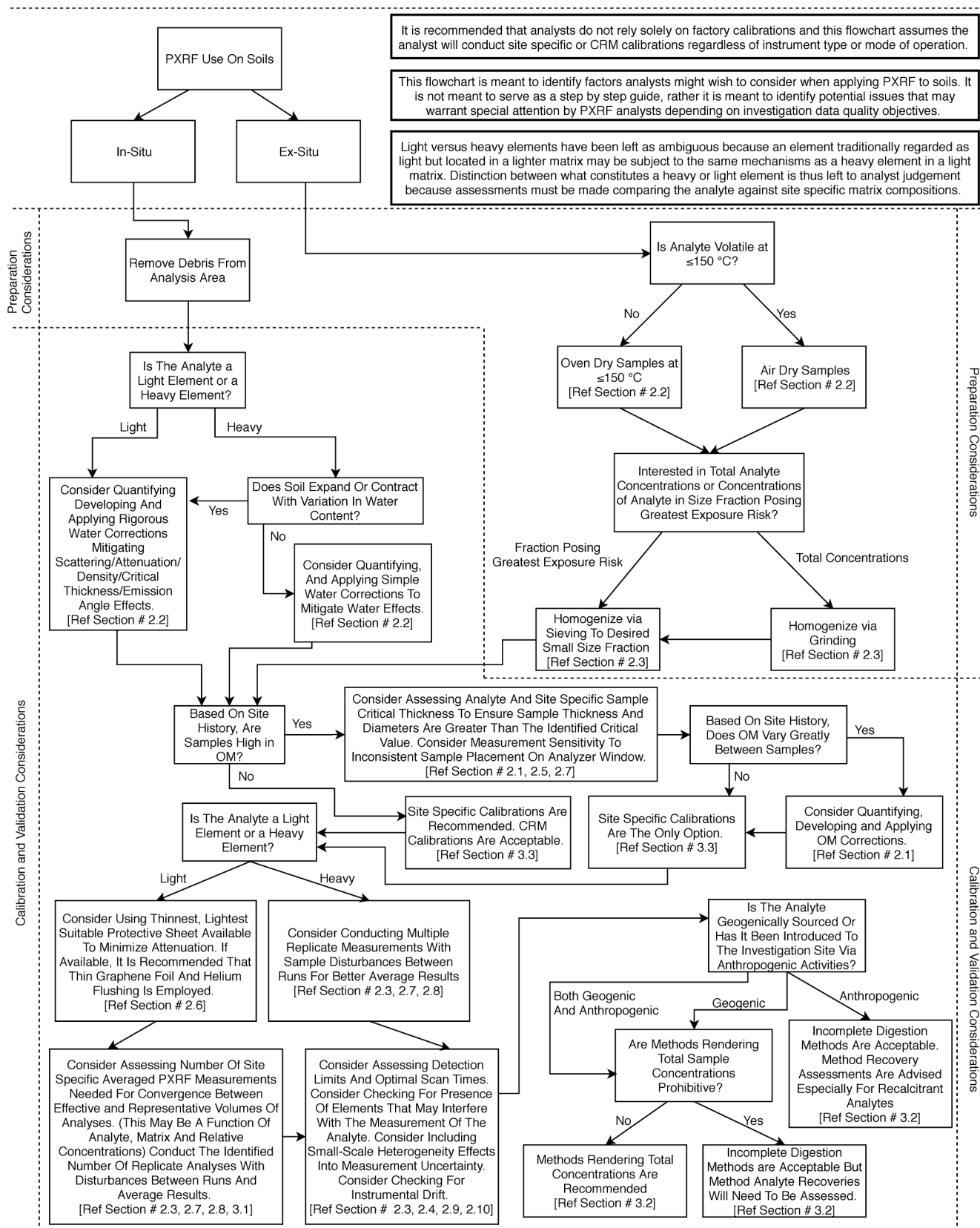
Fig. 1. Flowchart of some considerations identified in this review for the employment of PXRF on soils. This chart is intended to aide analysts recognize sources of variability in PXRF measurements for further consideration and potential mitigatory action to improve outputs.

Table 1

In-situ and ex-situ performance of portable X-ray fluorescence as indicated by coefficients of determination. Comparisons were drawn either between certified reference materials (CRM), inductively coupled plasma optical emission spectroscopy (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS). The ranges, median and average R^2 values listed in the table are across all the elements listed, including all elements reported in the study unless otherwise noted. The studies in this table are ordered by the average R^2 values for comparative measurements between PXRF and the listed methods. The general hierarchy of these PXRF average coefficients of determination follow this pattern CRM > Ex-situ (complete digestion) > Ex-situ (incomplete digestion) > In-Situ.

PXRF Instrument	Provided Matrix/Soil Information	Elements	R^2 Range	Median R^2	Average R^2	PXRF Application	Comparison Against	Digestion Type	Reference
Niton XLt 960	Unspecified – 8 CRMs	As, Pb, Cu, Zn	≥ 0.99	≥ 0.99	≥ 0.99	Ex-Situ	CRM	–	Hu et al. (2014)
Olympus Delta Premium	NIST 2586, 2587, 2709a, 2710a, 2711a, 1944, NRC BCSS-1, PACS-2, MESS-2, RM 8704 CRMs	Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Cd, Pb	0.87 to ≥ 0.99	≥ 0.99	0.97	Ex-Situ	CRM	–	Rouillon and Taylor (2016)
Niton XL3t GOLDD + 950	NIST 2586, 2709a, 2711a, NRCan Till 1, 2, 3, 4 CRMs	As, Cr, Cu, Fe, Mn, Pb, Rb, Sr, Th, Ti, V, Zn, Zr	0.84 to ≥ 0.99	0.99	0.97	Ex-Situ	CRM	–	Ravansari and Lemke (2018)
Niton XLt 792WY	Unspecified – 48 CRMs	As, Ca, Cd, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, Sr, Ti, V, Zn	0.74 to ≥ 0.99	0.98	0.96	Ex-Situ	CRM	–	Gutierrez-Gines et al. (2013)
Olympus Delta Premium	Various soils from Queensland and New South Wales, Australia	Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Cd, Pb	0.52 to ≥ 0.99	≥ 0.99	0.94	Ex-Situ	ICP-OES	$HNO_3 + HClO_4$ + HF (Complete)	Rouillon and Taylor (2016)
Niton XLt 960	Cambisol, China	As[A], Pb, Cu, Zn	0.68 to 0.93	0.74	0.76	Ex-Situ	ICP-MS[A]	$HNO_3 + HClO_4$ + HF (Complete)[A]	Hu et al. (2014)
Bruker Tracer III-V	Vertisol, New South Wales, Australia	Ca, Fe, P, Mn, Cr, K, Ti, Zn, Cu, Ni, Pb, As, Cr, Co, Sb	0.26 to 0.97	0.78[B,C]	0.72[B,C]	Ex-Situ	ICP-OES	aqua regia (Incomplete)	McLaren et al. (2012)
Innov X Alpha 4000	Abandoned mine soil, South Korea	Zn, As, Cu, Cd, Pb	0.02 to 0.95	0.92[F]	0.59[F]	In-Situ	Various[F]	HCl (Incomplete)[F]	Jang (2010)
Omega Xpress	Texture varied from clay to loam Baton Rouge, Louisiana USA	As, Co, Cu, Fe, Mn, Pb, Zn	0.35 to 0.96	0.48[D]	0.57[D]	In-Situ	ICP-OES	aqua regia (Incomplete)	Weindorf et al. (2012a)
Niton XLt 960	Cambisol, China	As[A], Pb, Cu, Zn	0.28 to 0.66	0.43	0.45	In-Situ	ICP-MS[A]	$HNO_3 + HClO_4$ + HF (Complete)[A]	Hu et al. (2014)
Niton XL-722	Erren River Basin, Taiwan	Pb, Zn, Ni, Cu,Cr, Cd	0.08 to 0.73	0.41[E]	0.43[E]	In-Situ	ICP-OES	aqua regia (Incomplete)	Wu et al. (2012)

[A] Arsenic analyses performed by Atomic Fluorescence Spectrometry (AFS) using aqua regia digestion.

[B] The authors report results for some light elements that are widely recognized as problematic to quantify via PXRF (silicon, sulfur, aluminium, magnesium and sodium). These elements have been excluded in the calculation of average R^2 (phosphorus is reported as optimisation for P analysis was the focus of this work).

[C] The authors compare the performance of the instrument operated under both factory and optimized settings. The best case R^2 values generated by the authors were used to construct this table.

[D] Barium and chromium were excluded from the list of elements. The authors reported values for those elements but identified those relationships as anomalous, ($R^2 = 0.07$ and < 0.01 respectively).

[E] Mercury was excluded from the list of elements ($R^2 = 0.01$) because of potential volatilization.

[F] The Korean Standard Test (KST) was employed which used HCl for extraction of all analytes with the exception of zinc for which aqua regia was used instead (Lim et al. 2009). Analyses were conducted at three different labs using different instrumentation (ICP-OES, atomic absorption spectroscopy).

Table 2
Criteria for Characterizing Data Quality as adapted from Kilbride et al. (2006); USEPA (1998). R^2 is the coefficient of determination. RSD is the relative standard deviation. All three indicated conditions (R^2, RSD, Inferential Statistics) must be met to qualify for the associated data quality level. For the definitive data quality tier, inferential statistics (test for slope and intercept) must indicate that the slope coefficient is not significantly different from unity, and the intercept coefficient is not significantly different from zero (at $\alpha = 0.05$).

Data Quality Level	R^2	RSD	Inferential Statistics Relationship	Description
Definitive	0.85 to 1.0	$\leq 10\%$	$y = x$	Data sets are statistically similar.
Quantitative "Screening Level"	0.70 to 1.0	$< 20\%$	$y = mx + b$ or $y = mx$	Data sets are statistically different.
Qualitative "Screening"	< 0.70	$> 20\%$	$y = mx + b$ or $y = mx$	Data sets are statistically different.

effect of water content on PXRF measurement.

$$C_c = \frac{C_f \times m_w}{m_d}$$

(1)

where C_c is the corrected concentration, C_f is the raw PXRF measurement, m_w is the wet mass of the sample and m_d is the dry mass of the sample (Shuttleworth et al., 2014). Ge et al. (2005) also developed and employed correction equations accounting for the scattering and attenuation effects of sample water content, noting satisfactory performance for their correction equations. Schneider et al. (2016) subsequently employed the corrections developed by Ge et al. (2005) for 11 analytes in soil samples that deviated in PXRF measurement accuracy between 14.9% and 99.8% due to varying water content, and noted satisfactory post-correction results ($R^2 > 0.92$, $0.90 \leq$ slopes ≤ 1.3). Theoretical correction procedures such as those employed by Ge et al. (2005) or empirical correction procedures such as an adaption of the methodology presented by Ravansari and Lemke (2018) may be useful in correcting for water content. Such approaches may be most useful for low Z analytes or soils prone to expansion or contraction with variable water content.

A confounding effect of soil water is its effect on soil swelling and thus critical thickness which is defined as the depth from which 99% of a fluorescence signal can originate (Kalnicky and Singhvi, 2001). This phenomenon could potentially explain the variation on the influence of water on PXRF measurements as demonstrated in Table 3. Changes to soil volume may partially explain the variation encountered beyond simple dilution, scatter or attenuation effects, in particular for soils that exhibit some shrink-swell behaviour. Further work is required to assess the performance of PXRF in such soils. As suggested by Potts and West (2008), for in-situ measurements, integration of a soil moisture sensor with the PXRF may enable quantification and correction of PXRF measurements for water content. Once the influence of such sources of variation are comprehensively accounted for through experimental development, in-situ PXRF measurements may provide a "truer" estimate of the composition of a field site than what might be achieved via other methods.

2.3. Heterogeneity

In addition to variability in organic matter and water content, soils have heterogeneous chemical composition, physical structure, and grain size distribution. Soil chemical heterogeneity is mitigated in ex-situ analysis by applying PXRF on the fine fraction of soil and by employing sampling and homogenization techniques such as grinding and sieving. A $< 250\,\mu m$ fraction is recommended by the USEPA (2007b) and has been used in various studies (Bugdalski et al., 2014; Clark et al., 1999; Ridings et al., 2000). Grinding and sieving fortify PXRF analyses against "nugget effects" in which a chunk of analyte may by chance be positioned in front of the analyzer window thereby increasing the analyte signal (Kalnicky and Singhvi, 2001). Such effects are especially prevalent for elements present at low total concentrations but existing within nugget prone accessory minerals such as zircon for zirconium (Zr) and pyrite for As (Rostron and Ramsey, 2017). These homogenization techniques do not fully immunize PXRF against potential problems caused by heterogeneity but recognition of this limitation and

mitigation of the problem is critical. Nugget effects may also be mitigated and uncertainty decreased by averaging multiple measurements conducted between analysis vial disturbances (re-homogenization), or instrument/sample repositioning between analyses (Ravansari and Lemke, 2018; Sharma et al., 2014). Argyraki et al. (1997) noted heterogeneity dominating the measurement uncertainty (for Pb) and suggested taking duplicate measurements of a sample to assess uncertainty arising from sampling and heterogeneity. Some PXRFs also give analysts an option to vary beam size (3 mm vs 8 mm) which may be used to quantify uncertainty due to heterogeneity by taking multiple measurements using different beam sizes (Rostron and Ramsey, 2017). Ravansari and Lemke (2018) analyzed soil samples via PXRF for As, chromium (Cr), copper (Cu), Fe, manganese (Mn), Pb, rubidium (Rb), strontium (Sr), thorium (Th), titanium (Ti), vanadium (V), zinc (Zn) and Zr, conducting analyses in triplicate while shaking the analysis vials between runs. They reported that the degree of variability in results was element dependent (e.g. heterogeneity component of variance for Ti = 52.7% vs As = 4.0%) which is to be expected because of elementally dependent effective volumes of analyses and mineral effects as noted above.

Bias in comparisons may exist when comparing PXRF measurements conducted in-situ (where un-sieved soil is often analyzed) versus ex-situ PXRF or ICP measurements (where soil is often sieved) (Ramsey and Boon, 2012). Different grain size fractions may have different metal concentrations, which may affect the apparent measured concentrations (Bugdalski et al., 2014; ITRC, 2012; Sutherland, 2003; Wang et al., 2006). Metals of anthropogenic origin are often introduced into the environment as fine particles and the fine fraction of soils presents a much larger surface area for sorption of metals compared with larger size fractions (Bugdalski et al., 2014; Sutherland, 2003; Wang et al., 2006). For example, Wang et al. (2006) conducted XRF measurements (Philips PW1400 instrument) on urban roadside soils obtained near the city center area of Xuzhou, China. They found that over 70% of anthropogenic Pb was contained in the 45–125 μm fraction and this pattern also held for antimony (Sb), As, barium (Ba), bismuth (Bi), cadmium (Cd), Cu, molybdenum (Mo), selenium (Se), silver (Ag), mercury (Hg) and Zn using other analytical methods. Anthropogenic trace elements released into the environment are often contained within the upper layer of the soil profile due to the low rate of soil formation and because this is where sorption processes take place after release and deposition (Teutsch et al., 2001). These processes result in comparatively higher anthropogenic metal concentrations in the finer fraction of the upper soil profile compared with coarser fractions or soils sourced from deeper within a profile (Acosta et al., 2009; Bugdalski et al., 2014; Sutherland, 2003; Teutsch et al., 2001; Wang et al., 2006).

Depending on whether the investigation is targeting total concentrations or concentrations in the fractions posing greatest exposure risk, project goals should inform sampling strategies and sample preparation methods employed (grinding versus sieving) (Fig. 1) (Kalnicky and Singhvi, 2001; USEPA, 2007b). In a study investigating playground soils, Acosta et al. (2009) suggested that metal concentrations in the fine fraction of soils were better for assessing exposure risk because of the higher risk of inhalation of dust or ingestion of fine particles. In practice, for surface in-situ PXRF measurements, heterogeneity is currently difficult to control due to nugget effects and this stratification of

Table 3

Organic content and water effects on soil volume, density (affecting depth of contributing signal origin) and/or PXRF analyses. If authors did not provide specific organic content or shrink-swell characteristics, this information was deduced based on the provided soil information (it was assumed that clays and organic rich soils will exhibit shrink-swell behavior as evidenced within the first three examples of this table).

Provided Soil Information	PXRF Instrument	PXRF Analytes	Organic Rich/ Shrink Swell	Highlights and Notes	Reference
Eutric Histosol Histic Gleysol	–	–	Yes/Yes	Volumes varied by 23.6 to 60.1% in response to wetting and drying cycles.	(Peng et al. 2007)
Calcic Gleysol Dystric Gleysol	–	–	No/Mixed	Volumes varied by 1.5 to 4.8% in the silty Calcic Gleysol and 3.6% to 15.1% in the clayey Dystric Gleysol in response to wetting and drying cycles.	(Peng et al. 2007)
Vertisol	–	–	No/Yes	Vertisol sample expanded > 19% with exposure to water.	(Wilson et al. 2013)
Humic-gley Podzolic Soil	–	–	–	The authors of the referenced papers investigated the effects of soil organic content on soil bulk density noting a correlation between the two. Soil bulk densities decrease with increasing organic content. Note: A well-established, tried and tested link exists between soil density and organic content.	(Adams 1973; Saini 1966)
Gelisols	Olympus Innov-X Delta	Ba, Ca, Cr, Fe, K, Mn, Pb, Rb, Sr, Ti, Zn	Mixed/Yes (ice)	The authors investigated the effects of ice on PXRF measurements for Alaska, USA soils. The majority of in-situ measurements on frozen soils significantly underestimated concentrations as compared to PXRF measurements conducted after sample preparations (drying, grinding). In-situ (frozen) and ex-situ (wet-melted) comparisons against dried, homogenized samples were similar but frozen sample performance was lower (R^2 0.81 versus 0.88 and slopes of 0.88 versus 0.92). Note: The volumetric expansion of frozen water may have contributed to these findings.	(Weindorf et al. 2014b)
Peat	Niton XL3t 900	Pb	Yes/Yes	The authors analyzed peatland soils for lead in-situ using PXRF and compared those measurements against ex-situ digestion derived values. Pre-moisture corrected in-situ measurements significantly underestimated concentrations. Post-moisture corrected in-situ measurements were comparable to ex-situ measurements although they noted slight consistent underestimation of the analyte. Note: Volumetric expansion of spongey organic soils with water may have contributed to these findings.	(Shuttleworth et al. 2014)
CRM[A]	Niton XL3t GOLDD + 950	As, Cr, Cu, Fe, Mn, Pb, Rb, Sr, Th, Ti, V, Zn, Zr	Mixed/No	The authors investigated the influence of organic matter on PXRF measurements by incrementally spiking a CRM[A] with organic matter surrogates. They noted elementally dependent attenuation of the PXRF signal with increasing organic content. The diminished response was beyond what was expected from pure theoretical dilutionary effects. Correction coefficients ranged between 0.76 and 1.34. Note: A decrease in soil density with increasing organic content and associated increase in critical thickness may have contributed to these findings.	(Ravansari and Lemke 2018)
Floodplain Soils	Niton XLt 700	As	Yes/Yes	The authors analyzed floodplain soils for trace arsenic using PXRF. They noted a 37% arsenic signal loss for a 20% gravimetric water content. They noted a severe underestimation of the importance of soil moisture in previous literature. Note: We reasonably assume these floodplain soils were organic rich and thus were susceptible to volumetric variability with variability in water content potentially contributing to these results. This may also explain the authors surprising findings that these soils were much more susceptible to signal deviation with variability in soil water content than what was expected based on prior literature.	(Parsons et al. 2013)
Various: Temperate and semi-arid regions of France	Niton XL3t 980 GOLDD +	Ba, Ca, Cr, Cu, Fe, Mn, Pb, Rb, Sn, Sr, Zn	No/Unknown	The authors investigated the influence of water on PXRF measurements. They noted significant decrease in PXRF signal with increasing water. Using the correction procedures outlined by Ge et al. (2005), the authors successfully corrected PXRF measurements for moisture content producing quantitative data. Note: The authors use a range of different soils. It is unclear if any of these soils were shrink-swell type clays however, given the correction procedures for moisture content producing the majority were not organic rich based on the organic content inferential statistics provided by the authors (organic carbon mean is 4.0% and third quartile is 5.3%). This may have contributed to the author's successful moisture corrections (less confounding factors).	(Schneider et al. 2016)

[A] Certified reference material was utilized (Natural Resource Canada Till-1).

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analytes within the soil profile. Some of these issues can be mitigated and measurement uncertainty estimated by conducting duplicated measurements (made feasible by the rapidity, cost-effectiveness, and portability of PXRF) (Argyraki et al., 1997; Ramsey, 1998; Ramsey et al., 2013; Taylor et al., 2004; Taylor et al., 2005). Extension of PXRF technology has already been developed to capture spatial heterogeneity via mapping technology such as the Bruker ARTAX 800 system. Given the stratification difficulties, nugget effects, and fluorescence penetration issues, a future avenue of PXRF development may include development of intrusive probe like devices to assist with mapping and quantifying vertically stratified variation as well as overcoming critical depth of outbound fluorescence penetration issues.

2.4. Analysis time

General instrumental limits of detection (LOD) are occasionally provided by PXRF manufacturers as is the case for the Niton XL3T 950 GOLDD + (Thermo-Scientific, 2010), but LODs are theoretically dependent on analysis times and in reality need to be determined uniquely for specific projects, preparation methods and analytes (Parsons et al., 2013). For example, using a Niton XLt 700 PXRF Parsons et al. (2013) demonstrated that instrumental LODs for soil As varied between 6 ppm and 10 ppm across different preparation methods. The accepted method for identifying project/instrument specific limits of detection is to compute three times the standard deviation on non-consecutive replicate measurements performed on a certified reference material with an analyte concentration near the instrument's expected detection limit (Kalnicky and Singhvi, 2001). It is recommended that the analysis time for this be determined based on analytes of interest, project goals, and detection limit requirements (Kalnicky and Singhvi, 2001). Analysis times from 30 to 500 s have been used (Grattan et al., 2016; Parsons et al., 2013). A longer analysis time can decrease measurement variability across replicate measurements up to a point, especially for light elements that exhibit lower fluorescence yields with an inverse relationship between fluorescence and auger yields for increasing Z (Kahoul et al., 2011). Temporal variability in the fluorescence signal is mitigated by analyzing samples over a minimum duration and averaging counts over time. Detection limits may be improved if longer scan times are used but this will decrease throughput. The law of diminishing gains applies with longer scan times as increasing scan times by some factor will only reduce detection limits by the square root of that factor (Potts and West, 2008).

It is thus important to optimize scan times (Kalnicky and Singhvi, 2001; Parsons et al., 2013). Increasing analysis times will reduce detection limits only up to a point before the signal to noise ratio becomes sub-optimal (Tighe et al., 2018). For example, Kilbride et al. (2006) demonstrated that ex-situ PXRF (Niton XLt 700) measurement data quality for As improved with increased scan times (lower relative standard deviation and higher R^2) reaching definitive level quality at 240 s. Beyond 240 s data quality decreased from definitive to quantitative (Table 2). Thus, the limits of detection and optimal scan times need to be determined using certified reference materials, as they are instrument, instrument set-up (e.g. utilized filters), project, element, and matrix dependent (Fig. 1) (Kalnicky and Singhvi, 2001; Parsons et al., 2013).

2.5. Stability and movement during analyses

Sample and instrument geometry influence PXRF measurements by altering detected fluorescence intensities (De Boer, 1989; IAEA, 2005; Kalnicky and Singhvi, 2001; Parsons et al., 2013). Both primary beam and fluorescence signals are affected by the distance to the target because photon intensity exponentially decreases with distance travelled and this can be varied by a range of operational stability influences. In the field, PXRF instruments are often operated by hand (Chakraborty et al., 2017), and hand movement instability will alter quantification. For example,

slight lateral movements of the analyzer window effectively change the area of analysis mid-measurement, or slight upright movements increase distance between sample and detector. Stabilisation devices are offered for in-situ measurements (e.g. the X-MET 920-P analyzer with swinging handle) (USEPA, 1998) to alleviate this but little used, although most operators adopt the benchtop stands offered for ex-situ operation that secure the instrument for operation in 'desktop mode' (e.g. the Innov-X Alpha series 4000 PXRF) (Kenna et al., 2011).

Numerous studies report that ex-situ PXRF analytical performance generally shows lower uncertainty compared with in-situ PXRF performance although operator hand stability is little considered in qualifying results. This is due to the aforementioned stability differences and additionally, ex-situ analyses are usually performed after basic sample preparations such as drying, grinding or sieving (Lemière, 2018). For example, using a 120 s scan time and a Niton PXRF, Ridings et al. (2000) compared As in-situ and ex-situ PXRF measurements against acid digestion protocols (EPA, 1996) and found that the PXRF performed better ex-situ (RSD 4% lower compared to in-situ). Ridings et al. (2000) attributed lower in-situ performance to interferences caused by moisture, heterogeneity and grain size where ex-situ analyses are usually performed after basic sample preparations such as drying, grinding or sieving. Nevertheless, ex-situ measurements may also be affected by variable sample placement on the analyzer window particularly if the matrix is light (e.g. peat or plant matter) relative to the analyte (e.g. cesium) as theoretically, critical thickness increases for light matrix samples and analyte signal contribution may occur from deeper and more lateral regions of the sample (Fig. 1). For example, critical thickness varies between 30 µm and 12 mm for potassium and cerium respectively within Rhyolite which is a solid rock (Parsons et al., 2013).

In soils, if the area from which signal contribution could occur were to be replaced with air (due to imperfect sample placement), then this could introduce additional variability into measurements. Heavier analytes are primarily quantified by PXRF using the L_α X-ray energy in lieu of their K_α lines. This is in part because current silicon based PXRF sensors are inefficient at capturing higher energy photons above 30 keV (Redus et al., 2009). Cadmium-telluride (CdTe) X-ray sensors have been developed which possess higher stopping power for high energy photons (Redus et al., 2009). The prospect of their integration into existing PXRF instrumentation to compliment the information captured by the silicon detector may be useful as this could enable better quantification of heavier analytes such as gold or uranium (Glanzman and Closs, 2007). Capturing the K_α characteristic lines for heavier elements will also theoretically increase the representativeness of the measurements obtained however, it may also necessitate further vigilance with respect to critical sample dimensions and sample placement. This is not a problem for in-situ measurements and is similar in nature to the "infinite thickness" issues discussed in Section 2.7. Elementally specific assessment of operator hand stability during in-situ measurements, and ex-situ sample placement for heavy-analyte light-matrix samples in particular remain research gaps to determine relative importance for uncertainty in quantitation (Ellison and Williams, 2012; Ramsey and Ellison, 2019). Development of a sample holder for ex-situ set-ups is recommended to increase consistency between measurements and prevent potential sample placement issues.

2.6. Protective thin film thickness and composition

Samples prepared for ex-situ PXRF analyses are typically sealed in containers by a protective thin film polymer preventing contamination of the PXRF instrument (Tighe et al., 2018). A range of film material and thicknesses have been used or recommended as depicted in Table 4 (e.g. 1.5 µm to 50 µm). The thin film acts as an additional barrier between sample and X-ray detector and will attenuate or scatter fluorescence signals to some extent (Parsons et al., 2013). Low energy fluorescence signatures from light elements are particularly susceptible to attenuation, however, thin films exert negligible attenuation effects on

Table 4

Variable X-ray thin films employed or recommended in different studies (different brands, thicknesses and materials).

Polymer Composition	Thickness	Provided Information or Author Commentary	Reference
Mylar, Kapton, Spectrolene, Polypropylene	2.5–6 μm	The polymer types and thickness ranges listed to the left can be used for instrumental protection.	USEPA (2007b)
Mylar, Prolene	1.5 μm	Micro-fine mylar film or prolene can be used for instrumental protection.	Tighe et al. (2018)
Polypropylene	4 μm	TF-240 film from Fluxana Bedburg-Hau, Germany	Shand and Wendler (2014)
Mylar	3.6 μm	Chemplex Mylar X-ray Film	Rouillon and Taylor (2016)
Polypropylene	4 μm	Premier Lab Supply Model TF-240–255	Ravansari and Lemke (2018)
Mylar or Polypropylene	5 μm	Recommended that if plastic bags are employed, the analyzer should be calibrated using the same plastic type and thickness to minimize effects.	Kalnicky and Singhvi (2001)
Mylar/LDPE	6 μm/50 μm	Protective film influence is negligible for arsenic but lighter elements are affected to a greater degree, particularly for thicker films.	Parsons et al. (2013)

heavier elements (Kalnicky and Singhvi, 2001) such as As (Parsons et al., 2013). In the context of these discussions, specific Z cut-offs for what constitutes a "heavy" versus "light" element are left as ambiguous because these attenuation effects will vary depending on the employed thin film properties and the analyte's fluorescence energy, therefore they should be judged on a case by case basis.

Use of thicker protective barriers such as 50 μm thick LDPE sample bags or protective X-ray thin sheets placed on the ground may be convenient for preventing instrumental contamination during in-situ analyses but significant effects on PXRF measurements for lighter elements may occur (Parsons et al., 2013). Calibrations including the barrier effects may mitigate this to some extent, but if the analyte is too light or the barrier too thick, sufficient signal acquisition may be impossible. The effects of protective barriers employed for both in-situ or ex-situ analyses must be determined on a case by case basis due to the influence of a variety of factors (sheet thickness, composition, density, analyte fluorescence energy, and the potential presence of impurities) (Fig. 1). For example, a 50 μm polypropylene barrier attenuates 94% of the aluminum K_{α} signal (Henke, 2019). X-ray attenuation and transmission through a material are related by a simple equation; the sum of attenuation and transmission is equal to unity. Convenient resources such as the United States Lawrence Berkeley National Laboratory's X-ray optics calculators are available and can be used to compute X-ray transmission values for a given material enabling analysts to gauge the effects of protective barriers on elementally specific analyte signals (Henke, 2019).

Graphene is potentially useful for serving as a protective X-ray film on account of its low attenuation and high tensile strength. Graphene paper is commercially available (Sigma-Aldrich, 2018) and its cost has been decreasing with time and is projected to decrease further (Novoselov et al., 2012; Ren and Cheng, 2014; Zurutuza and Marinelli, 2014). Graphene is comprised of only carbon atoms and possesses a tensile strength (TS) of 130 GPa (Novoselov et al., 2012) which is orders of magnitude greater than current X-ray thin films (Table 4) possessing TS in the megapascal range. This makes it a good choice to reduce the risk of accidental instrumental contamination due to protective thin film damage (Kolmakov et al., 2011). Graphene may be most useful for field applications where light element signal acquisition is required and rough field conditions necessitate good protection to prevent instrumental contamination. Others have used graphene materials as protective instrument/environment interfacial barriers (e.g. X-ray photoelectron spectroscopy (Kolmakov et al., 2011)) however, its specific employment for in-situ PXRF measurements was not found in the literature. Detailed reporting of film use is essential in any PXRF application and the use of emerging thin films should be investigated.

2.7. X-ray energies, sample thickness and width

Instruments may be fine-tuned for detecting specific analyte(s) by adjusting tube voltage settings so that the primary beam energy is slightly higher than the K_{α} or L_{α} energies of the elements of interest thus limiting excitation by the primary beam. This prevents the analyte signal from being "swamped out" by background noise and also limits potential interferences or false positives in the spectra due to secondary excitation (Tighe et al., 2018). Incident beam energy can be further controlled by applying filters to remove X-ray energies that are not of interest thus reducing noise and background signals (Gilmore, 1968). For example, McLaren et al. (2012) improved the USEPA (1998) quality classification of their data from quantitative to the definitive level (Table 2) for Mn in Vertisol soils using a Bruker Tracer III-V PXRF by controlling the instrument tube voltage and filter settings (e.g. 15 KeV for light and 40 KeV heavy elements). However, analysts should be aware that effective depth of analysis may be the most limiting factor when optimizing energy settings or filter use.

Elemental concentrations determined by PXRF are based on the detected egressing fluorescence. Egressing fluorescence critical thickness is the maximum path length analyte signals can travel within the sample's matrix before 99% of the signal is attenuated. When a sample's thickness is greater than the analyte specific critical thickness, the sample is considered "infinitely thick" for the given analyte. Sample thickness can affect PXRF measurements if analyses are not conducted on infinitely thick samples (Kalnicky and Singhvi, 2001) or if calibrations are created using such samples. For example, Holmes (1981) analyzed filter membranes (not infinitely thick) loaded with variable masses of powdered obsidian and demonstrated that at low membrane mass loadings XRF signal intensity is a linear function of the sample mass. This occurs because if samples are not infinitely thick, detected intensities may be lower because the area from which signal contribution could occur may be replaced by air. Analysts are also reminded that some soils expand and swell when exposed to water (Lee et al., 2001). For example, Wilson et al. (2013) showed that exposure of a Vertisol sample to water caused it to expand > 19%. Peng et al. (2007) showed that an organic rich Eutic Histosol and a Histic Gleysol varied in pore volume between 23.6% and 60.1% in response to wetting and drying cycles. These effects complicate measurements via competing factors such as increases in attenuation from the displacement of air within soil pore spaces and decreases in attenuation from potential swelling. Theoretically, variation in volume and critical thicknesses due to variable water content can affect detected fluorescence intensity which will increase variability in rendered measurements (most notably a decrease due to both scatter/attenuation and the narrower angle of detectable outgoing fluorescence as distance increases back to the detector) (Fig. 2). Deviation of PXRF measurements due to variability in critical thicknesses may also be applicable to soil organic content and may potentially explain the elementally dependent deviations in PXRF response from theoretical values observed by Ravansari and Lemke (2018) with increasing soil organic content. The literature is inconsistent regarding required sample thickness, and a consensus has not been reached on what constitutes a generalized infinite sample
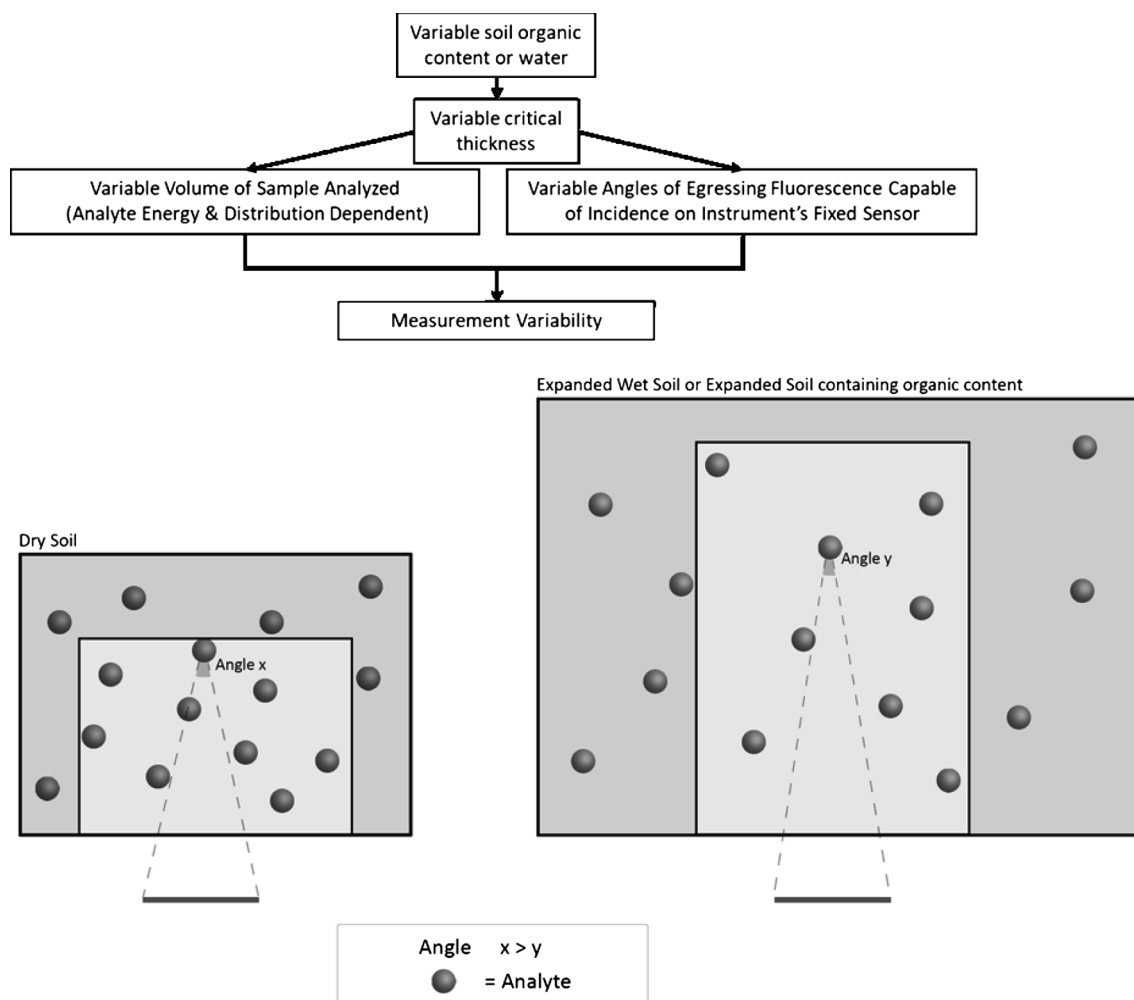
Fig. 2. Variability in soil organic content or water can affect shrink-swell or density characteristics of soils affecting depth of detectable egressing signal origin. Analyte signals originating deeper within the sample are less likely to be detected by the instrument because of the narrower range of egression angles capable of incidence upon the instrument's fixed sensor (Schoonjans et al., 2012). Additionally, this variability in depth of signal origin may also affect analyzed volumes of sample, and thus measurements. These phenomena introduce other dimensions of variability to PXRF measurements beyond attenuation and scattering. The effects and relative importance of these phenomena should be investigated using simulation methods, e.g. XMI-MSIM software developed by Schoonjans et al. (2012).

thickness. Some generalized cited values demonstrating this inconsistency include 5 mm (Kalnicky and Singhvi, 2001; Shand and Wendler, 2014), 5–6 mm (Morona et al., 2017), 1–2 cm (Palmer et al., 2009; Weindorf et al. ,2014b), 2 cm (Ravansari and Lemke, 2018), to 2.5 cm (USEPA, 1998) for a range of elements. Parsons et al. (2013) rightfully state that generalized sample critical thicknesses are invalid because a beam will penetrate a sample to varying degrees based on inherently unique sample properties such as density and internal constituents, i.e. a one size fits all approach is problematic.

As with problems posed by X-ray penetration depth, sample container diameter influences detected fluorescence because of potential lateral signal contribution, making it important to use analysis containers of infinitely wide dimensions (IAEA, 2005). Recommended values for containers range from 25 mm to > 40 mm with no general consensus (IAEA, 2005; Shand and Wendler, 2014; USEPA, 2007b). Both critical thickness and diameter values will vary greatly between different analytes and matrix types (Fig. 3). Issues relating to critical analysis dimensions are less problematic when performing in-situ PXRF measurements directly on soil profiles because the profiles can be considered infinitely thick and wide. However, if performing ex-situ analyses using sample containers or bags, infinitely thick and wide dimensions should be employed (IAEA, 2005; USEPA, 2007b). Special attention is required for high organic soils as critical dimension values may be unusually high. Matrix dependent critical dimension values for

the analyte with the highest X-ray fluorescence energy should be determined, as this analyte will require the highest sample thickness and width. A standard technique for assessing these critical dimensions is required and further work is needed. Fulfilling sample dimensional requirements for that analyte automatically satisfies the requirements for the other analytes within the study possessing lower fluorescence energies (Fig. 1).

2.8. Effective and representative sample volume of analyses

Representative volume [contemporarily referred to as representative elementary volume (REV) or representative volume element (RVE)] was first described by Hill (1963) as a unit volume that "is structurally entirely typical of the whole mixture on average." Low effective volumes of analyses characteristic of light elements are problematic because they may not be representative of the whole soil sample. For PXRF analysis of soils, as volume of analysis increases measurements will converge on the REV value (Ostoja-Starzewski, 2006). Low effective analysis depths cause low effective volumes of measurements which are problematic because those measurements may not be representative of the bulk sample. This problem is related to the previously discussed penetration depth issue but warrants a discussion here in the context of how these element and matrix specific penetration depths affect mass and volume of analyses which in turn affect
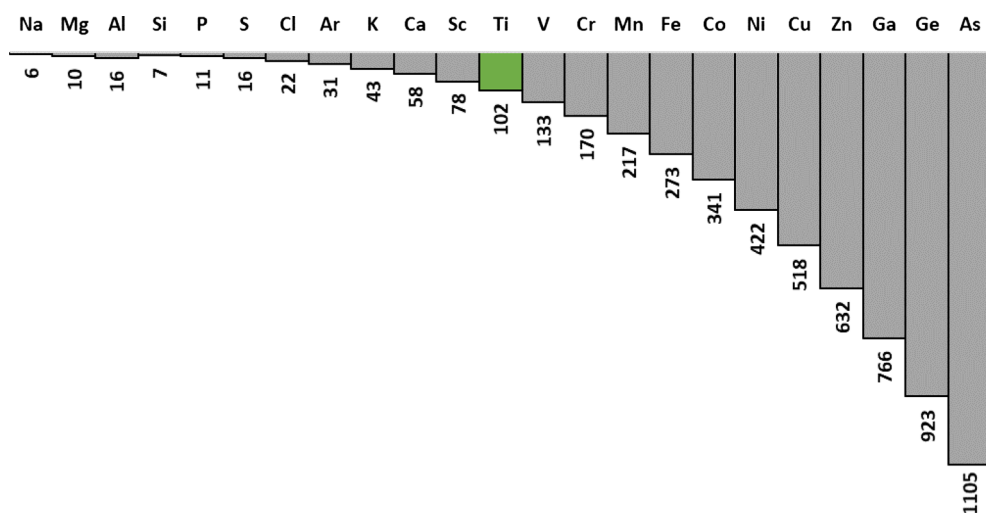
Fig. 3. Maximum egressing X-ray escape path length in µm for different elements contained in a solid slab of SiO_2 (Ti in green). This figure illustrates the maximum path length (effective depth of analyses) different element fluorescence signatures can take to escape a solid piece of SiO_2 before 99% of the signal is attenuated by the sample itself. The data used to compute and generate this figure was obtained from the XCOM Database (Nist et al., 2010) and the Transition Energies Database (NIST, 2005).

variability and representativeness of measurements. Both egression and penetration depths of X-rays vary depending on fluorescence energy and matrix. An example of this phenomenon is provided in Fig. 3, which shows the effective depths of analyses for different elements in a silica matrix as a simple surrogate for the effect in soil. Effective volume of sample analyzed decreases with decreasing Z due to the attenuation of the low characteristic fluorescence energies by the sample. Special considerations should be given to element specific effective volume of analysis (Ravansari and Lemke, 2018) to ensure representativeness of the sample, and to minimise the probability of a large nugget effect (high variance in measurements) for low Z elements (Rostron and Ramsey, 2017).

An example of this high variance stemming from low effective volumes of analysis is given in Fig. 4 for Ti. Even with concentrations well above the instrumental detection limits, Ravansari and Lemke (2018) noted large differences in results when the same sample was disturbed between analyses (52.7% heterogeneity variance component). A large portion of measurement variance for Ti stemmed from sample heterogeneity due to its low characteristic fluorescence energy and thus low effective volume of analysis – perhaps also further exasperated by its presence within nugget prone accessory minerals (Rostron and Ramsey, 2017). They concluded that effective volumes of analyses should be considered when conducting measurements using PXRF. A potential solution to this conundrum may be to artificially increase the volume of

analysis on a sample by performing replicate measurements between sample disturbances and averaging results. A control chart of the running average on repeated measurements may indicate that the average converges and stabilizes on the true REV concentration value and that the number of repeat measurements required to reach the REV may be elementally dependent. A higher number of repeat measurements may be required for lighter elements because of their lower effective volumes of analyses. Ramsey and Ellison (2019) recommends expressing uncertainty in a way that includes contribution arising from heterogeneity. A suggested area of further research is to develop a PXRF instrument consisting of a mobile sensor and/or source capable of movement to increase the effective volumes of analysis to REV levels and allow characterization of vertically stratified elements which are currently out of reach of conventional PXRF instruments. Development of an intrusive soil-specific PXRF device is recommended to mitigate these issues.

2.9. Interferences & detector resolution

Elements with similar fluorescence signatures may cause interference during quantification caused by an overlapped spectrum (USEPA, 2007b). The degree to which two elemental peaks can be differentiated is dependent on the instrument resolution, typically measured in electron volts (eV). If the resolution of the instrument is lower than the difference in characteristic fluorescence then X-ray counts between those elements cannot be resolved (Fig. 1), termed spectral overlap. For example, the Pb L_α and the As K_α energies are very similar (10.55 KeV and 10.53 KeV respectively) (Gałuszka et al., 2015; Kilbride et al., 2006). Lighter elements possess peaks that are closer to each other than heavier elements (Fig. 5). The resolution of silicon (Si) based X-ray detectors are dependent on the incident X-ray energies; however, they are typically reported by PXRF manufacturers only at the Mn K_α X-ray energy of 5.9 keV. The theoretical maximum resolution achievable by Si based energy dispersive X-ray detectors (referred to as the "Fano limit") is 118 eV for the Mn K_α X-ray energy of 5.9 keV (Lechner et al., 2004). This is of limited usefulness given that the range of analytes examined with PXRF are commonly much greater than Mn and that conventional detector resolutions are very near their theoretical limits. Instrument uncertainty is instead primarily limited by the PXRF's quality of build and ancillary components (e.g. 8 µm beryllium versus 1 µm graphene window affecting instrument signal acquisition (Bruker, 2018), or the employment of Kapton tape as a protective barrier). Manufacturers should provide and analysts should seek out overall instrumental resolution and precision information for multiple energy levels prior to instrument purchase to assess the suitability of the PXRF for its intended purpose e.g. soil light element measurements.
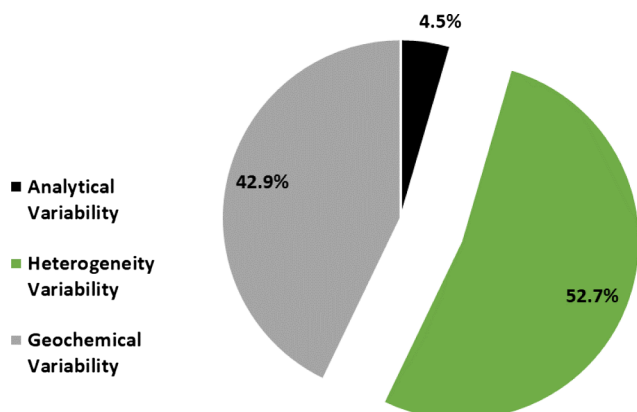

Fig. 4. ANOVA results on samples analyzed for Titanium (heterogeneity variance component for Ti in green). A large portion of variance arises from sample heterogeneity, which is attributed to the non-representative and low effective volume of analysis for Titanium. Data for this figure was obtained from Ravansari and Lemke (2018) and pie chart presentation . adapted from Argyraki et al. (1997)
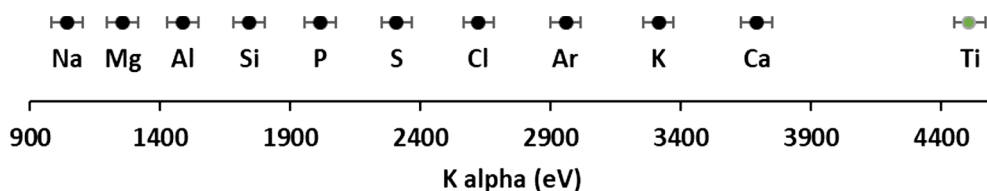
Fig. 5. K alpha fluorescence energies for select elements with atomic numbers 11–22 from left to right (Ti in green). The characteristic fluorescence energies for light elements are closer to each other which contributes to analytical variability (due to an overlapped spectrum) making lighter elements more difficult to measure via PXRF. Peak spacing increases with increasing elemental number thus overlapped spectrum problems are less severe for heavy elements. The spectral K alpha emission lines used to construct this figure were obtained directly from NIST (2005) and Bearden (1967). The error bars are associated with the **theoretical** maximum achievable **detector** resolution of 118 eV (i.e. ± 59 eV from the exact K_α) for Si based detectors at the Mn K_α X-ray line (Lechner et al., 2004).

Development of a standardized method for reporting of instrument precision and resolution at different energies by manufacturers for all advertised analytes is recommended.

2.10. Power source fluctuations and instrumental drift

Different battery packs are known to produce variability between replicate PXRF measurements. For example, Brand and Brand (2014) observed a 0.05% concentration change in Fe values (from 3.39% to 3.44% Fe) between battery pack changes. They suggested measurement variability caused by power source fluctuation could be mitigated by logging battery pack serial numbers with measurements thus enabling corrections, although little work is available to assess the usefulness of such an approach. Factors such as barometric pressure and humidity can also cause instrumental drift (Goodale et al., 2012; Merrill et al., 2018). For example Merrill et al. (2018) showed that light element signal acquisition was better at high altitudes due to the thinner atmosphere concluding that instruments lacking barometric pressure compensation tended to overestimate light element presence when measurements were conducted in a thin atmosphere environment (at high altitude). Other forms of PXRF instrumental drift are evident with long term repeated measurements under identical conditions showing signal deterioration over time especially for low Z elements (Kenna et al., 2011). Brand and Brand (2014) observed a 43% Si signal deterioration for an Olympus-Innov-X Delta Premium and a 40% Si signal deterioration for a Thermo-Niton XL3t GOLDD+ within a 2–5 month period. These signal changes may be due to increased leakage currents over time with deterioration of the silicon interface of detectors (Lechner et al., 2004) and is a consequence of the higher counts per second (cps) generated with new generation increased capability PXRF instrumentation (e.g. 250 k cps for a Bruker Tracer 5 g (Bruker, 2018)) and as high as 3 M cps for specialized R&D instrumentation (Barkan et al., 2015)). The high bombardment rates and higher rates of detector deterioration may necessitate close attention to signal change and regular maintenance. Therefore, it is critical that control charts and reference materials are applied throughout a project lifecycle (usually recommended as 1 in 10 samples, (USEPA, 2007b) to check for drift and verify the validity and applicability of calibrations developed in the past (and to re-develop calibrations if need be) (Fig. 1).

3. Considerations when utilizing comparative data in PXRF analysis

Portable XRF measurements are often validated against laboratory wet chemistry methods or independent CRMs so it is important to consider factors that may cause discrepancies between the two (McLaren et al., 2012; Parsons et al., 2013). Table 1 compares PXRF with various analytical methods.

3.1. Comparative volume of analysis

Wet chemistry techniques rely on acids to bring analytes of interest into solution to be subsequently analyzed via solution dependent instrumentation, such as inductively coupled plasma mass spectrometry (ICP-MS) (Shand and Wendler, 2014), flame atomic absorption (Flame AA) (Radu and Diamond, 2009), or inductively coupled plasma optical emission spectrometry (ICP-OES) (Yafa and Farmer, 2006). Acid digestion utilizes larger, more representative (0.5 g (USEPA (2007a)) volumes or masses of sample as compared with PXRF, which produces concentration measurements for the elementally specific effective volume of analyses (Ravansari and Lemke, 2018; Rostron and Ramsey, 2017). This can result in significant differences between the two outputs. Table 5 depicts the elementally dependent number of PXRF analyses required for the equivalent mass typically analyzed via digestion methods (0.5 g), e.g. 92 averaged replicate analyses for Ti. Analyzing the equivalent of 0.5 g is not necessary because soils are typically homogenized prior to ex-situ PXRF analyses and lower masses may be representative of the bulk sample. Analysts should consider that PXRF analysis of light elements may require higher number of averaged analyses with re-homogenization for convergence between measured and representative values (Fig. 1). Further work is required to define these convergence criteria for different analytes in variable matrixes.

3.2. Partial & total digestions

Even digestion methods using most strong acid combinations are incapable of total soil breakdown and thus tend to provide lesser concentration values as compared to PXRF or the less common total digestion methods (Sutherland, 2003). Depending on digestion methods employed, differences can be significant for soils derived from analyte rich parent material (high natural background levels) because such soils contain higher proportions of mineralogically recalcitrant elements inaccessible to partial digestion methods (Tighe et al., 2004; USEPA, 2007a). For sites with recalcitrant analytes, checks of recoveries on a small subset of site specific samples should be performed using a total measurement method such as hydrofluoric acid digestion or Neutron Activation Analysis (NAA) (Fig. 1). For example, McLaren et al. (2012) noted better (near 100%) recoveries and good correlations between XRF and NAA measurements for most elements in the NIST 2711a certified reference material as compared to aqua regia digestion. If use of strong solvents or NAA is not possible, CRMs may serve a similar purpose. Certified reference materials used are also important and should be similar to the study site soils. It may prove difficult to find suitable CRMs because soils are inherently site specific. However, for sites with low geogenic analyte presence, some partial digestion methods (e.g. aqua regia) may yield values close to total recovery digestion methods making measurements derived from such methods suitable for comparisons against PXRF measurements. Aqua regia is an incomplete digestion method and analysts need to check recoveries when making comparisons, but recoveries are often close to 100% for several elements of interest in contaminated or agriculturally relevant samples (McLaren et al., 2012; Tighe et al., 2004).

Comparability of measurements and appropriateness of validation between PXRF and wet chemistry methods can be assessed via total digestions (Parsons et al., 2013) or partial digestions that have repeatable known recoveries for a given matrix (Tighe et al., 2004). Data quality can be assessed using the criteria outlined by the USEPA (1998) (Table 2) and in many cases, it is the 1 to 1 criteria that excludes many relationships from the highest (definitive) tier of this hierarchy. In addition to assessing the performance of PXRF using confirmatory samples and these criteria, deviations from 100% recovery, and therefore bias caused by incomplete dissolution, may be corrected post-analysis. These types of relationships may be excluded from the

Table 5

Elementally dependent number of PXRF analyses required to analyze the equivalent mass typically analyzed via digestion methods (0.5 g). These numbers are unique to a solid SiO_2 matrix sample and were computed using the elementally dependent fluorescence effective depths of analyses presented in Fig. 3. For simplification, the depth from which 99% of signals can originate is considered "analyzed"; however, in reality there exists a gradient for detected signal contribution depending on how deep the analyte is located within the element and matrix dependent effective volume of analysis. A matrix density of $2.65\,g/cm^3$ and a detector area of $20\,mm^2$ is assumed. Readers are advised that these values are for illustrative purposes only and are meant to convey the general trend (higher energy fluorescence results in signal contribution from deeper within sample leading to a higher volume and mass of analysis).

Element	PXRF Analyses
Na	1587
Mg	962
Al	608
Si	1332
P	885
S	604
Cl	422
Ar	301
K	219
Ca	162
Sc	121
Ti	92
V	71
Cr	55
Mn	44
Fe	35
Co	28
Ni	22
Cu	18
Zn	15
Ga	12
Ge	10
As	9

"definitive" tier (Table 2) of the data quality assessment criteria set forth by the USEPA (1998) if digestion recoveries differ from total values, being classified instead as "quantitative – screening" or "qualitative – screening" even if the relationship is extremely strong. This is because PXRF values will not necessarily linearly scale with partial extraction or digestion values and analysts should consider these potential confounding factors when assessing PXRF performance using comparative measurements.

3.3. Calibrations

Many PXRF procedures exist to transform spectral information into concentrations, be it via empirical or factory calibrations. For example, empirical simple liner regression or theoretical fundamental parameters approaches have been used (Cuadros-Rodríguez et al., 2001; USEPA, 2007b) however, a discussion on these is beyond the scope of this review. A number of considerations for calibration can significantly improve quantitation and QA/QC. Soil specific or CRM calibrations are recommended instead of reliance on a PXRF's outputs (Fig. 1). In general, higher specificity in the soils used for calibration development may improve data quality (e.g. site-specific samples) although satisfactory results can be obtained with CRM or soil specific calibrations as well (USEPA, 2007b). Such empirical calibrations relating rendered concentrations or raw counts to reference values enable more accurate calibration of measurements on unknown samples (Rouillon and

Taylor, 2016). Portable XRF calibration curves developed using reference materials should be constructed using CRMs of similar composition to the samples undergoing analysis (USEPA, 2007b). Certified reference materials used for calibration cannot be used for any subsequent validation as they are not independent (Magnusson, 2014). Matrix matched calibrations relying on certified concentrations and empirical responses are not viable for organic rich soils because CRMs spanning a wide range in soil OM content with trace elements do not exist (Shand and Wendler, 2014) and in such cases, site specific or other specialized calibrations (section 2.1) are recommended instead (Fig. 1).

4. Conclusion

In this review, we have examined soil PXRF analyses and identified several aspects of its use and sources of variation that need further research to better ascertain their effects on outputs (including but not limited to water and OM). This review is not meant to serve as a step by step guide for using PXRF on soils, rather (given the complex nature of soils) it is meant to highlight considerations that may warrant vigilance from analysts. A new tool (Fig. 1) has been developed to elucidate considerations for would-be PXRF analysts. Despite noted knowledge gaps and the need for further research, PXRF application to soils has demonstrated highly repeatable and accurate results across a range of studies with low measurement uncertainty for heavy analytes present at concentrations well above instrumental detection limits. To advance our understanding of PXRF measurement variability, the relative importance of the noted potential sources of uncertainty should be assessed. Nevertheless, the largest component of PXRF measurement variance (especially for low Z elements) arises from sample heterogeneity theoretically exasperated by low effective volumes of analyses (particularly for in-situ measurements where soil is not often homogenized). Moving forward, analysts are reminded that water and OM *are* a part of soil matrix and can vary greatly within and across different soil types and sites affecting soil shrink-swell characteristics, critical thickness, the range of fluorescence egression angles capable of incidence on the detector depending on the depth of contributing signal origin, volume of analyses and ultimately PXRF measurements. Analysts are thus advised to tailor analysis regimens with analyte *and* matrix specific effective volumes of analyses in mind (Fig. 1).

Author contributions

R.R. and M.T. conceived the review. R.R. ideated and composed the review. M.T. and S.W contributed to the editing and writing of the manuscript.

Declaration of Competing Interest

The authors declare no competing interests.

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