PXRF METHOD DEVELOPMENT FOR ELEMENTAL ANALYSIS OF ARCHAEOLOGICAL SOIL*

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Portable X-ray fluorescence (pXRF) is now widely used for detecting the elemental composition of a material. Elemental analysis can enhance archaeological interpretations, such as mapping, preservation analysis and identifying anthropogenic activities. However, validated and reproducible protocols for analysing archaeological soil are still required. The elemental concentrations detected with three sets of preparation methods were compared: in-situ *(no preparation),* in-field *(analysing through plastic bags) and* ex-situ *analysis (laboratory-based preparation). Influential factors were also investigated: calibration parameter, moisture, homogeneity, sieve size and soil type. In-field analysis attempted to improve reliability without offsite processing, but instead substantially reduced elemental concentrations and skewed the proportional distributions.* Ex-situ *analysis significantly increased elemental concentrations and reduced variation. Proportional distribution was different between the three methods, but unchanged following homogenizing and sieving. These comparisons demonstrated that* ex-situ *analysis maximizes detection and ensures consistent samples.*

KEYWORDS: ARCHAEOLOGY, ELEMENTAL ANALYSIS, METHOD DEVELOPMENT, PORTABLE X-RAY FLUORESCENCE, SOIL ANALYSIS

INTRODUCTION

Interpretations of archaeological excavations can be enhanced through the use of elemental soil analysis for chemical visualization. Smejda *et al*. (2017) showed that human occupation caused long-term intensification of elemental content (P, K, S, Zn and Cu) over an extensive burial period at the Bronze and Iron Age settlement of Tel Burna. Gall (2012) used the intensified multi-elemental distribution at a farmstead to identify activity areas, cultural features and archaeological paints. Occupation phases and activities enrich the organic and calcium content of soil, and alter the distribution and forms of phosphorus present, distinguishing internal areas, domestic activities and food consumption zones (Middleton 2004; Migliavacca *et al*. 2013). Elemental soil analysis also allows mapping or surveying before excavation; Cannell *et al*. (2018) used P, Ca, Fe and Cu to delimit burial zones of an unmarked graveyard in Furuland. Preservation can be screened from soil; the abundance of Ti, Mn, Fe and Zr in soil contaminates artefacts and due to their insolubility result in diagenetic protection (Carvalho *et al*. 2004; Piga *et al*. 2011). In contrast, a high carbonate or Cl content will inform the urgency of conservation and the desalination process required (Neff *et al*. 2005). These applications show excellent capacity of elemental

analysis for visualizing the chemical conditions of an archaeological site. There remains a need for methods that provide accuracy and sufficient sensitivity without the accessibility, cost and destructive sampling issues in laboratory-based analytical techniques (Roxburgh *et al*. 2019).

Soil is a complex matrix of inorganic minerals, organic matter, water content and air (Wilson *et al*. 2008). Portable X-ray fluorescence (pXRF) is a technique used for the quantification of part of the inorganic elemental portion. It can be used for qualitative and quantitative analysis in a range of industries including agriculture, environmental, metalworking, plastics, textiles and archaeology (Weindorf *et al*. 2014b; Rouillon and Taylor 2016; Lemière 2018). Traditional XRF involves lab-based equipment, such as energy-dispersive XRF and wavelength-dispersive XRF (the latter achieving higher sensitivity at the cost of significantly more time and expense). In contrast, pXRF has received increasing use due to it being rapid, highly economic, portable and non-destructive (Peinado *et al*. 2010; Hayes 2013; Rouillon and Taylor 2016; Pîrnău *et al*. 2020). These features make pXRF more accessible and frequently applicable than lab-based XRF and other techniques for archaeological projects. Despite the frequent application of pXRF to archaeological material, the need and absence of valid, reliable protocols for archaeology is a recurring debate (Frahm 2013; Frahm *et al*. 2016; Goff *et al*. 2020). This paper investigates the key influential factors for enhancing pXRF analysis of soil through a systematic, controlled and experimental approach to produce a protocol ready for application to archaeological case studies. Quantifying these factors through such a systematic approach will allow well-informed recommendations.

PREPARATION METHODS FOR PXRF SOIL ANALYSIS

pXRF is a surface to near-surface technique, although the sample must be thick enough to absorb all the primary X-rays and fluoresce all secondary X-rays so that the material below the sample is not detected (otherwise known as infinite thickness; Markowicz and Van Grieken 2002; Sitko 2009). This ensures that that the elastically and inelastically scattered X-rays are contained within the sample, allowing an estimation of the density and mass from the measured signal. Inaccurate detections are reported when infinite thickness is not achieved (Markowicz and Van Grieken 2002; Sitko 2009). The X-ray penetration depth depends on the energy of the X-ray and the density of the material, with most of the fluorescence signal originating from the top several microns of the sample (Potts *et al*. 1997), though a sample thickness of > 2mm is generally deemed sufficient for achieving infinite thickness from soil (Kalnicky and Singhvi 2001).

Sample preparation is required for optimizing the sensitivity, reliability and elemental detection from pXRF. However, applications of pXRF to archaeology, geochemistry and other disciplines show a range of sample preparations available and may use reduced protocols when analysing soil (see Table 1 for a summary of previous applications). Some studies operate a 'point and shoot' approach without considering sample preparation, despite the wealth of method development (Frahm *et al*. 2016), such as the comparison of different sediment preparations when prospecting with pXRF by Hayes (2013).

hree distinct sets of protocols exist for pXRF analysis of archaeological soil, defined here as *in-situ*, in-field and *ex-situ*. The *in-situ* method consists of holding the pXRF directly against the soil and analysing it without extraction or sample preparation (Sahraoui and Hachicha 2017; Šmejda *et al*. 2018; Tian *et al*. 2018). The in-field method involves extracting a soil sample into a clear plastic bag and analysing it with the pXRF in contact with five different locations of the bag (Laiho and Perämäki 2005; Peinado *et al*. 2010; Thermo Scientific 2012; Shand and Wendler 2014; Backman *et al*. 2016; Rouillon and Taylor 2016; Tian *et al*. 2018). The *ex-situ* method involves extracting, fully drying, sieving and homogenizing soil before preparing it into

Table 1   *Summary of previous applications and preparation methods of soil portable X-ray fluorescence (pXRF) analysis*

Discipline	Methodology	Reference
Archaeology	Prospected a graveyard to identify potential graves. Calibrated pXRF, dried and homogenized soil (not sieved), and placed in sample cups with polypropylene film	Cannell *et al.* (2018)
	Air-dried, sieved and ground soil, pelleted with KBr. Analysed with calibrated XRF to identify the work and domestic areas of a house	Cook *et al.* (2014)
	Analysed moist soil and air-dried soil covered in polypropylene film. Next, dried, sieved and ground soil in a mortar to 120 μm, and analysed in a cup with polypropylene film	Hayes (2013)
	Analysed sieved, moist soil in sample cups for investigating the potential influence of pH	Kramer (2016)
	Compared bone against soil from an urn using soil ground into sample cups with Mylar film. Calibrated with Inductively Coupled Plasma (ICP) methods and used one measurement per sample	Pankowská *et al.* (2018)
	Milled and pelleted soil before scanning with XRF	Selskienė *et al.* (2017)
	Compared P analysis from pXRF with existing ICP data. Air-dried, sieved (2 mm, 250 μm, 125 μm) and ground samples with a mortar and pestle into cups with 4 μm Mylar thin film. Scanned for 180 s. Showed good comparability with ICP. pXRF could detect low P content in archaeological soil	Frahm *et al.* (2016)
	Human occupation results in long-term intensification of elemental soil content. Multi-elemental mapping with pXRF; direct contact (*in-situ*) for all samples in Soil Geochem mode (Innov-X) with 1-min scans. Nine were randomly selected for ICP, showing strong correlations	Smejda *et al.* (2017)
	Compared pXRF with ICP and acid extractions. pXRF: dried sediments (105° for 48 h), sieved at 2 mm, ground with a ball mill, placed into XRF cells with 4 μm film, scanned for 240 s in 'Mining Mode' (Niton XL3t). Showed good correlations, and applicability for pXRF in archaeological multi-element analysis	Lubos *et al.* (2016)
	Used pXRF to survey and delineate the topsoil of an archaeological fortress with multi-element analysis. Air dried and sieved soil samples (2 mm), analysed with 'Soil Mode' (Innov-X) for 60 s	Pîrnău *et al.* (2020)
	Surveyed soil by analysing in contact (without extraction) whilst 'Summer dry'. Submitted a selection of samples for ICP	Šmejda *et al.* (2018)
Contemporary soil	Ground soil dried in sunlight over 2 h and held in XRF sample cups with Mylar film	Bastos *et al.* (2012)
	Analysed samples in different containers (Chemplex and Mylar, food bag, Ziploc® bag) before and after drying. Internal calibration with certified reference materials	Mejía-Piña *et al.* (2016)
	Compared preparation methods on reference soil. Mixed soil by shaking in bag, sieved down to 74 μm, placed in XRF cup with Mylar film, analysed with factory calibrations	Rouillon and Taylor (2016)
	Analysed wet soil through a Ziploc bag, confirmed with ICP	Wu *et al.* (2012)

(*Continues*)

Table 1 *(Continued)*

Discipline	Methodology	Reference
Environmental and contaminant analysis	Sieved soil at 0–10% moisture to 2 mm and analysed through plastic bags after internal calibration	Peinado *et al.* (2010)
	Three pXRF comparisons: (1) field-moist; (2) dried, mechanically and manually ground into cups with 2 cm sample thickness and 3 μm Mylar film; and (3) samples pelleted with hydraulic press. All analysed in GeoChem mode. Compared against bench-top XRF. All three pXRF methods compared well with XRF, but sample preparation and calibration achieved the best results	Goff *et al.* (2020)
	Analysed soil *in-situ* followed by sieving. Showed contaminations of As, Cu and Pb in soil resulting from a nearby smelter	Fry *et al.* (2020)
	Compared scan modes and times using a Bruker pXRF for surveying tropical soils (air-dried, homogenized, 2 mm sieved samples in plastic bags), with scan mode having more impact	Silva *et al.* (2019)
	Analysed *ex-situ* pXRF data with kriging to produce maps that identified hotspots of heavy metal contaminations in soil	Chakraborty *et al.* (2017)
	Analysed soil with pXRF in direct contact to immediately inform where to focus subsequent *in-situ* scans when surveying a large site for heavy metal environmental contamination	Rouillon *et al.* (2017)
	Used pXRF to detect heavy metal contaminations in water samples, with comparisons against ICP showing good correlations and potential for a water-specific calibration in pXRF instruments	Pearson *et al.* (2018)
	Dried soil to < 20% moisture, sieved to 2 mm, homogenized sample in a bag and analysed through the bag. Recommended pelleting and additional scans for improved reliability	Laiho and Perämäki (2005)
Geochemistry	Scan soil through a plastic bag, typically in five different locations to improve reproducibility and scan quality	Backman *et al.* (2016)
	Topsoil survey with pXRF. Air-dried soil, homogenized with wood roller, sieved to 2 mm, mixed and analysed	Dao *et al.* (2012) Dao *et al.* (2013)
	Review of pXRF methods, but preparation not provided	Kalnicky and Singhvi (2001)
	Compared *in-situ*, dried, 40% moist and 'saturated' soil samples (sieved and pelleted)	Sahraoui and Hachicha (2017)
	Placed dry soil into sample cup with polypropylene film and analysed. Best consistency with ≥ 1.5 g of soil, low consistency with 0.5 and 1 g soil	Shand and Wendler (2014)
	Topsoil samples were ground and sieved to 2 mm. Compared field-moist, air-dried and sticky wet samples as they air-dried in one day	Stockmann *et al.* (2016)
	Analysed soil directly *in-situ*, followed by manual mixing and scanning through a plastic bag, then flattening bag and scanning (termed '*ex-situ*'), and finally air-drying, sieving to 2 mm and scanning through plastic bag. All scans were 30 s long	Tian *et al.* (2018)

(Continues)

Table 1   *(Continued)*

Discipline	Methodology	Reference
Guidelines	Instruction booklet on how to use pXRF. States soil should be prepared properly and placed in a sample cup. Scans should last a minimum of 30 s	Parsons Inc. (2016)
	EPA 6200 method for pXRF in-field screening of soil. Scanning in contact, or through plastic bags, must have a sub-selection submitted for laboratory analysis (dry if required, size to 2 mm, grind)	USEPA (2007)
	The Natural Resources Conservation Service (NRCS) detailed the calibration, standardization and scan modes for pXRF soil analysis. Limited information on preparation: air-drying, homogenizing and grinding samples (< 75 μm) achieves reproducibility	Soil Survey Staff (2014)
	Soil Science Society of America (SSSA) method: soil should be dried, grinded and sieved to 2 mm for pXRF analysis and to reflect typical soil preparation analysis with alternative techniques	Weindorf and Chakraborty (2016)
	International standards for onsite pXRF soil analysis provide limited information, with improved results achieved by holding samples in a plastic container, bag or cup, and optional sieving, drying and grinding steps	ISO (2013)
	Manual on how to use pXRF, stating to use sample cups and cotton wool to fill space (if needed) for infinite thickness	SERAS (2006)
Mercury detection	Calibrated pXRF with site-specific samples (homogenized but not sieved or dried), then analysed homogenized soil in direct contact	Brent *et al*. (2017)

vessels (plastic XRF sample cups), typically in lab-based applications (Thermo Scientific 2014; Parsons Inc. 2016; Lemière 2018). There is a range of practices encapsulated within *ex-situ* methods, such as milling, pressing and fusing powders (Lemière 2018; Goff *et al*. 2020). The *ex-situ* method used in this research involves manual grinding without pelleting because this does not require access to additional instrumentation.

The *in-situ* method is common for applications such as archaeometry, geology, mapping contaminated soils and sample screening due to the desire to exploit the rapid, simple and portable nature of pXRF in site-wide analyses (Hayes 2013; Frahm *et al*. 2016; Rouillon and Taylor 2016). The in-field method attempts to standardize the *in-situ* method whilst maintaining the portability and rapid data-gathering aspects of pXRF. However, matrix effects and moisture in unprocessed soil cause interference across all preparation methods and need accounting for with correction factors or by drying samples (Maruyama *et al*. 2008; Tian *et al*. 2018).

Moisture enhances the absorption of X-rays and scatters the primary X-rays, which together attenuate the refracting X-rays and effectively under-detect the 'true' value (Stockmann *et al*. 2016). Generally, soil moisture content < 20% is reported to cause nominal errors that may be ignored for admissible data (Piorek and Lopez-Avila 1998; Kalnicky and Singhvi 2001; Laiho and Perämäki 2005; Zhu *et al*. 2011; Mejía-Piña *et al*. 2016). However, several investigations into moisture content suggested that the effects have more impact than reported, but can be accounted for with correction formulae irrespective of the soil and archaeological site (Bastos *et al*. 2012; Stockmann *et al*. 2016; Sahraoui and Hachicha 2017). Padilla *et al*. (2019) showed that the Compton pXRF calibration cannot account for moisture despite reports suggesting it can, whereas the best results were achieved from dried samples with 10 cm thickness. *In-situ* analysis

in cold environments may require additional consideration; Weindorf *et al.* (2014a) showed significantly underestimated elemental concentrations in frozen soil samples, and higher elemental concentrations in refrozen samples due to enrichment by the melted ice sheets. These studies showed discrepancies in how detrimental moisture is when analysing archaeological soil. There remained a need to investigate soil across controlled, regular moisture intervals with the robust *ex-situ* methods to identify the point that moisture effects occur.

Ex-situ methods are recommended by manufacturers and research facilities but infrequently encountered in analyses of archaeological material (Table 1). The summary of pXRF applications in Table 1 emphasizes the absence of standardized sample preparation within each *in-situ*, in-field and *ex-situ* method. The direct impact of this variation on elemental concentration and validity remains unknown. Therefore, this paper investigated the impact of each stage of sample preparation to identify whether a necessity exists for *ex-situ* methodology as opposed to the more frequent *in-situ* applications of pXRF on archaeological soil. Although soil contains many elements, this paper focuses on those previously used in successful multi-elemental mapping of archaeological soil: Mg, Al, Si, P, S, Cl, K, Ca, Mn, Fe and Zn (Konrad *et al.* 1983; Middleton 2004; Wilson *et al.* 2008; Gall 2012; Smejda *et al.* 2017; Cannell *et al.* 2018; Horák *et al.* 2018; Šmejda *et al.* 2018).

METHODS

Commercial compost soil (John Innes No. 1, 3–4 nutrient range, pH6–7, 45% peat and high loam content) was examined following 13 stages of preparation (Table 2). Commercial compost was used to provide a consistent mixture of sediment and organic matter that may be encountered in archaeological applications that do not process soil. Chalk loam, chalk soil, clay loam, clay soil and sandy soil samples provided by UKGE Ltd were analysed with the *in-situ*, in-field and *ex-situ* methods in Table 2 after examining the preparation effects on compost to explore the implications for other soil types. The same samples were used to ensure comparability across each stage.

Samples were weighed before and after drying to determine the moisture content of the original sample using equation (1), resulting in a mean moisture content of 25.56%. Samples were manually homogenized with a mortar and pestle for 140 s per sample:

$$\text{Moisture content } (\%) = \frac{\text{Wet weight (g)} - \text{dry weight (g)}}{\text{Dry weight (g)}} \times 100 \qquad (1)$$

A Thermo Niton™ XL3t GOLDD+ pXRF with an Ag anode (6–50 kV, 0–200 μA max X-ray tube) was operated on battery power for all analyses. The pXRF was warmed up, system checked against the 1¼ Cr–½ Mo coupon (reference disc) inside the unit, and tested against blank and NIST 2709a standard reference material (SRM) to confirm that the pXRF unit was operating accurately ($y = 0.9731x - 0.0087$, $r^2 = 0.9998$, using the values provided in the NIST 2709a certification including: Mg, Al, Si, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Zr, Cd, Sb, Ba and Pb). The NIST 2709a is a San Joaquin soil, used because it was certified for most elements of interest within the single calibration sample. Samples were analysed in triplicate using the preinstalled fundamental parameters (Mining mode) unless specified otherwise, with 30-s scans with the main filter (50 kV, ≤ 50 μA), low filter (20 kV, ≤ 100 μA), high filter (50 kV, ≤ 40 μA), and 60-s scans with the light filter (6 kV, ≤ 200 μA).

Table 2   *Summary of the methodological stages for investigating the influences on the portable X-ray fluorescence (pXRF) analysis of soil*

Method stage	Description
0: Scan mode (equipment set-up)	Five dried, homogenized and 2mm-sieved compost samples were loaded into XRF sample cups (SPEX CertiPrep™ 3,529) until full, covered with 5μm polypropylene thin-film (SPEX™ SamplePrep 3,520 window film), and scanned in triplicate using Mining mode, followed by TestAll Geo mode. The same settings and filters used for both modes. The NIST 2709a SRM was scanned 20 times using Mining mode, followed by TestAll Geo mode
1: *In-situ* (unprocessed soil, contact scanning)	Unprocessed compost samples were loaded into cleaned sample cups with new film and scanned with the pXRF in contact with the film in three locations of the cup window
2: In-field (partially processed)	Samples from stage 1 were loaded into clear plastic sample bags and scanned with the pXRF in contact with the bag in three locations
3: *Ex-situ* (fully processed, laboratory-based)	Samples from stage 2 were dried overnight in an oven at 105°C, homogenized in a mortar and pestle by hand for 140s, sieved through a 2mm mesh sieve, loaded into sample cups with film and analysed. The mortar and pestle were cleaned with deionized water between each sample
Preparation effects on ex-situ *(laboratory-based) methods*	
4a: Heterogeneity	Samples were dried overnight, loaded into sample cups with film and scanned. Soil was weighed to 0.01g before and after drying to determine the moisture content
4b: Homogeneity	Dried samples were homogenized in a mortar and pestle by hand for 140s (forming the bulk), loaded into sample cups and analysed. The mortar and pestle were cleaned with deionized water between each sample
5a: 2mm sieve	Bulk, homogenized samples were sieved with a 2mm mesh sieve (forming the 2mm bulk), loaded into sample cups and analysed. This is the final preparation stage for typical *ex-situ* recommendations
5b: 425μm sieve	Samples were returned to the 2mm bulk, sieved through a 425μm mesh, disaggregated again, loaded into sample cups and analysed
5c: 300μm sieve	Samples were returned to the 425μm bulk, sieved through a 300μm mesh, loaded into sample cups and analysed
5d: 250μm sieve	Samples were returned to the 300μm bulk, sieved through a 250μm mesh, loaded into sample cups and analysed
5e: 106μm sieve	Samples were returned to the 250μm bulk, sieved through a 106μm mesh, loaded into sample cups and analysed
6: Moisture effects	Dried, homogenized and 2mm-sieved compost samples were portioned into seven sets of samples, placed into sample cups and analysed. Deionized water was added to 10g of these samples in 1g increments, resulting in 10% moisture content intervals up to 60% (1.2g increments for 10–20% moisture). The soil and water were briefly homogenized again to distribute the moisture evenly. Moistened samples were loaded into sample cups and analysed
7: Soil type	Five soil types (chalk loam, chalk soil, clay loam, clay soil and sandy soil, provided by UKGE Ltd) were scanned following the preparation in stages 1–3 (*in-situ*, in-field, *ex-situ*, respectively)

Note: The calibration parameter comparison stage was part of the experimental set-up and occurred first, but was not part of sample preparation, so was assigned to stage 0.

Data were analysed using R 3.4.0 (R Core Team 2017) using the *car* (Fox and Weisberg 2011), *DescTools* (Signorell 2016) and *PMCMR* (Pohlert 2015) packages. Data were first checked for normality using Q-Q plots of the residuals, and confirmed with Shapiro−Wilk tests. Data were

then checked for variance using Levene's tests. Only the comparisons with moisture content passed both assumptions; these were analysed using linear regression. All other comparisons were analysed using Kruskal–Wallis rank-sum tests, followed by Mann–Whitney *U*- or Nemenyi tests with chi-square (χ) distribution correction to identify significant differences between groups. The *ggplot2* package (Wickham 2016) was used to produce all graphs. Tukey box plots of the median and quartiles were produced to show the change in raw elemental concentration across method stages, faceted for each element. Additional faceted box plots were produced with proportional data (made relative to 100% of the total elemental content detected) to show the impact made to proportional elemental distribution between methods.

<div align="center">RESULTS AND DISCUSSION</div>

Experimental set-up: Calibration parameter

Three sets of calibrations were available for soil analysis: fundamental parameters (called *Mining* mode for Niton models, *Mining Plus* for Olympus Innov-X, and *Fundamental* or *GeoChem* for Bruker), Compton normalization (*Soil* for Niton and Olympus Innov-X, *Compton* for Bruker), and a hybrid of Compton–fundamental calibration (*TestAll Geo* for Niton, *Soils* for Bruker) (Conrey *et al*. 2014; Ross *et al*. 2014). Fundamental parameters detected elements Mg-Se, Ag and Au, whereas Compton normalization was excluded because it did not incorporate the light filter for elements Mg-S due to the calibration for quantifying traces of heavy elements (Radu and Diamond 2009; Migliavacca *et al*. 2013; Lemière 2018). Analysing compost soil with fundamental parameters and Compton–fundamental hybrid (Mining and TestAll Geo mode) showed no significant difference in overall concentration (the combined raw concentration of the elements of interest) ($F_{1,28} = 0.35$, $r^2 = 0.01$, $p = 0.56$), nor any elements individually except for Mn and Zn. Following this, the NIST 2709a standard was analysed 20 times using both parameters, resulting in a significantly higher overall concentration when using the Compton–fundamental hybrid ($F_{1,38} = 33.49$, $r^2 = 0.47$, $p < 0.001$), with most elements individually showing significant increases.

The objectives and target material must be considered when deciding which calibration parameter to use. The absence of significant differences with processed compost samples suggested that archaeologists could use either calibration parameter for analysing soil, although sample preparation still requires attention (e.g., McWhirt *et al*. 2012 showed that pXRF analysis of compost showed better error rates and correlations with ICP after drying). In contrast, increased concentrations from the NIST2709a were made when using the Compton–fundamental hybrid. Stapfer *et al*. (2019) observed similar effects, with fundamental parameters measuring Ti, V, Cr and Ba more accurately and Compton–fundamental measuring P, Ni, Cu and Pb more accurately. Both calibration parameters compared against the standards well ($y = 0.9731x - 0.0087$, $r^2 = 0.9998$ for fundamental and $y = 0.9931x + 0.001$, $r^2 = 0.9999$ for Compton–fundamental). However, TestAll Geo automatically selects the calibration parameter without informing the operator (Frahm *et al*. 2017; Lemière 2018; Stapfer *et al*. 2019). Furthermore, TestAll Geo has been removed from the Thermo Niton™ XL5. Therefore, fundamental parameters is more appropriate for most applications of analysing archaeological soils due to the consistency in calibration and between instrument models (Kalnicky and Singhvi 2001; Frahm *et al*. 2017; Lemière 2018).

Preparation method comparison

There was a significant difference in overall concentration (combined value of the concentration in the 11 elements of interest) across all sample preparation stages ($\chi^2 = 110.72$, d.f. $= 8$, $p < 0.001$)

(Fig. 1). There was also a significant difference in overall concentration when comparing the *in-situ*, in-field and *ex-situ* stages ($\chi^2 = 36.55$ d.f. $= 2$, $p < 0.001$). Nemenyi tests with chi-square showed that raw *ex-situ* concentration was significantly higher than *in-situ* and in-field concentrations for every element individually, except Mg and Mn (these were frequently below detection limits). The Nemenyi tests also showed that in-field concentration was significantly lower than *in-situ* concentration for Al, Si, P, S, K and Ca individually.

In-situ methods are not necessarily representative of the bulk composition, whereas processed soils are more representative and consistent but may introduce mineralogical effects (Kalnicky and Singhvi 2001; Laiho and Perämäki 2005; Maruyama *et al.* 2008). In-field methods use plastic bags to hold the soil sample, but analysing soil through the bags diffracts and dampens the X-ray signals (Shand and Wendler 2014). This was observed with the in-field method (stage 2) achieving a mean overall concentration 67% lower than the *in-situ* method (stage 1). In contrast, following full *ex-situ* sample and vessel preparation in stage 3 achieved a mean overall concentration 25% higher than stage 1. Given the Beer–Lambert law of attenuation, these effects vary depending on the bag and require correction (Parsons *et al.* 2013); this study used bags 3 mm
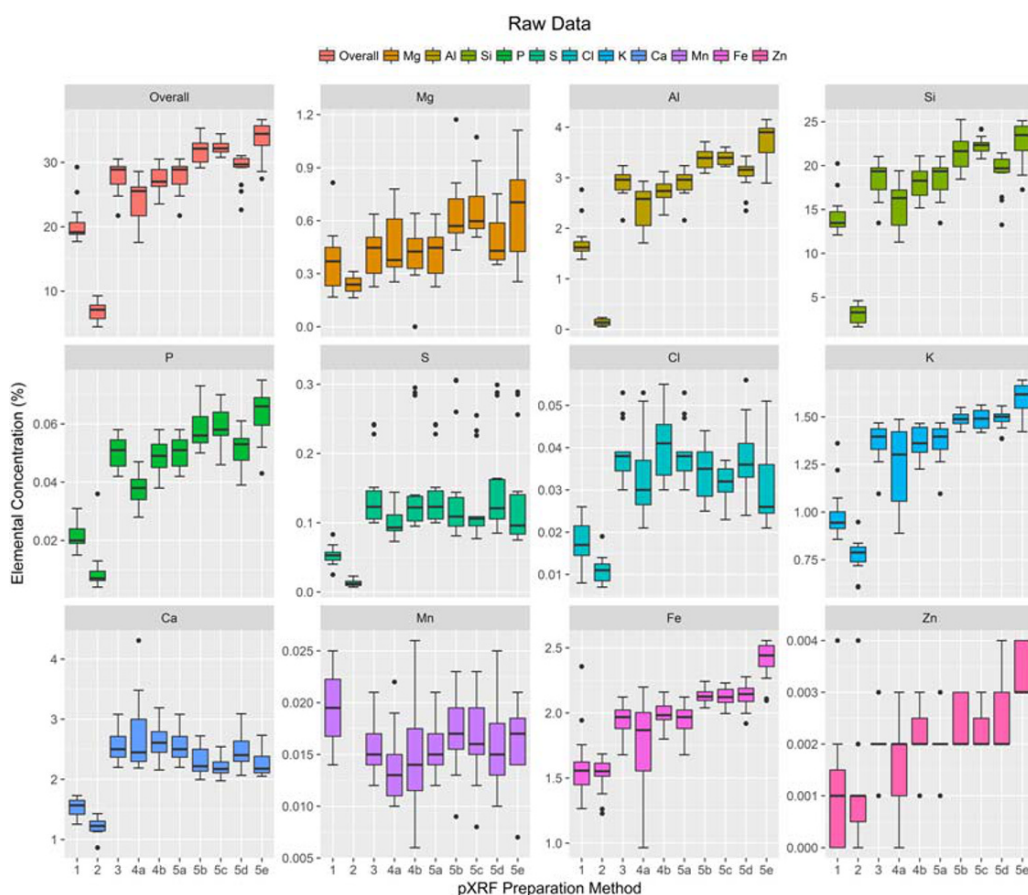

Figure 1 *Elemental concentration in compost across all preparation stages: stages 1–3 compare in-situ, in-field and ex-situ; stage 4 compares homogeneity; and stage 5 compares sieve size. Stages 3 and 5a are the same (dried, homogenized, sieved to 2 mm). [Colour figure can be viewed at wileyonlinelibrary.com]*

thick, whereas thinner bags or the 5 μm thin-film used *ex-situ* allow more signal through and thus detect higher elemental concentrations. These dampening effects were also demonstrated when Mejía-Piña *et al.* (2016) achieved highest elemental concentrations with Mylar XRF thin film and lowest concentrations with plastic and Ziploc® bags. Comparisons of thin film plastics show technological improvements, with polypropylene currently being the best option for optimizing signal and contamination although alternative films are available for specific applications (Parsons *et al.* 2013; Mejía-Piña *et al.* 2016; Ravansari *et al.* 2020).

Whilst raw elemental concentration was increased with *ex-situ* preparation methods, archaeologists might compare relative elemental content instead. However, Kruskal tests showed significant differences in the proportional concentration of individual elements across the three preparation methods. Most notably, the dampened signal effects caused by the plastic bags used with the in-field method produced a substantial, artificial increase in the proportion of K and Fe (Fig. 2). This means that investigating either raw *or* proportional elemental concentration with in-field methods is potentially unrepresentative of the soil and inappropriate for archaeological
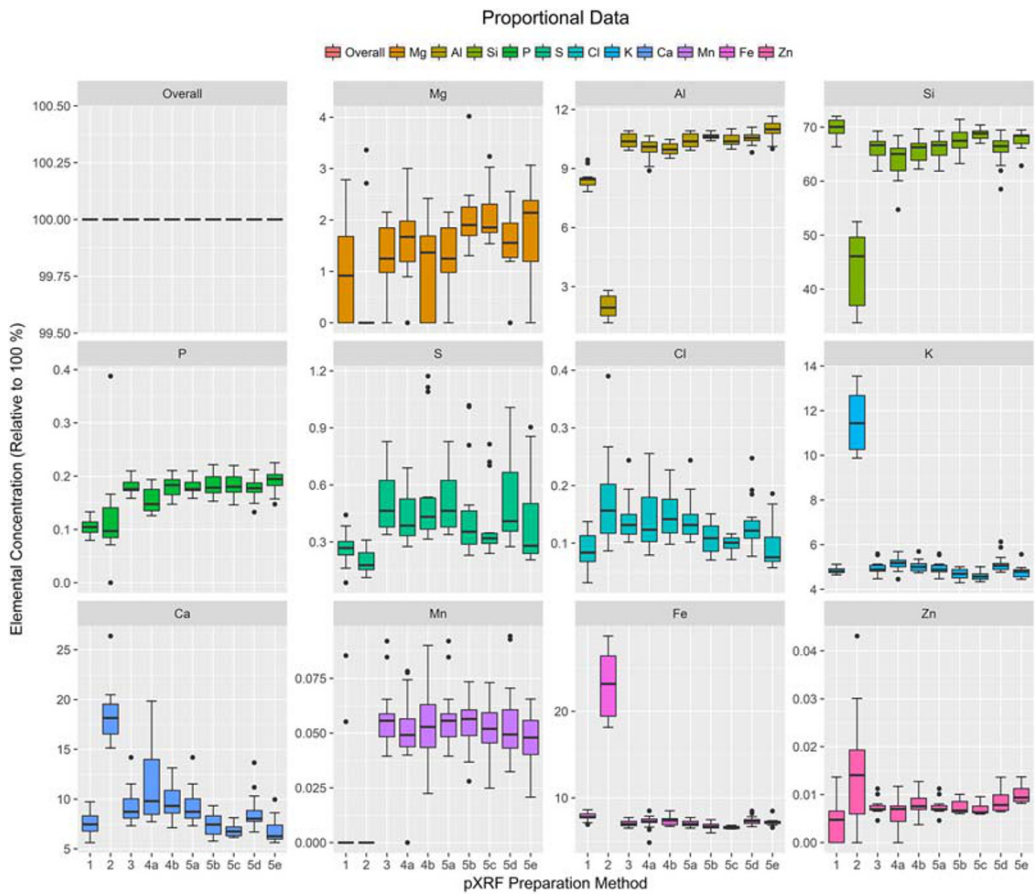

Figure 2   *Elemental concentration across all stages, proportional to 100% of the detected elemental content to show relative changes in distribution: stages 1–3 compare in-situ, in-field and ex-situ; stage 4 compares homogeneity; and stage 5 compares sieve size. Stages 3 and 5a are the same (dried, homogenized, sieved to 2 mm). [Colour figure can be viewed at wileyonlinelibrary.com]*

applications. The differences in proportional concentration also meant that ratios or proportional elemental content do not provide comparability between *in-situ* and *ex-situ* preparation methods, emphasizing the need for consistent sample preparation (Lemiere *et al.* 2014). This is relevant for all elements of interest.

Drying, homogenizing and sieving also contributed toward the sharp decline in the coefficient of variation (CV) of overall concentration from 15% with *in-situ*, or 20% with in-field, down to 7% with *ex-situ* (CV accounted for the substantial differences in concentration across stages). This was because homogenization provided a stable matrix for analysis by reducing the variability caused by the concretions, nodules, redox features and mineralogical characteristics that comprise soil. Overall, this clearly demonstrated the need for the robust *ex-situ* methods to ensure accurate and reliable pXRF analysis of soil.

Moisture effects

There was a significant decline in raw overall concentration when increasing the moisture content ($F_{10,64} = 118.2$, $r^2 = 0.94$, $p < 0.001$), with significant differences against the intercept observed at
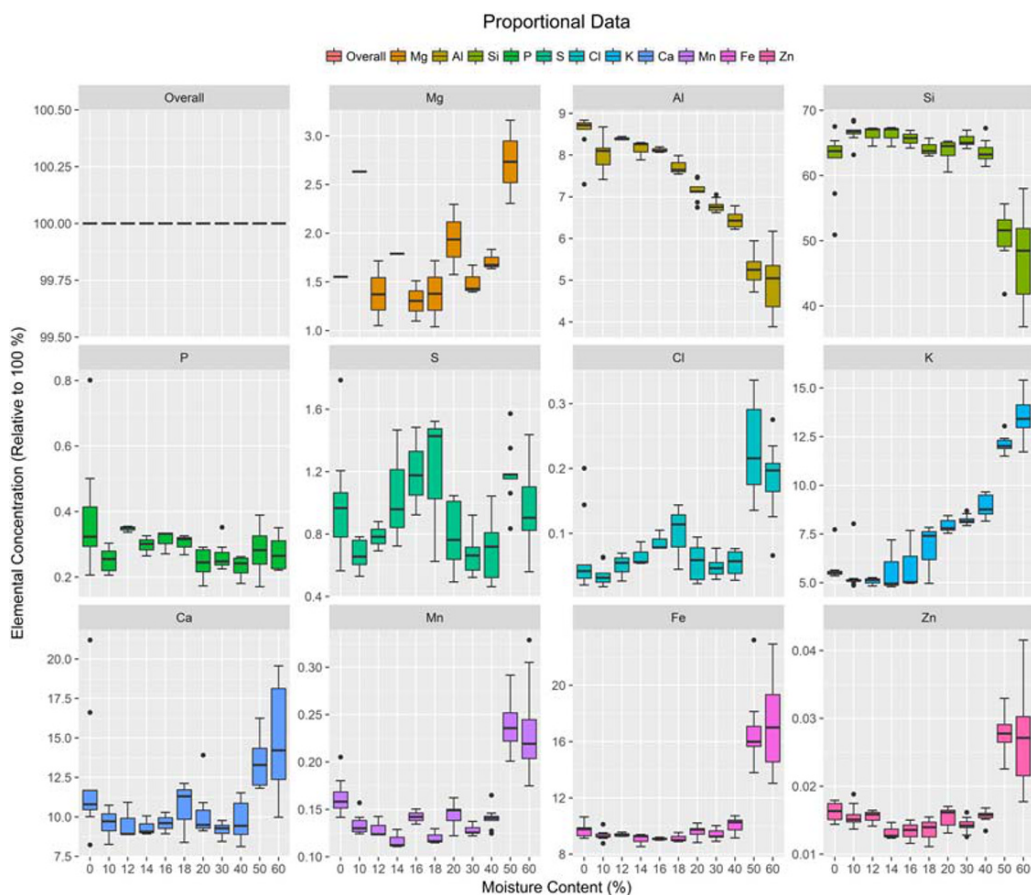

Figure 3   *Elemental concentration with increasing moisture content, proportional to 100%. [Colour figure can be viewed at wileyonlinelibrary.com]*

16–60% moisture. Individual Kruskal tests on the proportional elemental concentration (assumption tests failed) showed significant differences in the concentration of all elements individually with moisture content, except for Mg due to the frequent non-detections (Fig. 3).

The in-field protocol attempted to improve the detection quality and reproducibility from *in-situ* analysis, but still suffered from moisture effects. This investigation showed that moisture < 20% had significant effects on raw elemental concentration, contrasting with the nominal and admissible error conclusions by Kalnicky and Singhvi (2001) and Piorek and Lopez-Avila (1998). Less aggressive drying procedures such as air-drying soil may be sufficient for improving the concentration detected over unprocessed soils (Hayes 2013; Cook *et al*. 2014; Stockmann *et al*. 2016), although the low moisture content will need confirming before analysis.

In addition to the impact on raw elemental concentration, moisture significantly affected the proportional elemental concentration in soil. Reflection characteristics such as scattering and absorption are different for each element (Tjallingii *et al*. 2007; He *et al*. 2017). For example, the signal dampening effect from moisture is more significant on light elements, particularly Al and Si (Kido *et al*. 2006), whereas there is relatively little change observed in heavy elements (Tjallingii *et al*. 2007). This was demonstrated clearly in the proportional comparisons in Figure 3. Furthermore, the closely spaced K- and L-lines (transitional and heavier metals) of an atom can cause spectral interferences between elements, resulting in over- and underestimation with wider error ranges when one element is in particular abundance and overlapping elements are in trace amounts (Gallhofer and Lottermoser 2018; Lemière 2018; Ravansari and Lemke 2018). Removing moisture and amending the calibrations accounts for spectral interference in these situations (Goff *et al*. 2020; Ravansari *et al*. 2020). This has key implications for archaeological investigations, such as when comparing relative concentrations of elements across an excavation or between sites (Wilson *et al*. 2009; Horák *et al*. 2018), or when investigating the interaction between traces of P, S and Fe in vivianite-rich archaeological sediments (Taylor *et al*. 2019). Generic moisture correction formulae are inappropriate considering the variation across elements (Bastos *et al*. 2012; Stockmann *et al*. 2016; Sahraoui and Hachicha 2017). Examining fully dried soil is therefore more appropriate than estimating the corrected elemental content of moist soil.

Homogeneity

There was a significant difference in overall concentration after homogenizing dried soil samples ($\chi^2 = 7.61$, d.f. = 1, $p<0.01$) (stages 4a and in Fig. 1). Individual comparisons using Mann–Whitney *U*-tests with paired comparisons showed that Al ($V = 19$), Si (14), P (1), S (19), Cl (17.5), Fe (24), Zn (9) and overall concentration (13) were significantly higher with homogenization. Nemenyi tests showed no significant differences in the proportional concentration of any elements before and after homogenizing soil (Fig. 2).

The key purpose of homogenizing soil is to break down the large clumps of soil and mix the elements throughout the soil matrix (Laiho and Perämäki 2005; Brent *et al*. 2017; Luo and Bathurst 2017; Goff *et al*. 2020). These results showed that whilst homogenizing soil is required to increase the concentrations detected, there is no artificial impact on the relative distributions of all elements of interest. Whilst this may suggest that homogenizing soil may be unnecessary, it was essential for ensuring consistency across samples. Homogenizing soil also reduced the variation in concentration, such as reducing the CV of overall concentration from 8.92% to 8.16%. Homogenized soil can then be easily prepared more compactly into sample cups, assisting the establishment of infinite thickness (Markowicz and Grieken 2002; Sitko 2009; Lemière 2018).

These observations are supported by Brent *et al*. (2017), where repeated XRF scans showed variation due to soil homogeneity and not the method capabilities.

Sieve size

There was a significant difference between the concentration of all elements and decreasing sieve size ($\chi^2 = 54.30$, d.f. $= 5$, $p<0.001$) (stages 5a–e in Fig. 1). Nemenyi tests showed that unsieved samples (stage 4b) and samples sieved through a 2 mm sieve (stage 5a) were not significantly different for any individual elements, whilst they were both significantly different to 425, 300 and 106 μm for most elements individually. However, there were no significant differences in the proportional concentration of elements across all sieve sizes, except for K and Fe (when comparing 300 and 250 μm).

The differences in elemental concentration between sieves was expected to be small because the sizes used were relatively close together. When determining the necessary sieve size for *ex-situ* preparation, there was some conflict in the size to sieve soil. Laiho and Perämäki (2005) compared samples sieved to different sizes (not sieved, sieved to 2 mm, < 2 mm and < 0.5 mm), resulting in better and more consistent detection with smaller sieves. Other studies sieved with smaller meshes, including 1 mm (Cook *et al*. 2014; Theden-Ringl and Gadd 2017), 120 μm (Hayes 2013) and 74 μm (Rouillon and Taylor 2016). Whilst the current study observed some increases in raw concentration when sieving to 106 μm, proportional distributions were unchanged. Similar effects were observed by Maruyama *et al*. (2008), where small increases in concentration were observed with decreasing sieve size until sharp spikes in concentration were produced < 150 μm. Sieving soil to 106 μm was considerably unrepresentative of the original environment due to mineralogy sorting effects (Elliott and Cambardella 1991; Alostaz *et al*. 2008).

Recommended protocol

This study investigated the impact of soil preparation steps and compared the *in-situ*, in-field and *ex-situ* methods. As a result, the following protocol is recommended for archaeological soil analysis: extract soil samples from the site, dry overnight at 105°C, homogenize the soil, sieve with a 2 mm sieve and prepare into appropriate XRF cups with XRF film. Sample cups should be filled with soil to ensure infinite thickness of the target material (Shand and Wendler 2014), as opposed to packing empty space with cotton wool (SERAS 2006).

Scan times and settings appropriate to both the pXRF unit and target material should be used. Archaeological applications of pXRF colloquially cite scan times as short as 10 s per filter to be appropriate (e.g., Frahm *et al*. 2014). However, short scan times have significant error and inaccuracy, whereas excessively long scan times do not further improve accuracy (Kilbride *et al*. 2006; Hall *et al*. 2014; Parsons Inc. 2016; Schneider *et al*. 2016). A 30-s scan per filter, with an extra 20–30 s to fully detect the light elements (Huang *et al*. 2016), is deemed fast and accurate for most applications of pXRF including soil (Kilbride *et al*. 2006; Parsons Inc. 2016; Schneider *et al*. 2016).

Soil type

The examiner should remain aware of soil type when following the provided recommendations. Considering the range in soil type combinations and how their matrices contrast (Burnham *et al*. 1980; Blott and Pye 2001), analytical techniques that operate effectively irrespective of soil type are required. The elemental composition of the burial environment can contaminate artefacts

and, without consideration, may interfere with interpretations (Wilson *et al.* 2008; Wilke *et al.* 2016; Cannell *et al.* 2018).

Kruskal–Wallis tests showed a significant difference in overall concentration between the *in-situ*, in-field and *ex-situ* analysis of all soil types (Fig. 4): compost ($\chi^2 = 36.55$ d.f. = 2, $p < 0.001$) chalk loam ($\chi^2 = 23.143$, d.f. = 2, $p < 0.001$), chalk soil ($\chi^2 = 23.143$, d.f. = 2, $p < 0.001$), clay loam ($\chi^2 = 22.586$, d.f. = 2, $p < 0.001$), clay soil ($\chi^2 = 23.143$, d.f. = 2, $p < 0.001$) and sandy soil ($\chi^2 = 23.143$, d.f. = 2, $p < 0.001$). The in-field method consistently achieved the lowest concentration of each element individually whereas *ex-situ* preparation was consistently the highest. The wide variation in the concentration of each element between soil types was due to natural differences in the composition of soils.

These results showed that *ex-situ* preparation method is required for all soil types and not just compost. The interaction between elemental concentration and moisture content will be emphasized in certain soils (Stockmann *et al.* 2016). Sandy soils with a low saturation limit (< 30% moisture) will be more easily affected than samples with high saturation limits such as clay soils
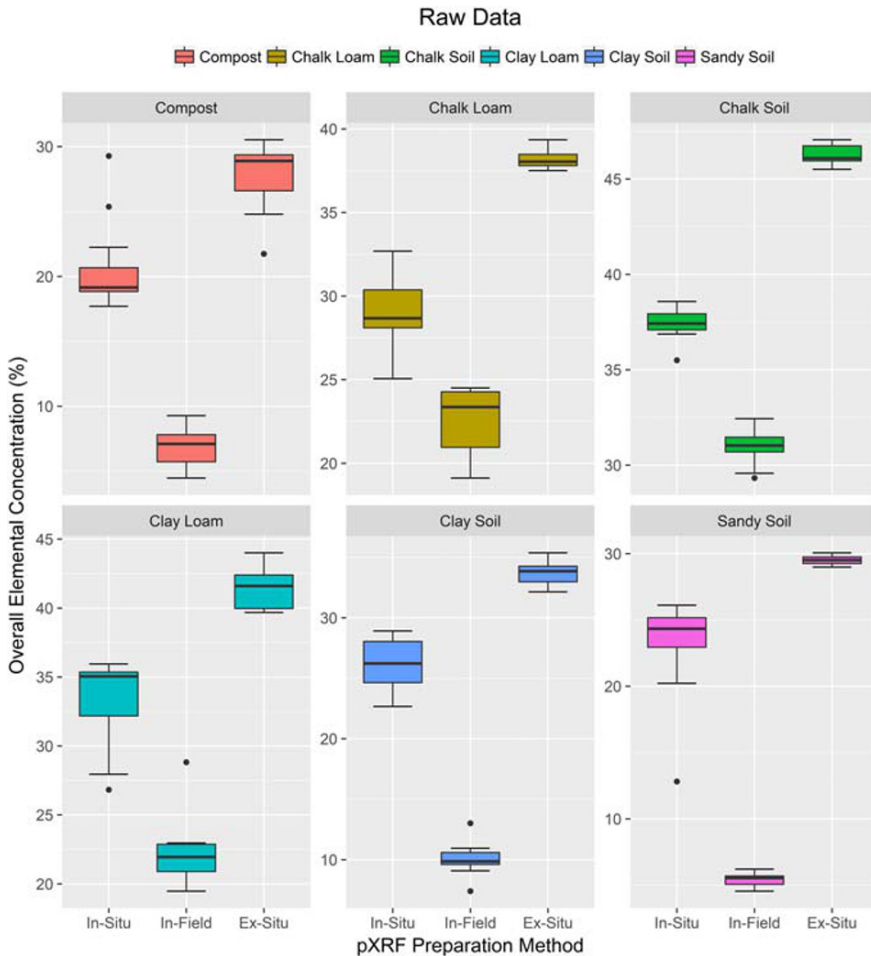

Figure 4   *Change in overall elemental concentration detected in the six different soil types when using the in-situ, in-field and ex-situ methods (stages 1–3). [Colour figure can be viewed at wileyonlinelibrary.com]*

and compost (35–50% and 40–60% saturation limits; Fulton 2009). Furthering the conclusions from moisture effects, establishing correction formulae that account for the wide range of soil types, their homogeneity, sieve size and interaction with moisture is unlikely (Laiho and Perämäki 2005; Bastos *et al*. 2012; Stockmann *et al*. 2016; Sahraoui and Hachicha 2017).

CONCLUSIONS

This paper sought to quantify systematically the influential factors on pXRF analysis of soil to identify and evaluate whether a necessity exists for sample preparation and the extent of preparation required. The significant and substantial increase in the detection of both *overall* elemental concentration and the concentration of *individual* elements achieved with the *ex-situ* method will prove invaluable for enhancing archaeological interpretations. Using the *ex-situ* method to increase the concentrations detected by pXRF improves the likelihood of identifying elemental traces surviving in soil over an extensive burial period. Furthermore, the impact on proportional concentrations showed that comparing proportional concentrations and ratios across sites, or investigating interactions between elements, is inappropriate without correct sample preparation. This was demonstrated clearly with the artificial bulking of the proportion of Fe and K content and non-detection of Mg with the in-field method, invalidating interpretations of these partially prepared soils. Using generic correction factors for partially processed soil is ineffective due to the variation on raw and proportional elemental concentration observed across each preparation stage.

Whilst each preparation step is important, demonstrating the insignificant difference in proportional concentration across *ex-situ* stages limited the preparation steps required for accurate data. Instead, the key advantage of homogenizing soil was for operational reproducibility and reduced variation (Luo and Bathurst 2017; Theden-Ringl and Gadd 2017). Sieving soil to remove debris, larger particles and assist with homogeneity is a standard stage of preparing soil for analysis, and should be applied to archaeological soil analysis, although sieving < 2 mm induced soil-sorting effects (Elliott and Cambardella 1991; Shand and Wendler 2014; Thermo Scientific 2014). Overall, this study showed that whilst pXRF can be operated without sample preparation for rapid surveying, improved elemental detection and reliability are achieved when following the recommended preparation procedures: complete drying of soil, homogenizing, sieving to 2 mm and loading into appropriate vessels. Whilst this does diminish the advantages of pXRF being a portable technique, analysis can still be completed in unfixed locations and does not require specialist sampling equipment, laboratory instrumentation or high operating costs. The recommendations provided in this paper enhance the capacity for pXRF in routine soil analysis and standard archaeological practice.

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<div align="center">SUPPORTING INFORMATION</div>

Additional supporting information may be found online in the Supporting Information section at the end of the article.

Data S1. Supporting information.