



Niall Hugh Marsay

Evaluation and Adaptation of Portable X-ray Fluorescence and Data
Fusion Techniques for Non-invasive Characterisation of Metal-
Contaminated Environments

Faculty of Engineering and Applied Sciences

PhD

Academic Year: 2020–2024

Supervisor: Carmen Alamar Gavidia

Associate Supervisor: Pablo Campo Moreno, Stuart Wagland

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Abstract

Metal extraction and refinement has left a legacy of brownfield and post metallurgical sites, which present risks to health and the environment. However, these sites present an opportunity to provide the critical resources needed to meet the global energy transition to net zero. A key barrier to the resource recovery and remediation of these sites is the expensive and slow surveying methods currently in use. Addressing this barrier, this PhD aimed to develop an innovative rapid, non-invasive method for quantifying elemental and speciated metals in contaminated soils using portable X-ray fluorescence (pXRF) and visible-near infrared (Vis-NIR) spectroscopy. Research investigated the applicability of these methods and evaluated the influence of sample preparation and inter-sample interferences through four objectives.

Firstly, when investigating the effects of sample pre-processing on ex-situ pXRF measurements of samples collected from a post-metallurgical site; it was identified that sieving and grinding improved pXRF precision (average relative standard deviation fell by 7.17% and 8.37% respectively); while drying and grinding enhanced pXRF accuracy (average r^2 increased by 0.03 and 0.10 respectively).

Secondly, the correlation of pXRF and geophysical measurements was investigated for the first time ever at a heterogeneous post-metallurgical site. No correlations ($r^2 < 0.46$) were observed between the two approaches, which was attributed to the differing sample volumes and depths measured by these methods. It was concluded that matrix heterogeneity and the scale disparity between geophysical and chemical sampling present significant challenges to rapid methodologies.

Thirdly, to overcome the interference caused by moisture and soil organic matter (SOM) on in-situ pXRF measurements, a novel data fusion framework using pXRF and Vis-NIR was developed. During its development, it was identified, for the first time, that moisture had an elementally dependent non-linear trend with substantial underpredictions by pXRF at ~15% moisture. Furthermore, this

research also showed, for the first time, that SOM caused an insubstantial but significant difference in performance of pXRF predictions. However, the data fusion framework successfully accounted for both moisture and SOM in all elements measured, with Ca showing the largest improvement ($r^2 = 0.308$).

And fourth, to predict to determine the feasibility of predicting metal speciation, a simplified, artificial sample matrix containing multiple iron compounds was again measured with both pXRF and Vis-NIR. This novel approach demonstrated for the first time that speciated Fe concentration can be accurately predicted ($r^2 = 0.96$) in a heterogeneous solid sample.

This PhD thesis proposes a best-practice methodology for ex-situ pXRF analysis, addressing the effects of sample preprocessing. The methodology can be immediately implemented to reduce financial cost of collecting data in contaminated land surveys. Additionally, through further development of the data fusion framework for in-situ measurements, significant time and cost savings can be achieved, allowing for increased data collection and the generation of qualitative models in the early stages of contaminated land assessments. Furthermore, this research demonstrates the potential to predict metal speciation, with the possibility of reducing the cost of speciation data acquisition. Such advancements would enable more targeted remediation and resource recovery efforts at contaminated sites

Keywords:

Portable X-ray fluorescence spectroscopy, heavy metals, data fusion, post-metallurgical sites, contaminated land, in-situ analysis, visible-near infrared spectroscopy, critical raw materials.

Acknowledgements

This thesis is dedicated to Shela Marsay,

My supportive and beloved Grandma.

I would like to express my deepest gratitude to my mum and dad for their unwavering support throughout my entire life. Without their encouragement, I would not have been able to begin, let alone complete, this thesis. Your support has been invaluable.

I would also like to thank my supervisors, Carmen, Pablo, and Stuart, for their guidance and feedback throughout my PhD. Without their input, this thesis would not have reached its current form, and I would not have developed into the scientist I am today.

Ben, from the start of this PhD to the end, you have been by my side as both a flatmate and a friend. Whether supporting each other's research or disagreeably agreeing on our cycles to university, living with you has been one of the highlights of the past four years.

Vanessa, thank you for being my friend all these years and for supporting me during the most challenging months of this journey, whether close by or from a distance.

To all my friends in the office, the technicians in the labs, and Jackie, Clare, and Tania, thank you for the time and energy you have devoted to supporting my work and me.

Lastly, Celeste, thank you for all the rants we have shared over the phone in the past 12 months your time will come too.

Thank you all for being an integral part of this journey.

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List of Abbreviations

portable X-ray fluorescence spectroscopy	pXRF
basic oxygen steelmaking	BOS
certified reference materials	CRM
coefficient of determination	R^2
conceptual site model	CSM
electrical resistivity tomography	ERT
electromagnetic induction	EMI
Granger-Ramanathan averaging	GRA
induction-coupled plasma	ICP
induction-coupled plasma mass spectrometry	ICP-MS
limit of detection	LOD
Lin's coordination correlation coefficient	r_c or ccc
mid-infrared spectroscopy	MIR
multiplicative scatter correction	MSC
nonlinear iterative partial least squares	NIPLS
ordinary least squares	OLS
outer-product analysis	OPA
partial least square regression	PLSR
partial least square support vector machine	PLS-SMV
Pearson's squared correlation coefficient	r^2
potentially toxic elements	PTE
potentially valuable elements	PVE
rare earth elements	REE
ratio of performance to interquartile range	RPIQ
relative standard deviation	RSD
root mean squared error	RMSE
soil organic matter	SOM
standard normal variate	SNV
support vector machine	SMV
U.S. Environmental Protection Agency	EPA
visible-near infrared spectroscopy	Vis-NIR
X-ray fluorescence spectroscopy	XRF

1 Introduction

1.1 Background: Post-metallurgical sites a problem and a solution.

Developed economies are increasingly extracting and refining heavy metals during their transition to green technologies. [1–3]. However, environmental sustainability remains an issue within this industry due to a poor record in the disposal of waste [4]. Between 2000 and 2013, 1,035 sites across the UK were identified which were contaminated with metal or metalloids. This accounts for 60% of all sites contaminated with potentially toxic chemicals identified by the environment agency (EA) [5]. Such sites can be sources of mobile pollution [6] which harm the environment and human health [7] and occupy otherwise valuable land. As such, remediating these sites is a pressing issue [8].

The current method of site investigation is a key barrier to the remediation of these sites. Currently, site investigations are designed according to the international standards ISO 2136:2020 and ASTM E2531 using a conceptual site model (CSM) methodology.

A CSM comprises three phases of increasing detail. The first phase is primarily a desk-based study gathering information site history, geology and hydrology with the potential for a brief “walk over” survey. If potential contamination cannot be ruled out the second phase “exploratory investigation” collects samples of soil and water to generate a qualitative model. If contamination is identified, then a third phase “detailed investigation” is required to generate a quantitative model of pollution concentrations and locations across the site. [9–11].

When investigating metal/metalloid contaminated sites samples are analysed in the laboratory using induction coupled plasma emission spectroscopy/mass spectrometry (ICP-ES/MS) and bench X-ray fluorescence spectroscopy (XRF). These instruments are effective at low concentrations with limit of detection (LOD)s of <0.01 and $<10 \text{ mg kg}^{-1}$, respectively, and can measure more than 20 elements simultaneously [12,13]. Despite this, these technologies are limited to laboratory analysis and can incur substantial costs due to the length and

complexity of sample preparation and quantification processes. In addition to these costs, current legislation requires site investigators to focus on identifying hazards to human health, waters, property, or ecological systems [5]. The combination of current legislation and instrumentation results in a missed opportunity to identify economically viable resources within these sites and potentially recover costs while contributing to the circular economy.

By 2026, the International Energy Agency forecasts that 95% of new global power capacity built each year will be renewable [14]. Renewable energy needs both more diverse and larger quantities of metals than previous technologies. As such, the European Union have identified 43 critical raw materials [15] while other studies have identified longer lists [3]. All of these are candidates to be included in site investigations to make their remediation more cost-effective as well as contribute to the circular economy.

1.2 Research project rationale: the limitations of portable spectrometers.

There is an evident need for new methods to be developed and implemented to enable rapid site investigations while simultaneously widening the scope of analytes. Portable X-ray fluorescence spectrometry (pXRF) [16], portable visible-near infrared (Vis-NIR) and mid-infrared (MIR) spectroscopy [17] have all shown promise as rapid on-site low-cost tools, that require minimal sample preparation for measuring heavy metals. While subsurface geophysical measurements, such as electromagnetic induction, have been combined with ICP-MS to predict subterranean metal concentrations [18]. However, limitations of each device have been identified such as interference from moisture and soil organic matter (SOM) for pXRF [16]; or models to predict metal concentrations from IR spectra being site-specific [19]. Moreover, both pXRF and IR are limited to measurement of samples at the surface or excavated from the site. Combining pXRF and IR spectroscopy using data fusion has also shown the potential to overcome their limitations and improve overall accuracy [20]. While the combination of portable instrumentation with sub-surface geophysical measurements may allow for the rapid three-dimensional modelling of a site [21].

Use of rapid analysis techniques (including pXRF and geophysical methods) has become widespread within the literature for analysing metal contamination in soil [16]. Yet a knowledge gap remains as these methods have not been applied to post-metallurgical sites. The ground at these sites is composed of a slag matrix, which is different to soil. This difference means methods applied previously to soil matrixes require reappraising to confirm their viability [16] in this new context. Teesworks has a history of over 170 years of steel-making and is now Europe's largest brownfield site [22]. At the eastern side of the site lies the long acres area which contained steal workings from the 1890s to 1970s. Later, it was used as a dumping ground for basic oxygen steal-making slag, creating an 18 m by 0.5 km² iron slag heap [23]. Making it an ideal location for the trial of untested methods. The findings of this study will have an impact on future site surveyors who will know which elements can be analysed by pXRF on slag sites and which elements will require analysis with traditional methods. As well as to avoid the use of geophysics as a way to define elemental concentrations in surface deposits.

Many studies have highlighted moisture and SOM as limitations of pXRF that can cause significant interference [24–26]. This interference is particularly important for in-situ measurement of contaminated sites given their dependence of moisture on weather and time of measurement or SOMs variation across a site. Despite their significance, only one study has investigated the effect of SOM while controlling other variables in a systematic manner such as element concentration [27]; and no studies have looked at moisture. Furthermore, few studies have investigated compensating for these effects using rapid measurement techniques [28]. Finally, studies have always focused on quantifying the total elemental concentration of metals [16], even though metals come in many distinct species (compounds) which have varying risks to the environment and require varying methods of extraction [29]. Therefore, to address this second knowledge gap research is required to investigate the effects of these interferences free from other variables to ascertain if they can be accounted for. Understanding and accounting for these interferences would increase the viability of in-situ measurement, as well as providing speciation/risk of the metals present at a site. Ultimately, it will increase the speed and accuracy of contaminated site surveys.

To fill the knowledge gaps identified, this PhD thesis aims to further the development of rapid characterisation methods underpinned by in-depth scientific analysis of inter-sample interferences, determining the limitations of established spectrographic approaches. The research makes a clear scientific contribution to knowledge by identifying the optimal method of sample processing to obtain the highest accuracy of ex-situ pXRF measurements; identifying the limitations of combining pXRF and geophysics; discerning the relationship between organic matter, moisture and pXRF signal; developing a data fusion method to account for these interferences; and discovering a novel combination of pXRF and diffuse Viz-NIR to predict metal concentration and speciation in a solid mixture.

1.3 Aims and Objectives

This PhD aims to further develop rapid, non-invasive methods for quantifying elemental and speciated metals in contaminated soils using portable X-ray fluorescence and the fusion of its data with visible-near infrared spectroscopy. The research will investigate the applicability of these methods and evaluate the influence of sample preparation and inter-sample interferences.

Objective 1. Determine the effects of pre-treatment on the accuracy of pXRF measurements of weathered ferric slag.

Objective 2. Investigate if pXRF and geophysical data correlate in post-metallurgical waste sites and develop a method to generate higher spatial resolution maps than would be practically possible with pXRF alone.

Objective 3. Develop a data fusion framework using pXRF and IR, to increase the accuracy of pXRF measurements of heavy metals in environmental matrixes.

Objective 4. Develop a data fusion framework using pXRF and IR spectrometry to predict metal speciation and concentration.

1.4 Thesis Outline

This thesis has been written in a paper format with the chapters written as individual papers (Chapters 2 – 5). As a result, there are elements of repetition in describing previous literature and methods.

Chapters within this thesis are grouped into two themes: (i) analysis of a post-metallurgical site with varying methods; and (ii) creation of an artificial sample to understand the effect of different variables on portable spectrometer measurements (Figure 1.1).

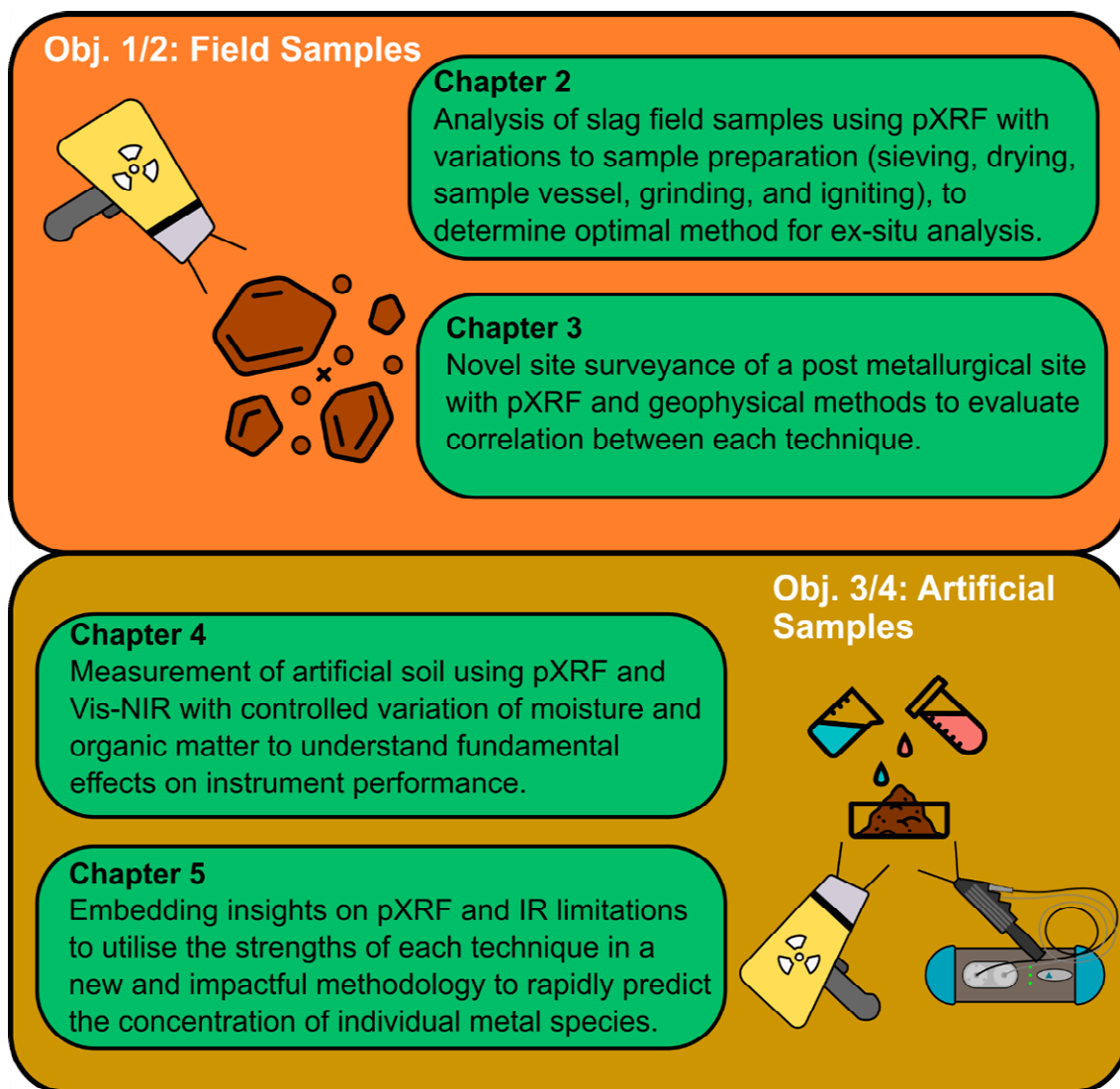


Figure 1.1 A summary of thesis structure and links between objectives and chapters.

Chapter 2 investigates the effects different sample pre-processing techniques have on pXRFs data quality when measuring slag matrix samples. Samples collected from a post-metallurgical site were sequentially sieved, dried, ground, ignited and measured with pXRF before and after each step. The pXRF performance was then evaluated against ICP-MS data. Based on this work, best

practice for ex-situ methodologies was identified as well as the limitations of applying pXRF to slag matrices.

Chapter 3 presents the results of a site investigation using pXRF and four geophysical methods. Different methods of data fusion are explored to rapidly generate a high spatial resolution map of the site. This study highlights the limitations of such approaches and proposes the steps necessary to create viable methods in the future.

Chapter 4 compares the performance of just pXRF against the data fusion of pXRF and Vis-NIR spectroscopy when predicting heavy metal concentrations in artificial soil samples with controlled variation in moisture and SOM. This study sought to understand the fundamental effects of moisture and SOM on pXRF heavy metal predictions. And utilise that knowledge to correct pXRF predictions.

Chapter 5 evaluates a novel methodology of combining pXRF and Vis-NIR spectroscopy to predict both elemental concentrations and ratios of different species. This chapter highlights an important avenue for future work which could lead to a method that can predict not only metal concentration but the quantities of its various species. This is important information that is not cost effective to collect at present and would allow site remediators to apply the most effective method of remediation for the speciation found.

Chapter 6 provides an overarching discussion of the results presented in the previous chapters. Contributing to a better understanding of the application of portable spectrometers for the measurement of heavy metals in post-metallurgical sites. Moreover, the implications of this thesis on industry practices, the environment, academic research, and wider society are highlighted and discussed. This chapter also outlines recommendations for future research in the field of portable spectroscopy and the analysis of heavy metals in the environment. And finally, concludes with the key findings from the thesis, discussing the scientific contribution to knowledge, highlights limitations of this work and proposes further work to the new science developed as part of this PhD.

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2 Development and optimisation of ex-situ portable XRF analysis for weathered slag.

2.1 Abstract

Portable X-ray fluorescence spectroscopy (pXRF) is widely used for rapid measurement of heavy metals in soils, however thorough evaluation of common pre-processing methods and their effectiveness is limited. This study addresses processing methods using samples collected at a high heterogenetic post-metallurgical site containing; basic oxygen steelmaking (BOS) slag and soil; the former being an important source of potentially toxic and valuable elements. Impact of pre-treatment processes, including sieving, drying, grinding, sample vessel, and ignition on the accuracy of pXRF measurements was compared against ICP-MS measurements.

Of the twelve elements detected, four showed qualitative (Cr and Fe $r^2 \geq 0.60$, $RSD \leq 30\%$) or quantitative (Mn and Ca $r^2 \geq 0.70$, $RSD \leq 20\%$) measurements for raw samples. This improved to six elements after pre-processing (Sr qualitative, and Pb, Cr, Mn, Ca, Fe quantitative). Sieving and grinding improved precision (average RSD fell by 7.17% and 8.37% respectively), while drying and grinding enhanced accuracy (average r^2 increased by 0.03 and 0.10 respectively). This study provides the first evidence that organic matter does not significantly impact pXRF accuracy. The two distinct matrices (BOS slag and soil) on-site resulted in a bimodal concentration distribution and a negative correlation for Ti. Importantly, this research proposes that not all common pre-processing steps are necessary to generate high-quality data, thereby increasing the speed and reducing the cost of data collection. Further analysis is required to develop a methodology to generate high-quality data across all elements of interest within BOS slag, or other relevant high heterogeneity samples.

2.2 Introduction

Globally, demand for rare and heavy metals continues to grow at a steady pace, with the demand for Cu and Nd, as an example, expected to triple by 2045 [1]. However, the extraction and refinement of these resources has not been an

efficient process, leaving a legacy of brownfield or post-metallurgical sites [2]. Sites are comprised of contaminated soils, waste slag or mine spoil and can be sources of mobile pollution such as acid mine drainage [3]. Between 2000 and 2006, 1,035 of these metal/metalloid contaminated sites were identified in the UK making up 60% of all contaminated sites identified in the UK [4].

Most site surveys focus on nine toxic metals (As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Zn) [5], as these elements are present in 98% of such sites [4]. While potentially toxic elements (PTE) are given full attention in site surveys, other non-toxic but potentially valuable elements (PVE) are often overlooked. Examples of PVE include Fe, Cu, Pt, Rh, and rare earth elements (REE) [6]. Since the current demand for PVE outstrips supply [7], there will be a significant challenge in meeting the Paris Agreement and enabling the transition to Net Zero by 2050 [1]. Therefore, there is a need for significant growth in the extraction of these elements from virgin deposits or from previously ignored opportunities.

Post-metallurgical sites such as former steel works can have concentrations of over 40% w/w Fe, 1.5% w/w Zn and 0.5% w/w Mn [8]. These concentrations were not economically viable for extraction by refineries at the time of production. However, with novel techniques such as bio- or chemical leaching [8], extraction may become profitable, creating new feedstocks for heavy industry and the circular economy, while reducing the cost of site remediation.

Site survey and quantification processes are still a barrier to expedited remediation and recovery of resources. International standards ISO 2136:2020 and ASTM E2531 prescribe that site surveys be carried out using a conceptual site model (CSM) [9,10]. A CSM comprises four phases of increasing detail: desk-based study, limited survey, focused survey and if necessary, a supplementary survey [9,10]. The CSM's tiered approach can take years to complete at complex sites [5], but minimises the risk of overlooking potential contamination while avoiding unnecessary site surveying. Current legislation places the focus on PTE [11] but since PVEs are often ignored in surveys, there are missed opportunities for recovering costs and contributing to the circular economy.

Samples collected for metals during CSMs are currently quantified by induction-coupled plasma mass spectrometry (ICP-MS) and bench X-ray fluorescence spectroscopy (XRF). Both instruments provide high-accuracy measurements with limits of detection (LOD) of <0.01 and $<10 \text{ mg kg}^{-1}$ for ICP-MS and XRF, respectively [12,13]. While these techniques can analyse more than 20 elements simultaneously, they require sample preparation such as acid digestion [14] or LiBr compressed disk formation [15]. These processes are time-consuming at a significant cost for batch sampling, which limits the amount of data collected, especially in the first stages of a CSM.

To overcome these challenges and increase the economic viability of site remediation, novel analytical methods are needed. Portable XRF (pXRF) is a compact hand-held device which can be deployed in-situ or ex-situ, providing elemental concentrations without further data processing [16]. However, pXRF still requires some preparation and has three well-known limitations. When sample moisture reaches 20% or more, reported metal readings are suppressed [17]. This effect has been attributed to water displacing air in the matrix, which attenuates X-rays by effectively reducing the distance the pXRF penetrate [17]. Similarly to moisture content, soil organic matter (SOM) interferes with X-rays [18].

The pXRF performance is also impacted by sample chemical heterogeneity. pXRF measures a volume of sample which is dictated by the critical thickness of any matrix (the maximum distance X-rays can penetrate and still be detected by pXRF). In soil-like matrices, this distance can be as low as $16 \text{ }\mu\text{m}$ for Al [16], meaning a single scan by pXRF will measure only 0.001 g of sample [19]. Well below the 0.2 g recommended minimum mass for analysis of certified reference materials [20]. As such, pXRF is more vulnerable to heterogeneity than other methods which measure larger masses of sample such as ICP [21].

Due to the aforementioned limitations, in-situ pXRF performs quite poorly. Across several studies identified by Ravansari and Lemke (2020), in-situ pXRF showed an average r^2 of 0.59 to 0.43 when compared to ICP. To overcome these challenges, the following sample preparation techniques have been

implemented: moisture removal by air drying [22]; oven drying [23]; homogenisation (sieving, grinding) [24]; and removal of SOM by ignition [18]. The application of these ex-situ measurement approaches resulted in a higher accuracy average with r^2 of 0.72 – 0.94 [16]. The disadvantage of these preparation methods is longer processing times, reducing pXRF's benefits over traditional methods. Despite the widespread use of ex-situ methods within the literature, their methodologies are inconsistent. In addition, there have been no studies investigating which processing steps make the largest difference in improving accuracy.

Another variable of importance is the matrix of a sample as this has a major effect on the accuracy of pXRF. Hence, it is important to validate pXRF on a given matrix before performing quantitative measurements. To date, there have only been two studies using pXRF on weathered slags. One investigated non-ferrous slags in Namibia [25], while the other reported results on basic oxygen steel flue dust [8]. Despite the importance of accurately assessing the performance of pXRF on new matrixes such as basic oxygen steal-making (BOS) slag, there is a lack of research in this area. A knowledge gap which needs addressing given the growing demand to remediate post-metallurgical sites and the potential resource recovery pXRF can enable.

As such, this study aims to determine the effects of pre-treatment on the accuracy of pXRF measurements of weathered BOS slag after different processing steps. To provide a best practice method for ex-situ measurements as well as an appraisal of pXRF's performance on this new matrix and how it can be most appropriately used. Based on previous assumptions held in the literature, this study hypothesises firstly that in-situ pXRF measurements will meet the EPA quantitative screening level. Secondly, each sample processing step will result in a significant improvement in pXRF's correlation to ICP-MS. And thirdly, ground pXRF measurements will meet the EPA's definitive level. To achieve this, ferric slag samples collected from a disused spoil heap were processed by sieving, oven drying, grinding, and loss on ignition before being digested for ICP-MS. pXRF analysis was conducted before and after each sample treatment.

2.3 Methodology

2.3.1 Sample material

Teesside, UK, is home to Europe's largest brownfield site covering an area of over 1500 ha [26]. Comprised of the former Redcar steelworks, South Bank coke ovens, South Lackenby effluent management system and several other heavy industries and steel working sites (Figure 2.1). This site has a history of heavy industry and steel refinement stretching over 160 years [27]. For this study, a ferric slag heap measuring 0.5 km² by 18 m tall located in the Long Acers district on the east of the brownfield site was selected (Figure 2.1). Documentation for the site is notably scarce. However, historical maps indicate a continuous history of steel working on the premises from 1890 to 1990, with a significant increase in material disposal occurring after the 1970s [27,28]. Documentation suggests that most waste deposited in the site is classified as BOS slag including minorities of refractory and cantina waste. However, due to the limited documentation the presence of other forms of steel making slag such as Bessemer steelmaking slag cannot be ruled out due to the long history of steel production at Teesside. After recorded waste deposition ended, soil was added to cap the site as such there are areas of mostly slag or mostly soil matrix with no clear horizon between the two. Samples were collected from the surface and sub-surface (~20 cm depth) of 17 locations selected to overlap with geophysical measurements (See Chapter 3 and [29]) which captured the full range of conditions observed on-site (Figure 2.1). Locations were categorised by eye as either slag or soil based on the majority of the matrix. But it should be noted that categorisation was subjective and there is overlap between the grouping due to the heterogeneity of the site with some soil samples containing substantial amounts of slag (Figure 2.1.E). Where present, vegetation was cleared before sample collection. Surface samples were collected by scraping the surface with a trowel while sub-surface samples were collected from the side walls of a ~30 cm deep hole excavated with a pickaxe. At each location and depth, three replicates (~500 g each) separated by 20 cm of distance were collected. Samples were stored in airtight polypropylene bags at room temperature for later analysis.

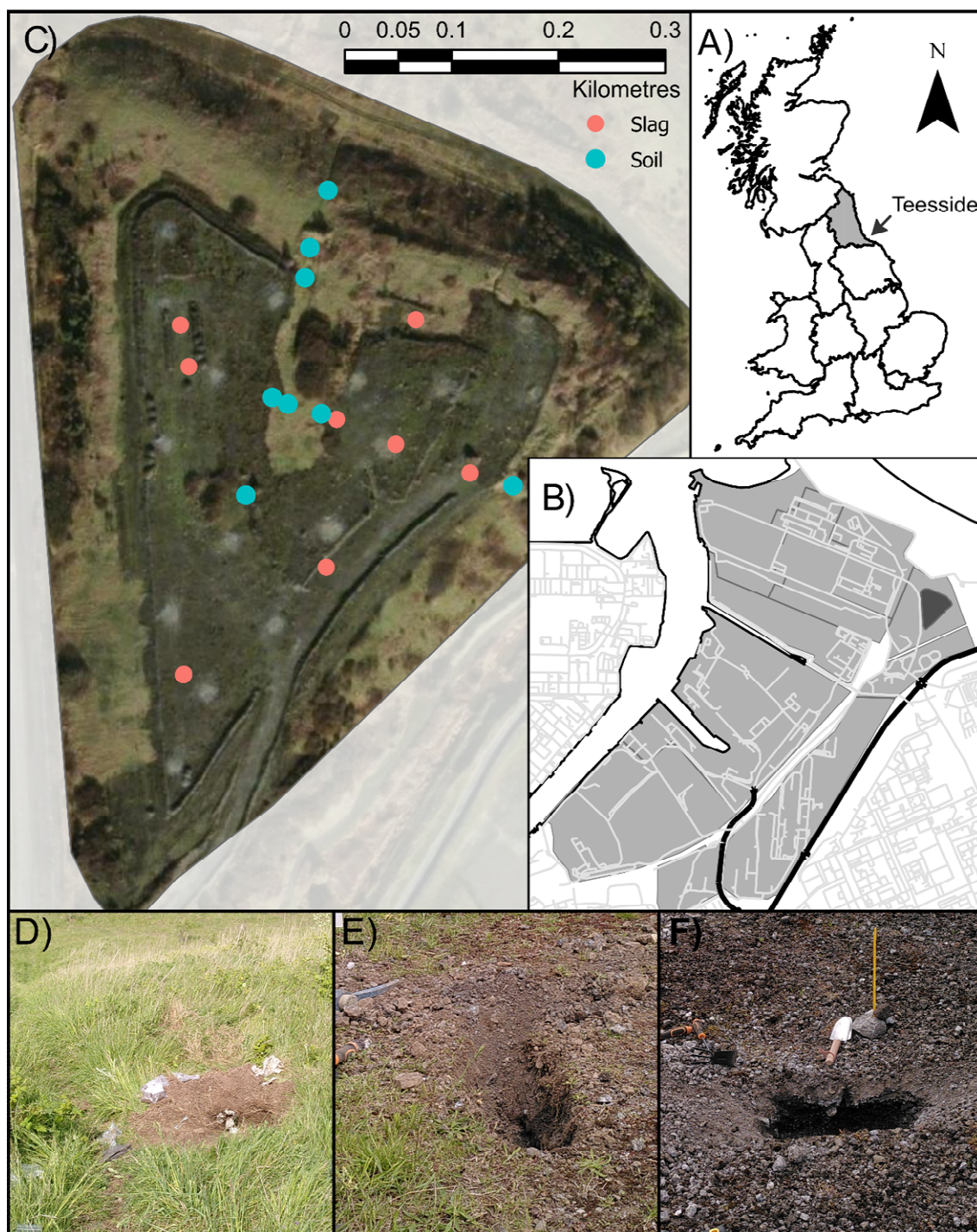


Figure 2.1: A) Teesside (UK), and the B) Long Acres study location (dark grey) located within the larger Teesworks former industrial area (light grey). C) blue sample locations were predominately soil matrix; red sample points were predominately slag matrix. D) soil sample location comprised of soil with little to no slag matrix present. E) soil sample location with substantial slag matrix present in sample. F) Slag sample location with no soil matrix present.

2.3.2 Experimental design and sample preparation

Samples (238-865 g per sample) were transported to Cranfield University for further processing. In sequence (Figure 2.2), samples were sieved through a 2 mm mesh and the <2 mm fraction (which varied between 75 g and 350 g in weight) and was then dried following standard (ISO 11465:1993) procedures at 105 °C for a minimum of 24 h to remove all moisture. After drying, the sample was mixed by rotating the sample bag in-between aliquots until a representative 30 g were collected, to be carried forward to be ground with a disk mill (Siebtechnik Germany) for 18 s to a fine powder (<0.125 mm, 30g), and further heated to 450 °C for 4 h to remove all SOM in line with (BS EN 13039:2000). Finally, all samples underwent microwave-assisted acid digestion following (ISO 11047:1998). Briefly, 0.5 g of sample was dissolved in aqua regia (HCl 6 mL, HNO₃, 2 mL FisharBrand UK) followed by the standard microwaving program. After cooling, the digestate was filtered and diluted in deionised water in volumetric flasks (100 mL) and stored at room temperature until analysis.

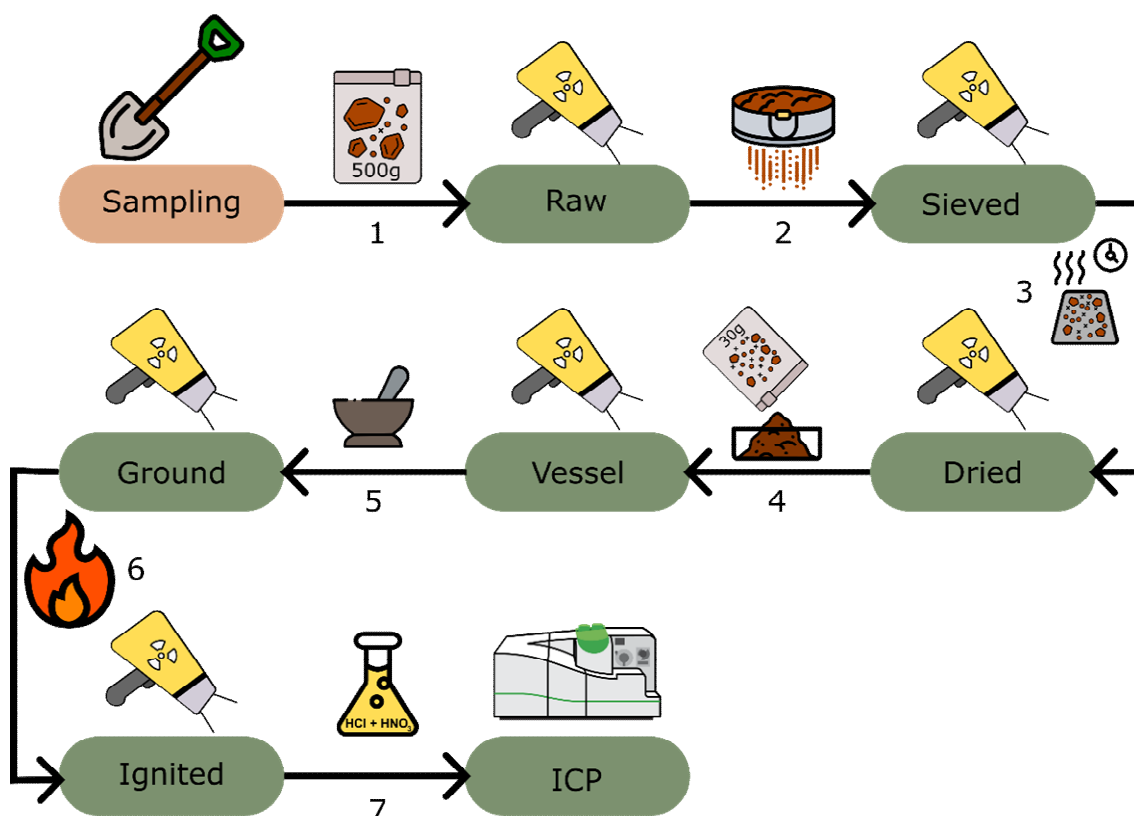


Figure 2.2: Sequential analysis and processing of samples (n=102) collected from Teesside, UK. The process consisted of seven steps: 1) samples were stored in polypropylene sample bags for transport and analysis; 2) samples were sieved through 2mm mesh; 3) samples were oven-dried for 24 hours at 105 °C; 4) samples were transferred to pXRF cups with Proleen® windows; 5) samples were ground to a fine powder and 6) ignited at 450 °C; 7) samples underwent acid digestion and analysis by induction coupled plasma mass spectroscopy (ICP-MS).

2.3.3 pXRF & ICP-MS

pXRF measurements of 26 elements (Table 2.1) were taken before and after each sample pre-processing step (except for acid digestion) with a Delta Premium (Olympus USA). According to manufacturer guidance, the analyser's Rh X-ray tubes were operated in soil mode using the steel suitcase accessory; beams 1 (40kV, Filter 3, 10 s), 2 (40kV, Filter 1, 10s) and 3 (15kV, Filter 5, 30 s) were active for a total scanning time of 50 s. The first three processing steps (raw, sieved and dried) were scanned 5 times through polypropylene sample bags with shaking in-between scans; the final three stages namely, vessel (which only shows the effect of changing sample vessel), ground and ignited were scanned

6 times through XRF sample cups with Proleen® windows (Chemplex USA) (Figure 2.2) with samples being returned to the bag and shook in-between scans. A Steal 316 Alloy coin was used to perform twice daily calibration checks [30]. Factory LOD are listed in appendix A.1.

ICP-MS measurements (Table 2.1) were taken by a NexION 350D ICP-MS (PerkinElmer, USA); uranium (U) was the internal standard. Twenty-two individual element standards (1000 mg kg⁻¹, PerkinElmer, USA) were used to create a 5-point linear calibration curve. See Appendix A.2 and A.3 for calibration ranges and LOD respectively.

Table 2.1: Elements measured by pXRF, and ICP-MS in basic oxygen steelmaking slag samples collected from an iron slag heap in Teesside, UK. Elements marked in bold are measured by pXRF only (see Appendix A.1 for LOD).

NexION 350D ICP-MS	Delta Premium pXRF
P, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag Cd, Sn, Sb, Ba, Hg, Pb.	P, S , Cl , K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb , Sr, Zr , Mo, Ag, Cd, Sn, Sb, Ba, Hg, Pb.

2.3.4 Data Analysis and Quality Evaluation

To show the effect of each sample processing step results were not adjusted, hence raw and sieved results are of the concentrations of the wet mass while dried, vessel, and ground results are concentrations of the dry mass and ignited and ICP results are the concentrations of the dry incinerated mass. No anomalous data points were identified or removed for Ti, Sr, Ca, and Fe. Data points greater or lower than the median $\pm$ two times the interquartile range for all processing steps were treated as anomalous and removed for P, K, Cr, Mn, Zn, and As. But for Ni only ICP data had this filter applied. For Pb, the two highest values were removed for all processing steps. For consistency elements are referred to in the order of concentration measured by ICP-MS “As, Pb, Sr, Cr, Ni, Ti, Zn, P, K, Mn, Ca, Fe” in all tables, figures and text. Violin plots were used to show the distribution of ICP-MS measurements. Box plots were used to show the RSD distribution for each element and processing step to evaluate precision.

Finally, pXRF measurements at each processing step were plotted against ICP-MS measurements for comparison purposes.

Relative standard deviation (RSD) for pXRF was calculated from the replicate scans of each sample. Mean RSD (the mean across a dataset with multiple RSD values calculated from each sample location's replicate measurements), Pearson's Squared correlation coefficient (r^2), y-intercept and slope were calculated in accordance with data quality levels defined by the U.S. Environmental Protection Agency (EPA) [31] shown in Table 2.2. The author has added a "no correlation" level as the agency does not provide a lower limit to qualitative screening but r^2 of <0.6 or negative slopes are ill-advised for use.

Further, goodness of fit statistics including Lin's coordination correlation coefficient (r_c or ccc), ratio of performance to interquartile range (RPIQ), and root mean squared error (RMSE) have been provided (Appendix A.7) to aid comparison to other studies in the field. All graphs and statistical analysis were completed with the following packages in R studio v2023.09.1: tidyverse, tidymodels, scales, cowplot, patchwork and RColorBrewer [32–37]. All code is available in our CORD repository (doi.org/10.57996/cran.ceres-2601).

Table 2.2: US EPA levels for establishing data quality. Pearson's Squared correlation coefficient (r^2), relative standard deviation (RSD).

Data quality level	Statistical requirement
Definitive	$r^2 = 0.85 - 1.0$. RSD $\leq 10\%$. Inferential statistics indicate statistical similarities. (At the 5% level) i.e., relationship $y = x$ accepted.
Quantitative screening	$r^2 = 0.70 - 1.0$. RSD $< 20\%$. Inferential statistics indicate statistical differences. i.e., relationship $y = mx$ or $y = mx + c$ accepted.
Qualitative screening	$r^2 < 0.70$. RSD 20 – 30%. Inferential statistics indicate statistical differences.
No / Unreliable Correlation	$r^2 < 0.6$. Negative slope. RSD $> 30\%$.

2.4 Results

2.4.1 Descriptive statistics of ICP-MS data

In this study, samples were analysed by pXRF and ICP-MS. With pXRF, 18 elements (As, Ba, Ca, Cr, Cu, Fe, Hg, K, Mn, Ni, P, Pb, Rb, S, Sr, Ti, Zn, Zr) were detected in more than 15% of the samples. Concurrently, ICP-MS detected 12 elements (P, K, Ca, Ti, Cr, Mn, Fe, Ni, Zn, As, Sr, Pb) in more than 15% of the samples. Hence, this paper will focus on these 12 common elements, which can be compared on both instruments.

Fe and Ca showed the highest concentrations on average (Figure 2.3), at 115,592 and 98,875 mg kg⁻¹ (11.0 and 9.8% w/w), respectively. Mn and K amounted to 13,518 and 5,225 mg kg⁻¹, respectively, followed by Zn, P, Ti, Ni, Cr, Sr, Pb, and lastly As at 35 mg kg⁻¹. Additionally, XRF included three elements (Ba ~325, Cu ~25, and Hg 18 mg kg⁻¹) undetected by ICP-MS.

ICP-MS results also showed bimodal distributions for Cr, Ti, P, Zn, Mn, Ca and Fe. Whereas Pb, Sr, Ni, and K had log-normal distributions.

Moisture concentrations measured by oven drying ranged from 2.0% to 30.0% while SOM concentrations measured by loss on ignition ranged from 0.0% to 13.0%. (see Appendix A.11)

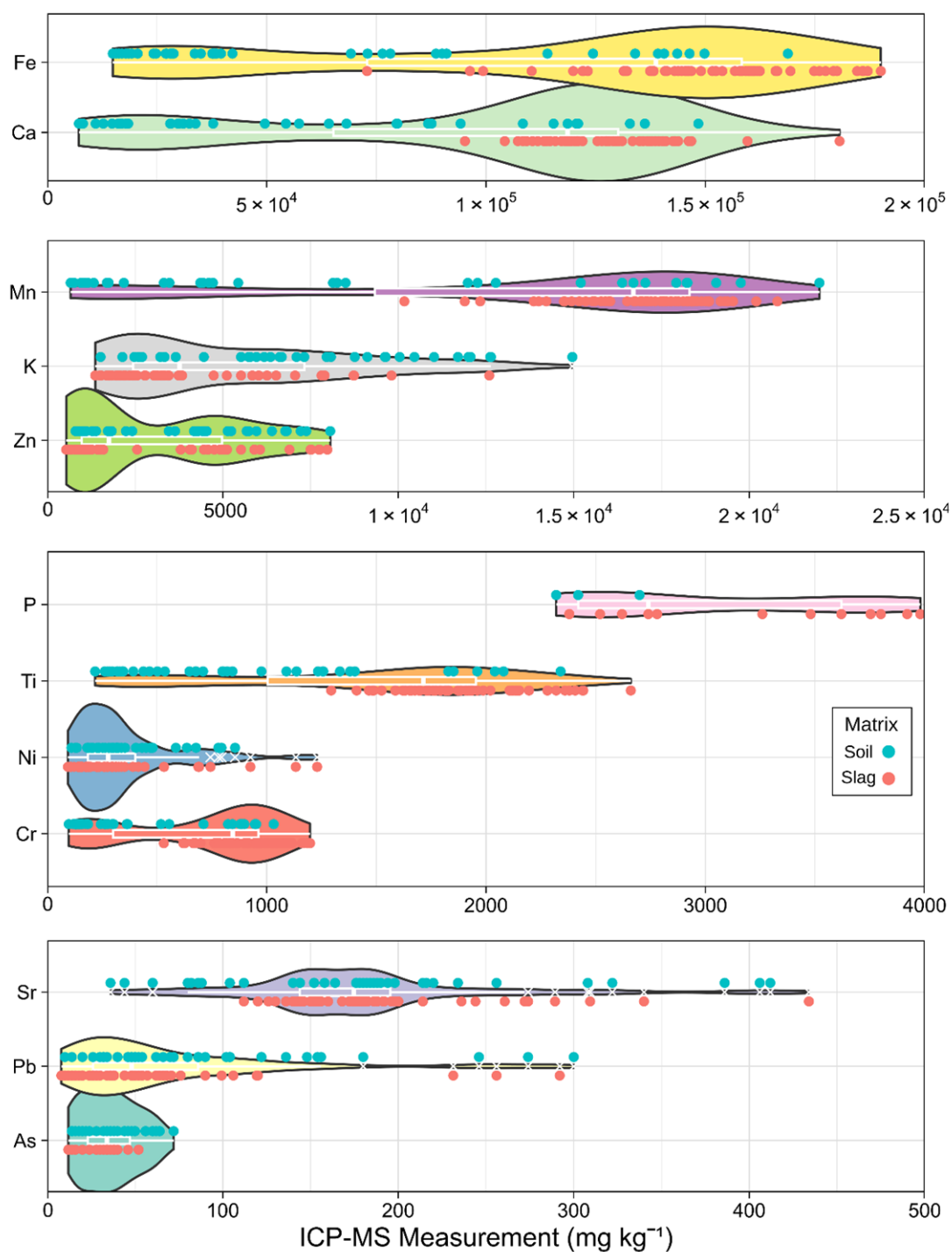


Figure 2.3: Range and distribution of all elements detected by ICP-MS in samples (n=102) collected from an iron slag heap in Teesside, UK. Blue (soil) and red (slag) dots indicate the matrix and measurements of individual samples.

2.4.2 Precision

To evaluate the precision of pXRF, RSD was calculated after each stage of pre-treatment from the replicate pXRF and ICP-MS scans of each sample (

Figure 2.4). ICP-MS had very good or excellent mean RSD for all elements (<10% EPA definitive level) except As and P whose RSD were 77% and 23%, respectively.

For raw samples, measured by pXRF six elements (Sr, Cr, Ni, P, Mn, and Fe) showed good mean RSD (<20% EPA quantitative level). While the other six elements (As, Pb, Ti, Zn, K, Ca) showed satisfactory mean RSD (<30% EPA qualitative level). No element showed an unsatisfactory RSD of more than 30%. Sieving made a substantial difference for eight elements (Sr, Cr, Ti, Zn, K, Mn, Ca, and Fe) reducing their mean RSD by 8% on average. Values for K, Ca, and Fe dropped below 10%, whereas Sr, Cr, Ti, Zn, and Mn resulted in <20%.

Grinding made the largest difference to the mean RSD of nine elements (Pb, Sr, Cr, Ti, K, Mn, Ca, and Fe) decreasing by an average of 7%, whilst improving six of them (Sr, Cr, Ti, K, Mn, Ca, and Fe) to an excellent level of precision (<5% mean RSD) and Pb to a very good precision 9.30%. Only As, Ni, and P still had good RSD after grinding (19.80%, 13.86%, and 12.90%, respectively). After all sample treatments As, Pb, Sr, Cr, K, Mn, and Fe were as precise as ICP-MS while As, Ti, P, and Ca were more precise than ICP.

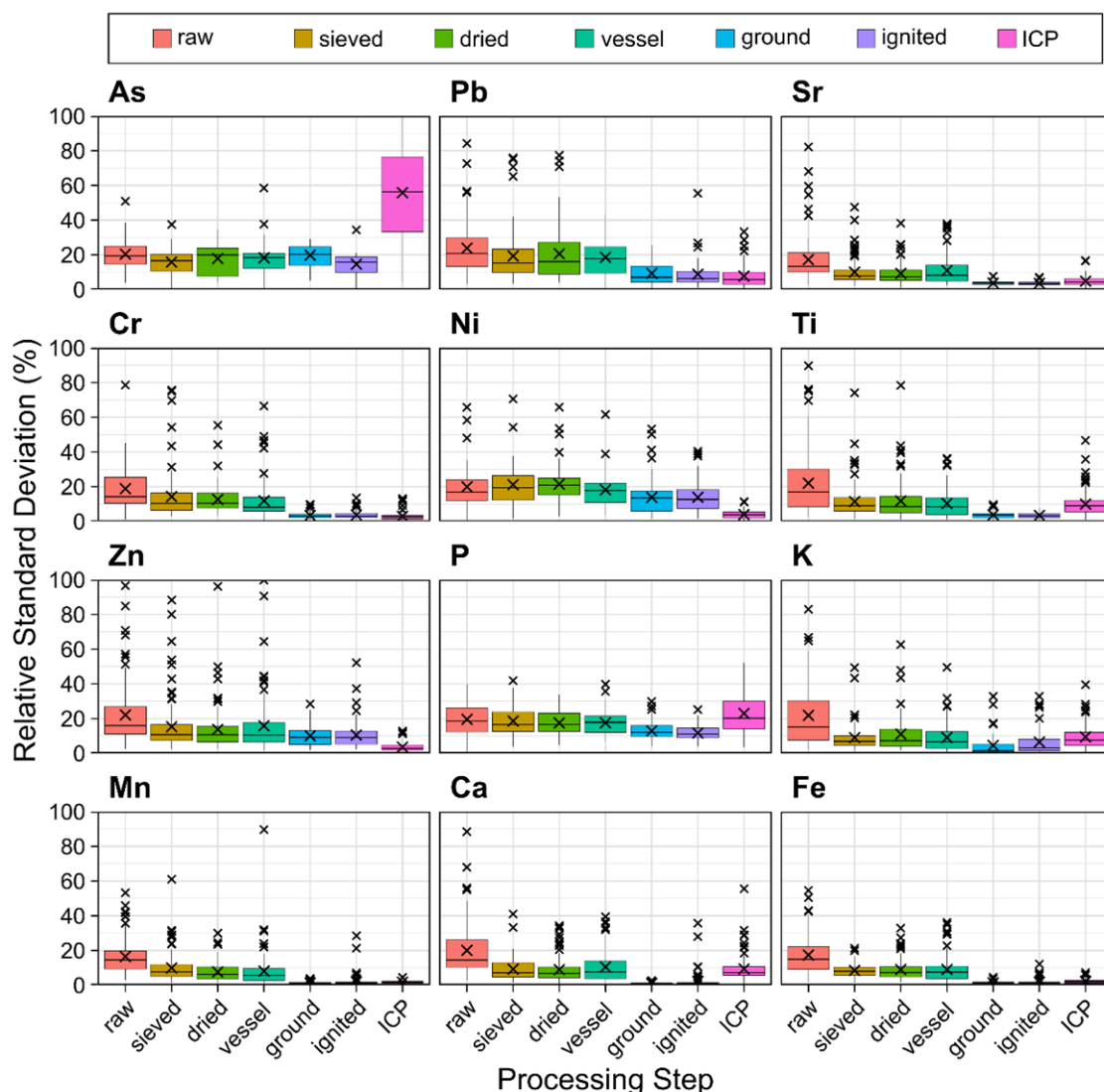


Figure 2.4: Distribution of relative standard deviations calculated across replicate scans of each sample (n=102) collected from an iron slag heap in Teesside, UK, after each processing step measured by pXRF and after acid digestion by ICP-MS.

2.4.3 Accuracy

To measure accuracy, pXRF measurements at each pre-treatment stage was plotted against ICP-MS measurements in Figure 2.5 –Figure 2.7, and the statistical analyses required to assess performance against EPA data quality levels were presented in Table 2.3. Across all 12 elements, six elements Pb, Sr, Cr, Mn, Ca, and Fe (Table 2.3) met the qualitative ($r^2 < 0.70$) or quantitative ($r^2 > 0.70$) screening level as defined by the EPA (Table 2.2) while six elements As, Ni, Ti, Zn, P, and K showed no correlation (Table 2.3, Appendix A.3)

Fe performed the best with an r^2 of 0.66 which increased to 0.88 after all processing steps. For raw and sieved samples pXRF is under-reported compared to ICP-MS. After drying, inferential statistics showed a linear relationship; grinding samples further increased r^2 to 0.88, but it also increased the slope to 1.61, meaning that pXRF over-reported Fe compared to ICP-MS.

Ca showed a clear correlation with r^2 of 0.75 for raw measurements rising to 0.85 after grinding. However, drying reduced r^2 to 0.68. In addition, Ca was the only element over-predicted by pXRF when measuring raw samples, with a slope of 2.3. This was only increased by sample pre-processing, in particular the change in sample vessel, which increased the slope to 4.39.

Mn, Cr, and Sr all showed similar changes in accuracy with grinding being the only step to make a substantial change, increasing r^2 by ~ 0.1 . Similarly, grinding increased the slope of Mn and Cr by ~ 0.2 , but Sr saw no substantial change in slope.

Pb, unlike the first five elements, did not show a trend of increased sample processing leading to improved r^2 or slope. For example, drying samples increased r^2 to 0.80 but changing sample vessels decreased r^2 to 0.67.

Of the elements that did not show correlations (A.3), As and P had ICP-MS results with RSD which did not meet the definitive EPA level ($r^2 < 0.85$) and hence their accuracy when measured by pXRF cannot be assessed in this study. Zn and Ni both showed little variation in the pXRFs range which was $< 10\%$ and $< 30\%$ of the total ICP-MS range respectively and resulting in slopes of ~ 0.00 . K showed slopes ranging from 0.65 to 1.26 but did not reach a r^2 higher than 0.12. Ti unexpectedly had a negative slope ranging from -1.00 to -1.72.

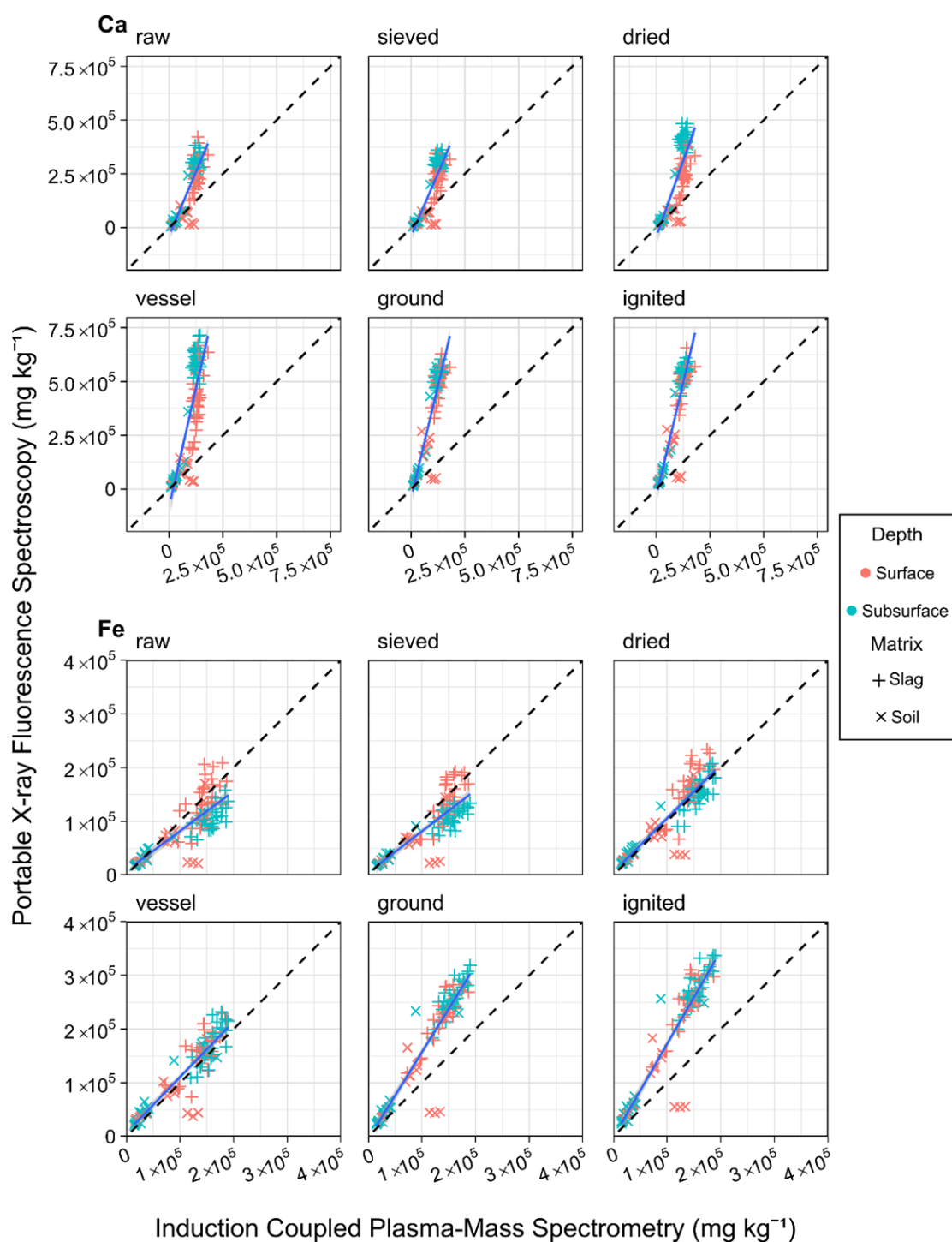


Figure 2.5: Regression of samples (n=102) collected from an iron slag heap in Teesside, UK, showing Fe and Ca concentrations measured by pXRF after each processing step (y-axis) against ICP-MS measurements (x-axis). OLS regression (blue solid line); ideal 1 to 1 relationship (black dashed line); slag matrix (horizontal cross); soil matrix (diagonal cross); surface samples (red cross); subsurface samples (blue cross). error bars in Appendix A.4.

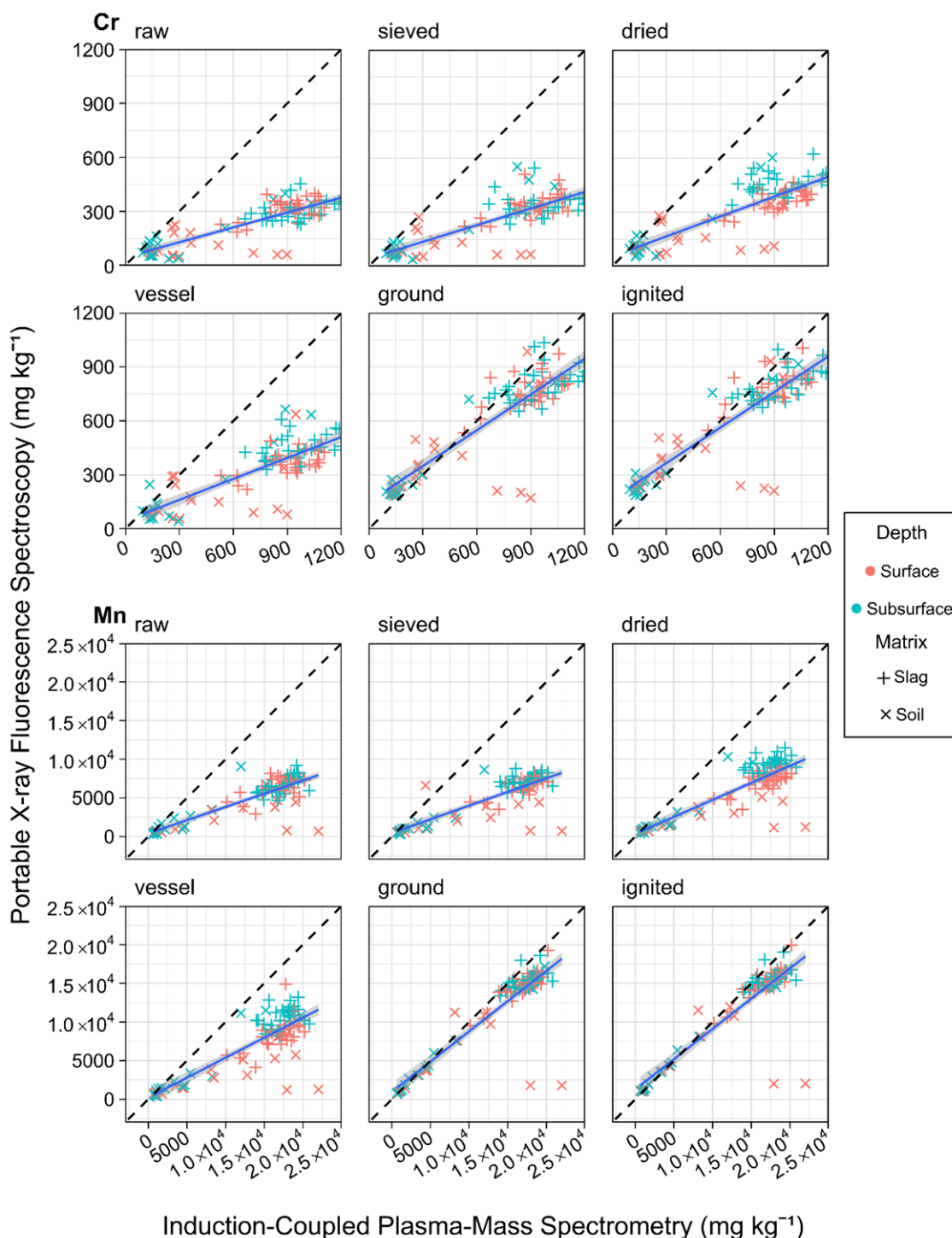


Figure 2.6: Regression of samples (n=102) collected from an iron slag heap in Teesside, UK, showing Cr and Mn concentrations measured by pXRF after each processing step (y-axis) against ICP-MS measurements (x-axis). OLS regression (blue solid line); ideal 1 to 1 relationship (black dashed line); slag matrix (horizontal cross); soil matrix (diagonal cross); surface samples (red cross); subsurface samples (blue cross). error bars in Appendix A.5.

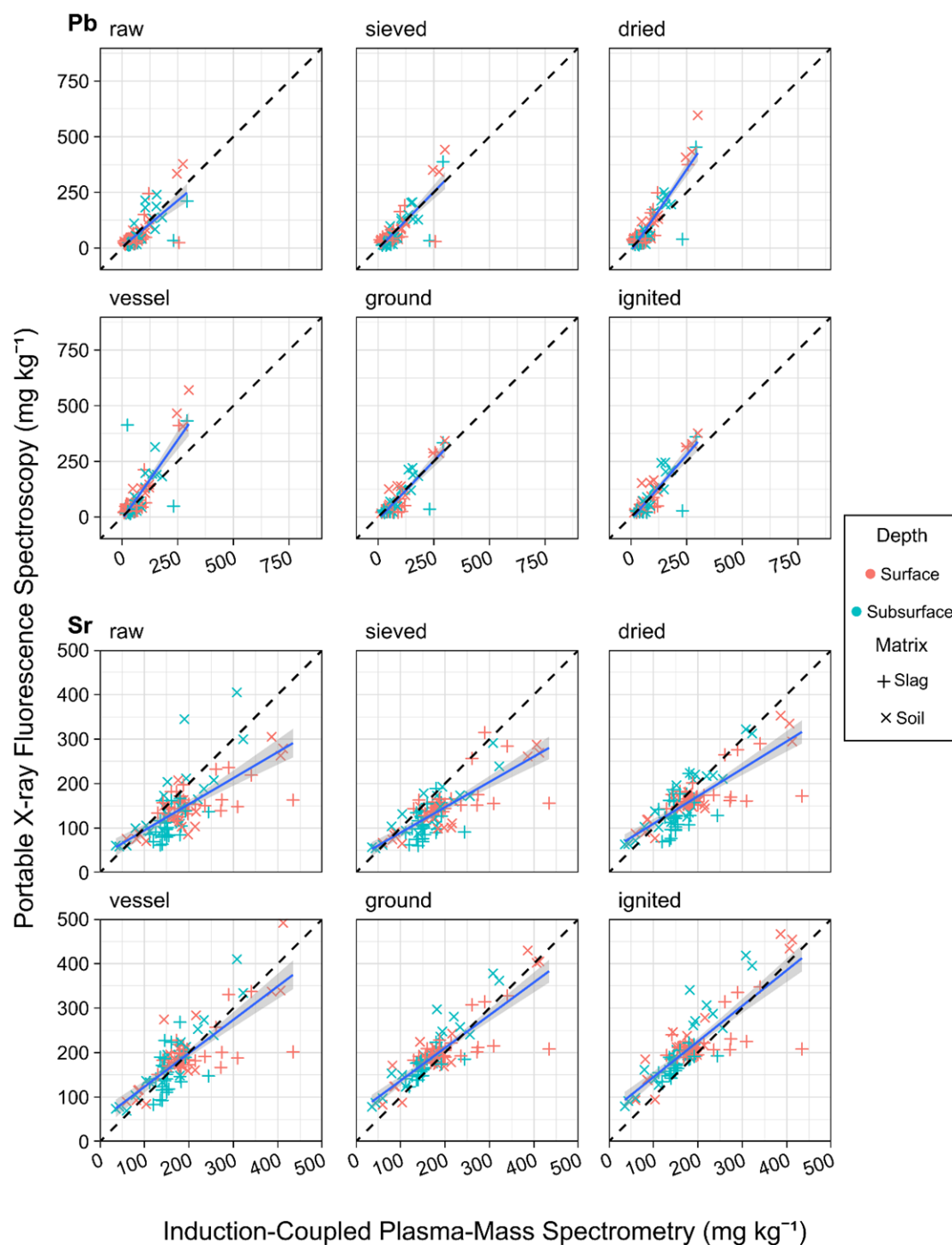


Figure 2.7: Regression of samples (n=102) collected from an iron slag heap in Teesside, UK, showing Pb and Sr concentrations measured by pXRF after each processing step (y-axis) against ICP-MS measurements (x-axis). OLS regression (blue solid line); ideal 1 to 1 relationship (black dashed line); slag matrix (horizontal cross); soil matrix (diagonal cross); surface samples (red cross); subsurface samples (blue cross). error bars in Appendix A.6.

Table 2.3: Data quality assessment levels as defined by EPA [31] and summary statistics of ordinary least squared regression on pXRF and ICP-MS measurements of samples (n=102) from an iron slag heap. Further statistics can be found in Appendix A.7.

Statistic	variable	As	Pb	Sr	Cr	Ni	Ti	Zn	P	K	Mn	Ca	Fe
n	raw	32	86	102	99	40	101	95	57	75	100	102	102
	sieved	33	82	99	96	44	98	92	58	69	97	99	99
	dried	31	88	102	98	52	102	94	65	74	100	102	102
	vessel	40	88	102	96	59	101	93	100	79	100	102	102
	ground	21	61	102	100	97	102	90	100	52	100	102	102
	ignited	20	56	102	100	99	102	90	100	61	100	102	102
r ²	raw	0.199	0.529	0.486	0.688	0.001	0.537	0.003	0.000	0.398	0.713	0.751	0.655
	sieved	0.196	0.667	0.597	0.650	0.100	0.530	0.011	0.005	0.359	0.706	0.756	0.724
	dried	0.251	0.802	0.612	0.689	0.005	0.594	0.005	0.021	0.390	0.713	0.682	0.800
	vessel	0.138	0.670	0.608	0.664	0.000	0.563	0.008	0.051	0.415	0.700	0.716	0.823
	ground	0.251	0.767	0.702	0.770	0.042	0.424	0.004	0.069	0.231	0.813	0.850	0.881
	ignited	0.085	0.754	0.670	0.786	0.027	0.426	0.007	0.120	0.302	0.811	0.852	0.884
Mean RSD	raw	20.5%	25.1%	18.2%	18.8%	19.9%	22.0%	22.1%	19.6%	21.8%	17.5%	20.1%	17.3%
	sieved	15.8%	19.3%	10.0%	15.2%	21.2%	11.4%	15.3%	18.6%	9.0%	11.8%	9.3%	8.4%
	dried	17.8%	22.0%	9.2%	12.7%	21.5%	11.8%	14.7%	17.4%	11.0%	7.6%	9.0%	9.0%
	vessel	18.3%	19.8%	11.0%	11.9%	18.2%	10.3%	15.8%	17.6%	9.1%	8.1%	10.5%	9.0%
	ground	19.8%	9.3%	3.7%	3.4%	13.9%	3.8%	10.1%	12.9%	4.5%	1.3%	1.0%	1.4%
	ignited	14.6%	8.9%	3.6%	3.7%	14.8%	3.4%	10.5%	11.7%	6.5%	1.9%	2.1%	1.8%
Slope	raw	0.154	0.832	0.587	0.275	-0.002	-1.005	-0.002	-0.043	0.650	0.342	2.361	0.740
	sieved	0.087	1.020	0.571	0.308	0.017	-1.046	-0.003	-0.208	0.629	0.354	2.325	0.768
	dried	0.131	1.471	0.618	0.369	-0.004	-1.429	-0.002	0.521	0.894	0.439	2.816	0.999
	vessel	0.126	1.426	0.754	0.388	0.000	-1.723	-0.003	3.299	1.357	0.518	4.387	1.032
	ground	0.056	1.050	0.737	0.663	0.076	-1.059	0.001	5.449	1.026	0.783	4.171	1.614
	ignited	0.044	1.161	0.802	0.660	0.071	-1.154	0.002	7.238	1.268	0.782	4.211	1.734
Intercept	raw	6	5	36	47	37	2837	134	15629	1324	405	-35600	7913
	sieved	6	-4	33	44	29	3006	141	15471	2029	459	-38360	4689
	dried	7	-15	48	55	42	3981	164	19156	2102	345	-43470	5600
	vessel	9	-10	48	46	49	4885	167	26479	2375	209	-78703	7489
	ground	9	-11	63	150	132	3916	77	39451	3633	961	-41432	-4578
	ignited	11	-11	65	167	149	4162	83	37014	2043	1288	-34098	-1506
Data Quality	raw	No Correlation	No Correlation	No Correlation	Qualitative	No Correlation	No Correlation	No Correlation	No Correlation	No Correlation	Quantitative	Quantitative	Qualitative
	sieved	No Correlation	Qualitative	No Correlation	Qualitative	No Correlation	No Correlation	No Correlation	No Correlation	No Correlation	Quantitative	Quantitative	Quantitative
	dried	No Correlation	Quantitative	Qualitative	Qualitative	No Correlation	No Correlation	No Correlation	No Correlation	No Correlation	Quantitative	Qualitative	Quantitative
	vessel	No Correlation	Qualitative	Qualitative	Qualitative	No Correlation	No Correlation	No Correlation	No Correlation	No Correlation	Quantitative	Quantitative	Quantitative
	ground	No Correlation	Quantitative	Quantitative	Quantitative	No Correlation	No Correlation	No Correlation	No Correlation	No Correlation	Quantitative	Quantitative	Quantitative
	ignited	No Correlation	Quantitative	Qualitative	Quantitative	No Correlation	No Correlation	No Correlation	No Correlation	No Correlation	Quantitative	Quantitative	Quantitative

2.4.4 Impact of moisture / SOM on pXRF performance

Effects of drying and igniting samples were of significant interest due to SOM and moisture being highlighted as key interferences that require further study [16] as such a more detailed analysis is reported below.

In the case of ignition, no substantial difference was seen in r^2 or the slope for any element (Table 2.3). Drying also made no substantial difference in slope or r^2 for nine elements (As, Sr, Cr, Ni, Ti, Zn, P, K, and Mn). However, drying did substantially increase r^2 for Fe and Pb from 0.72 to 0.80 and 0.67 to 0.80 respectively. Unexpectedly, drying decreased r^2 for Ca from 0.76 to 0.68. Additionally, drying increased the slope of all 3 elements with Fe increasing from 0.77 to 1.00, Ca from 2.32 to 2.81, and Pb from 1.02 to 1.47.

To further investigate if moisture and SOM were important interferences, pXRF measurements of sieved/dried samples and ground/ignited were regressed against each other for moisture and SOM respectively (Table 2.4). Removing SOM from samples made no substantial difference to pXRF measurements with slopes for elements that met EPA data quality levels (Pb, Sr, Cr, Mn, Ca, Fe) ranging from 0.89 to 1.01 and r^2 of ≥ 0.98 .

However, the removal of moisture from samples did make a substantial difference to pXRF measurements for all elements with the slope ranging from 0.74 – 0.88 and r^2 ranging from 0.86 – 0.95 meaning pXRF measurements were consistently higher for all elements.

Table 2.4: Regression analysis of pXRF measurements before and after A) drying and B) igniting samples (n=102) collected from an iron slag heap in Teesside, UK. Further Goodness of fit statistics, confidence intervals and regression plots are available in Appendix A.8, A.9, and A.10.

	A) Moisture			B) Soil Organic Matter		
Element	r²	Slope	Intercept	r²	Slope	Intercept
As	0.65	0.61	2.34	0.55	0.71	2.00
Pb	0.86	0.70	5.50	1.00	0.90	1.02
Sr	0.90	0.88	-4.85	0.98	0.89	9.66
Cr	0.82	0.74	20.50	0.98	1.01	-18.90
Ni	0.50	0.66	5.67	0.79	0.79	20.84
Ti	0.97	0.77	-8.74	0.99	0.91	107.79
Zn	0.85	0.84	-2.13	0.97	0.85	5.32
P	0.00	-0.02	15281.36	0.98	0.98	-1346.72
K	0.98	0.73	249.89	0.98	0.92	248.47
Mn	0.91	0.77	388.10	1.00	1.00	-264.07
Ca	0.95	0.76	12114.79	1.00	0.99	-7300.37
Fe	0.94	0.79	-1049.73	1.00	0.93	-3113.28

2.5 Discussion

2.5.1 Pre-processing step's varying impact on pXRF performance

2.5.1.1 Raw measurements

This study hypothesised that raw pXRF measurements will meet the EPA quantitative screening level. Cr and Fe achieved qualitative ($r^2 < 0.70$) screening levels while Mn and Ca achieved a quantitative ($r^2 > 0.70$) screening levels (Table 2.3) for raw measurements. However, these results underperformed those found elsewhere, who measured raw samples in sample bags, as done herein, r^2 ranged from 0.02 – 0.99 (0.62 mean) [38–42]. Compared to an r^2 range of 0.00 – 0.75 (0.41 mean) across the 12 elements measured in our study. This inconsistency between raw pXRF measurements and those of other studies may be due to the matrixes measured. Most studies utilising pXRF on unprocessed samples measure soil [16] which will often have a narrower range of particle size i.e. <2 mm. Whereas the raw slag samples had a wide range of particle sizes ranging from gravel <4 mm to pebble <60 mm sized material. This is consequential as larger particles will occupy more of the pXRF's window and leave large air gaps in between, resulting in lower precision and accuracy.

While four elements met EPA data quality levels and could be assessed in a rapid field sampling program, implementing such a program would be of little benefit as samples would need to be collected and analysed ex-situ to survey all other PTE and PVE.

2.5.1.2 Sieving and Grinding

It was hypothesised that each sample processing step would result in a substantial improvement in pXRF's correlation to ICP-MS. Both sieving and grinding made substantial reductions to the RSD of eight elements (Figure 2.4). These processing steps increase homogenisation and hence reduce random error [21]. Despite the EPA publishing guidance in 1998 recommending the assessment of pXRF with RSD [31] only five journal articles could be identified that reported mean RSD values. These values were calculated from repeat scans of certified reference materials (CRM) which would be equivalent to ground

samples in our study. These studies [43–46] reported RSD ranges for As 6.1 – 10.6%, Pb, 0.6 – 9.0%, Sr 8.1%, Cr 4.1 – 9.0%, Ni, 4.6 – 11.5%, Ti 0.58%, Zn 0.82 – 5.3%, Mn 0.8 – 0.9%, and Fe 0.2%. These values are broadly similar to the mean RSDs recorded in this study, except As which was substantially less precise than other studies. These steps remove variations in physical structure, grain size distribution and chemical composition. The latter being caused by the “nugget effect”, where an anomalous high-concentration chunk of analyte may randomly be placed in front of the pXRF aperture [19], but with reduced particle size variation, the nugget effect is substantially reduced. Finally, both slope and concentration measured by pXRF were increased by grinding for Cr, Mn, and Fe (Table 2.3); Peralta et al (2020) reported similar effects for Pb and Zn attributing the difference to the exposure of elements contained within the particles [47].

The results from this study suggest best practice to achieve the highest performance with pXRF includes grinding samples to increase homogeneity and precision. In addition, where particles are suspected to have differing concentrations between their interior and the exterior grinding will be needed to obtain measurements of the entire matrix as opposed to just the surface of the matrix. However, this processing step adds substantial time and requires specialist grinding equipment due to BOS slag's hardness. A suitable compromise of only sieving samples may be acceptable, as this brought all 12 elements within the EPA's quantitative screening level (RSD < 20%) and 6 within the EPA's definitive level (RSD < 10%).

2.5.1.3 Drying

Previous studies [17] have highlighted moisture as an important cause of interference for pXRF. In this study, drying made no substantial difference to the RSD of any element (Figure 2.4). Moisture is well documented as scattering or attenuating incident and fluorescence X-rays [17]; an effect that introduces systematic error and does not affect precision. When sieved and dried samples were regressed against each other showing substantial differences for all six elements with the slope ranging from 0.74 – 0.88 and r^2 ranging from 0.86 – 0.95 (Table 2.4). Meaning the removal of moisture substantially increased

concentrations reported by pXRF. This finding is consistent with that of Sahraoui et al (2017) who reported slopes of 0.67 – 0.94 and r^2 of 0.96 – 0.98 for Pb, Cr, Mn, Ca, and Fe when regressing ex-situ and dried pXRF measurements [48].

Most studies of moisture's effect on pXRF have only focused on comparing pXRF measurements before and after drying samples, not comparing change in pXRF measurements to the accepted standard methods (i.e. ICP-MS or bench XRF). This study only found substantial differences in the regression between sieved / ICP-MS and dried / ICP-MS for Pb, Ca, and Fe (Table 2.3). Furthermore, only the change to pXRF measurements of Fe resulted in a higher accuracy. In the case of Pb, its slope was increased from 1.02 to 1.47 and for Ca, r^2 decreased from 0.76 to 0.68 and its slope increased from 2.32 to 2.28. Data was complex to interpret due to contradictory results, however, results (Table 2.3) suggest that while removing moisture from the sample increases pXRF measurements, it does not always increase accuracy. This is most likely due to the limitations of the pXRF's factory calibration and results could potentially be improved with a CRM calibration [46].

Based on the results of this study it is inconclusive whether drying samples is best practice when using pXRF ex-situ, suggesting further work is necessary. However, comprehensive published literature highlights moisture effects, therefore, drying should be included in ex-situ methodologies. It is important to note this may lead to overprediction if factory calibrations are relied upon.

2.5.1.4 Sample vessel

The impacts of the sample vessel were investigated in this study as pXRF manufacturers recommend that elements lighter than Ti be measured through XRF sample cups with Proleen® windows as the lower energy fluorescence X-rays of these elements are significantly attenuated by thicker sample containers [16]. As such, changing the sample vessel made no substantial change to RSD (Figure 2.4). Furthermore, the only element that showed a substantial change in slope and accuracy was Ca. This finding corroborates the previous body of literature [16] stating that sample cups are not necessary for the analysis of heavier elements.

2.5.1.5 Ignition

This study sought to assess the importance of sample pre-processing steps for the improvement of both the accuracy and precision of pXRF measurement. Ignition made no substantial difference to the RSD of any element, in accordance with previous literature [18], as scattering or attenuating incident and fluorescence X-rays introduce systematic error and does not affect precision. This also applies to the accuracy of pXRF before and after igniting samples when compared to ICP-MS measurements (Table 2.3). Furthermore, no substantial difference was seen in pXRF when comparing ground and ignited samples directly against each other (Table 2.4). This contradicts previous studies such as Ravansari et al (2018) who found a clear reduction in pXRF response as organic matter increased in the sample matrix [18]. However, the paper has a limited sample size of a single CRM and used cellulose and sugar as surrogates for SOM which is not truly representative. Furthermore, that study did not acknowledge the large level of uncertainty in their measurements which makes their inference of difference due to SOM dubious.

It should also be noted that a subsequent literature review by Ravansari et al (2020) highlighted SOM as a key interference referring to their own and other literature [16]. However, revaluation of their references could not identify any reports that these studies identified SOM as an interference to their measurements [49] or that their references referred back to Ravansari's original study [50]. More recently, Chen et al (2021) incorporated SOM measurements into a corrective model to improve the accuracy of Pb. But the performance was negligible increasing r^2 from 0.911 to 0.976. Furthermore, Chen et al (2021) is limited in that its samples contained a SOM range of 0.3 – 3.33% meaning trends should not be extrapolated to cover the full range of SOM concentrations possible in samples. In addition, their study focuses solely on model creation and does not discuss the effects of SOM or other interferences present in their study [40].

Results in this study require further consideration as the removal of organic mass when analyte and other matrix masses are preserved, must result in a higher concentration of analyte within the sample. There are several possible

explanations for this result. Firstly, to remove SOM, samples in this study were combusted at 450 °C. However, it has previously been reported that iron-rich samples can gain mass during this process due to Fe oxidising and hence gaining mass and offsetting loss of organic mass [51]. But such a process would have resulted in no measured mass change and as such can be dismissed.

A second theory may be possible when considering how pXRF measures a sample. The intensity of the signal in a pXRF measurement of a sample is a product of three factors [16]. i) The energy of the incident and fluorescence x-rays. ii) The absorption/scattering ability of the matrix. The first two factors together dictate the critical thickness of a sample. The final factor is iii) the mass of the analyte within the critical thickness of the sample. As density positively correlates with absorption [16] and SOM contains lighter elements than the heavy elements in BOS slag, it can be assumed that the critical thickness would be reduced after removing SOM. If this is the case, then despite the increase in analyte concentration the reduced critical thickness may mean pXRF receives the same intensity of signal and hence reports the same concentration as before the removal of SOM.

The results for removing SOM in this study cast some doubt on the need for such procedures when measuring ex-situ with pXRF. However, SOM did not exceed 15% in this study, thus this may not apply at higher SOM-containing samples. Further work is required to establish the effects of SOM on critical thickness and pXRF performance. Such research could involve repeating Ravansari et al (2018) work with a wider range of samples and organic matter or better statistical analysis. In addition, modelling work may be appropriate to understand the effects at play using software such as XMI-MSIM developed by Schoonjans et al (2012) [52].

2.5.2 ICP-MS as a gold standard method for BOS slag

This study aimed to determine the effects of pre-treatment on the accuracy of pXRF measurements of weathered ferric slag. As such a gold standard method was needed to compare against, therefore ICP-MS was used, as is the wider practice throughout the literature [46]. BOS slag CRMs [53,54] were identified but

were unweathered and hence would not be representative of Teesside BOS slag due to the weathering. For instance, Ca, which was produced as CaO [55], has several reaction pathways. Specifically, CaO reacts with CO₂ to produce CaCO₃ [56], which can further react with H₂CO₃ found in acid rain, resulting in Ca(HCO₃)₂, a water-soluble compound. Consequently, Ca is likely to have been mobilized at Teesside, leaving the site via the watershed. Meaning there is a need to obtain CRMs that are as representative of the site as possible. Unfortunately, there are no CRMs of weathered BOS slag currently available. As such any study setting out to effectively validate its methodologies will have to create their own at great cost. However, these findings may be somewhat limited as BOS CRMs were not analysed by in-house ICP-MS. Therefore, it is not viable to exclude the possibility that these discrepancies are due to errors in the methodology of this study.

Further challenges were encountered by ICP-MS which did not detect Ba, Cu, Hg, or Sr. However, pXRF detected them at concentrations less than 326, 24, 17, and 136 mg kg⁻¹, respectively. Notably, the ICP-MS's LOD for these four elements was lower than pXRF's measurements by 0 – 2 orders of magnitude. However, pXRF can overpredict concentrations in comparison to ICP-MS by an order of magnitude as is the case for Ca (Figure 2.5). Thus, it is likely that the concentrations of these elements were below ICP-MS's limit of detection.

As and P were also close to their LOD (mean As -48.76, P -3410 mg kg⁻¹ LODs As -8.34, P -2220.55 mg kg⁻¹). This proximity to LOD is probably the cause of ICP-MS's relatively poor precision for As and P (Figure 2.4). As it has previously been demonstrated that as the concentration of sample analyte decreases, the RSD of the ICP-MS signal will increase [57] Due to the high concentrations of Fe and Ca, a dilution factor of 200,000 was necessary to place them within the upper range of the ICP-MS's calibration curve. However, if the samples were rerun with reduced dilution, there might have been a possibility of detecting Ba, Cu, Hg, and Sr and increased precision for As and P. Yet, in less dilute samples, the effects of Ca, Fe, and other matrix components would become more pronounced. These effects can interfere with the measurement of lower-concentration elements. For

example, Ca isotopes form $^{46}\text{Ca}^{16}\text{O}^1\text{H}^+$ and $^{40}\text{Ca}^{16}\text{O}^1\text{H}^+$ in ICP-MS plasma which interfere with ^{63}Cu and ^{65}Cu spectral lines making measurement challenging [58]. Modern ICP-MS's makes use of internal standards and mathematical correction equations [59] to compensate for spectral interferences. However, the use of these tools requires skilled operators at further time and expense. These findings cast some doubt on ICP-MS viability as a gold standard method when measuring matrixes containing disparate abundances of elements such as BOS slag. As such caution should be advised in future studies.

One final limitation of ICP-MS may have been identified below but the interpretation of these results is somewhat speculative as BOS CRMs were not analysed by both instruments to validate interpretations. A significant observation was the over-reporting of Fe by pXRF after grinding compared to ICP-MS. In contrast to earlier findings, this study reported a slope of 1.61 (Figure 2.5) much higher than the 0.87 and 0.98 reported previously [60,61]. However, one other study reported a similar slope of 1.70 [62] which unlike the previous two also measured anthropogenic waste sites. These studies and the findings reported herein used aqua regia as a digestion reagent, which cannot dissolve certain recalcitrant forms of Fe common in slag such as iron spinels [63]. However, pXRF would detect all forms of Fe within the sample regardless of speciation. ICP-MS can overcome this potential limitation using hydrofluoric acid (HF) digestion. However, as many site surveyors are interested in PTE, missing recalcitrant elements is not a concern since they are not mobile or bioavailable and hence pose little risk. Furthermore, the use of HF poses significant health and safety issues [64]. However, this limitation has implications for those looking to survey and recover PVE from a site. As knowledge of recalcitrant may be useful as new extraction methods are developed such as hydrometallurgy or biohydrometallurgy [8].

This and previous studies assumed that aqua regia and ICP-MS was an accurate and gold standard method to compare pXRF performance against. However, this study shows that when applied to post-metallurgical sites with disparate elemental concentrations this assumption is incorrect. Future research on such

sites should include representative CRMs as part of their validation procedure that have been created using total extraction methods. These findings may have implications for current site surveyors who use ICP-MS as their primary methodology. Although as previously stated, recalcitrant elements are generally not mobile or bioavailable and hence do not require inclusion in risk analysis.

2.5.3 Overall performance of pXRF on slag

This study set out to determine the effects of pre-treatment on the accuracy of pXRF measurements of weathered ferric slag. In the case of raw pXRF measurements, the mean r^2 was 0.41 (0.64 for 6 good elements) while ignited (ex-situ) was higher at 0.44 (0.79 for 6 good elements).

These results did not meet the hypothesis that pre-processed samples would meet the EPA's definitive data quality level ($r^2 > 0.90$). Furthermore, recent studies measuring soil with pXRF had substantially higher r^2 values than results presented within this study with average r^2 values of 0.62 for raw measurements [38–42] and 0.79 for ex-situ measurements [24,41,44,60–62,65–67] with maximums of 0.97 for raw [40] and 0.99 for ex-situ [62,67]. This difference could be due to the substantial differences in slag and soil matrixes. For example, the concentration ranges observed within the study herein (Fe max: 190,000 mg kg⁻¹) (Figure 2.3), were substantially higher than the maximum observed in any other pXRF study (Fe max: 71,990 mg kg⁻¹ [68]). However improved methodologies may also be the cause, several studies have made use of CRMs to create calibration curves for pXRF [45,60]. A method developed by Rouillon et al. (2016) [46] increased the accuracy of pXRF to the point of outperforming ICP-MS (mean recovery for Fe 99.0% and 94.1% from 5 CRMs for pXRF and ICP-MS respectively). Rouillon's methodology was considered for our study, to improve accuracy and to validate our ICP's accuracy, which was assumed based on previous studies. But as discussed earlier no representative CRMs of weathered BOS slag are currently available.

Despite correlations for six of the twelve elements analysed, this study found that increased sample processing did not always lead to improved correlations. As such, best practice requires that, pXRF be validated against ICP-MS at every site

and sample preparation methodology used to provide correction equations (i.e., $y = mx+c$) as recommended by Ravansari et al (2020). Based on the study's results, pXRF can only be recommended for the analysis of Pb, Sr, Cr, Mn, Ca, and Fe in BOS slag matrixes. Limiting the benefit of pXRF as a rapid analysis tool if ICP-MS analysis will need to be carried out for other elements of interest. Especially if PTE are of interest as only two (Pb, Cr) of the nine elements currently of interest to site surveyors [5] were of useful data quality.

2.5.4 Bimodal distributions in concentrations

The following section explores the bimodal distribution encountered within the samples collected at Teesside and highlights the challenges in measuring such distributions. Previous studies serving waste sites often observed high heterogeneity with multiple matrixes present and a lack of clear horizons [69]. Therefore, it was an expected finding to observe a bimodal distribution of Fe, Ca, Mn, Ti and Cr (Figure 2.3) in the data which correlates with the two matrixes found on-site. The soil matrixes populated the lower end of the distributions, as expected, considering that the soils present were added to the site as a cap, rather than originating as a waste product from the BOS process [70]. However, Zn and P's bimodal distribution could not be associated with the sample matrix. This discrepancy may involve leaching processes from the slags, transferring Zn or P from the slag to the surrounding soil. Although, recent research contradicts this notion, suggesting that BOS slag is a stable material that does not generate significant leachate [71].

Ti exhibited a negative correlation (slope -1.0 to -1.7) across all processing steps (Appendix A.3), which was attributed to opposing cluster patterns around the matrix for pXRF and ICP-MS. This outcome is contrary to previous studies which have reported positive correlations as high as r^2 0.97, and slope 0.89 when measuring Ti CRMs [46]. However, the results presented herein are the first to be measured across multiple matrixes and show that pXRF will not perform consistently under these conditions; challenging the notion that pXRF will operate with uniform performance across heterogeneous waste sites. This is an important issue for future research and one avenue of investigation may be applying the

Rouillon et al (2016) CRM calibration method but with the addition of CRMs of differing matrixes to make such a calibration effective at heterogeneous waste sites.

2.6 Conclusion

This study showed pXRF produced qualitative (Cr and Fe) or quantitative (Mn and Ca) measurements for raw samples which improved after pre-treatments with Sr showing qualitative, and Pb, Cr, Mn, Ca, and Fe showing quantitative pXRF measurements. Sieving and grinding improved precision, while drying and grinding enhanced accuracy. However, this study provides the first evidence that organic matter does not significantly impact pXRF accuracy. The two distinct matrixes on-site resulted in a bimodal concentration distribution and a negative correlation for Ti. Results herein highlighted the challenges of using ICP-MS for BOS slag due to elements falling below detection limits and incomplete digestion of recalcitrant Fe by aqua regia.

Although the analysis in this study was carefully controlled, this study is limited by a lack of validation for ICP-MS and by the sequential setup of sample pre-processing meaning each step must be considered in the context of previous steps. Further work is required to establish the effect of SOM on pXRF measurement given the results of this study contradict previous literature. In addition, further research should utilise CRMs of different matrices to construct a multi-matrix calibration that may improve pXRF's performance on complex sites such as the one measured in this study. Finally due to aqua regia's inability to dissolve recalcitrant elements present in BOS slag future studies should employ total digestion by HF for the assessment of pXRF performance.

The results herein highlight the benefits of sample pre-processing to improve the effectiveness of pXRF and suggest a recommended methodology of sieving, drying, and grinding samples to achieve the highest accuracy and precision from pXRF and to measure samples through pXRF cups if lighter elements are of interest. However, in-situ results must show a correlation otherwise pre-processing will not improve pXRF's performance. Furthermore, given the significant variance in pXRF accuracy, validation must be advised at every site.

Finally, site surveyors need to measure significantly more than the six elements accurately measured by pXRF in this study, as such ICP-MS analysis will need to be performed on every sample, meaning practitioners may be best avoiding the additional analysis and expenditure of using pXRF on BOS slag sites. However, focusing solely on the six key elements, the methodology identified in this study significantly reduces both analysis time and cost enabling the recovery or remediation of contaminants at post metallurgical sites.

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3 Combining pXRF with Geophysical Data for Rapid Surveys of Heavy Metals

3.1 Abstract

Geophysics has previously been combined with induction coupled plasma to map heavy metal content. However, the viability of integrating portable X-ray fluorescence (pXRF) with geophysical methods to expedite heavy metal mapping remains unassessed. Therefore, this study set out to investigate the viability of combining pXRF and geophysical methods, including electromagnetic induction and electrical resistivity tomography, to rapidly map heavy metal concentrations at a highly heterogeneous post-metallurgical site. pXRF accurately predicted Fe, Ca, Mn, and Cr ($r^2 > 0.7$). Furthermore notable ranges in concentrations of Fe (2 – 20% w/w) and Ca (0 – 40% w/w) were detected. However, despite the wide concentration ranges, no correlations ($r^2 < 0.46$) were observed between pXRF and geophysical data, which was attributed to the differing sample volumes and depths measured by these methods. The study concludes that matrix heterogeneity and the scale disparity between geophysical and chemical sampling present significant challenges to rapid methodologies. Future work should focus on higher-resolution geophysical surveys and alternative sampling strategies to enable rapid and cost-effective mapping of high heterogeneity post-metallurgical waste sites.

3.2 Introduction

Reducing global carbon emissions requires an international transition to a green economy. This transition is fuelling the demand for heavy and rare metals [1] due to their application in low carbon technologies. However, their extraction and refinement is unsustainable, having produced more than 300,000 post-metallurgical sites across Europe alone [2]. Such sites can be sources of mobile pollution [3] and pose a risk to the environment and human health [4]. These sites can have concentrations as high as 40% (w/w) Fe [5] and with emerging technologies such as bio- or chemical leaching [5] contaminated sites may become new circular sources of critical raw materials.

To apply these new technologies, sites will need to be surveyed for their critical raw materials. As described in chapter 2, site surveys are carried out by developing conceptual site models (CSM) [6], However, this approach can take years to complete [7], at substantial expense. Due to the large numbers of samples required to build a detailed site survey and lengthy sample preparation needed for the current lab-based analysis using induction-coupled plasma emission spectroscopy/mass spectrometry (ICP-ES/MS) (Chapter 2) [8]. In addition, due to current legislation, attention is primarily focused on quantifying risks whereas opportunities to identify and recover potentially valuable elements (PVE) are overlooked [9].

Methods such as portable X-ray fluorescence spectroscopy (pXRF) [10], and geophysics [11] have been studied as tools for the measurement of heavy metals in contaminated sites. In particular, pXRF shows promise due to the limited data processing required. Previous studies have achieved correlations (r^2) as high as 0.7 [12] and 0.8 [13] between pXRF and ICP-MS, which is usable as a quantitative screening tool according to the US Environmental Protection Agency (EPA) [14].

In chapter 2 the limitations of pXRF such sample heterogeneity were discussed and overcome with ex-situ sample processing. However, this increased the cost and time required to generate data negating the benefits of pXRF. Alternatively sample heterogeneity may be overcome with large numbers of replicate scans on the same sample. As larger number of scans translates into a more effective sample measurement, so that the average of these replicates will provide a more accurate composition [15]. However, the number of scans necessary to reach representative volumes can range from 15 for heavier elements (e.g. Zn) to 162 for lighter (e.g. Ca) [10]. As a result, obtaining accurate predictions from pXRF can take between 15 minutes and one hour per sample, making high-frequency sampling programs non-viable. In addition, pXRF is limited to the measurement of samples at the surface of a site. Measurement of the depths of a site can be overcome via bore holing, but this comes at a significant expense and risks creating pathways for pollution to mobilise along.

Geophysics covers several methods including electromagnetic induction (EMI) or electrical resistivity tomography (ERT). Both of which have been increasingly applied to the identification of contamination due to their ability to provide continuous underground information rapidly, at low cost [16]. As such, ERT and EMI are used to identify subsurface structures and layers of material by archaeologists [17] and geomorphologists [18]. Unlike pXRF, geophysical measurements provide electrical resistivity or conductivity of the subsurface rather than concentrations of metals. This measurement is a result of multiple factors including water saturation, mineralogy, particle sizes, and the porosity of the analysed material [19]. When combining geophysical measurements with ICP-MS or bench XRF analysis of limited borehole samples, the concentrations of metals across a site can be predicted. For example, Srećko Bevandić et al. (2020) used a combination of ERT and bench XRF to quantify the total extractable mass of 279.9 t of Pb and 373.3 t of Zn at a former tailing pond in Belgium [11]. Another study by Barago et al. (2021) found a significant correlation ($r = -0.975$) between the electrical resistivity measured by ERT and total metal concentrations at a tailing impoundment in Northern Italy [20].

To date, studies combining geochemical and geophysical analysis have relied on lab-based ICP-MS or bench XRF and, as such, there is still a knowledge gap of whether portable pXRF can be combined with geophysical methods to predict metal concentrations rapidly across a contaminated site. This study aims to investigate if pXRF and geophysical data correlate across a post-metallurgical waste site and to develop a method to generate higher spatial resolution maps than would be practically possible with pXRF alone.

3.3 Methods

3.3.1 Site history and sample collection

As described in detail in Chapter 2 this study collected samples from slag heap in Teesside (UK) measuring 0.5 km² by 18 m tall (Figure 3.1.B) due to its potential for resource recovery. Documentation [21,22] suggests the deposits were mostly basic oxygen steel-making (BOS) slag with minorities of refractory and cantina Bessemer steel making slag and waste. Full sampling procedure can be found in

chapter 2, but in brief a total of 17 samples (3 replicates, 20 cm depth, ~1kg) were collected from the sub-surface at locations selected to overlap with geophysical measurements [23], Samples were stored in an airtight polypropylene bag at room temperature for later analysis, to avoid loss of moisture.

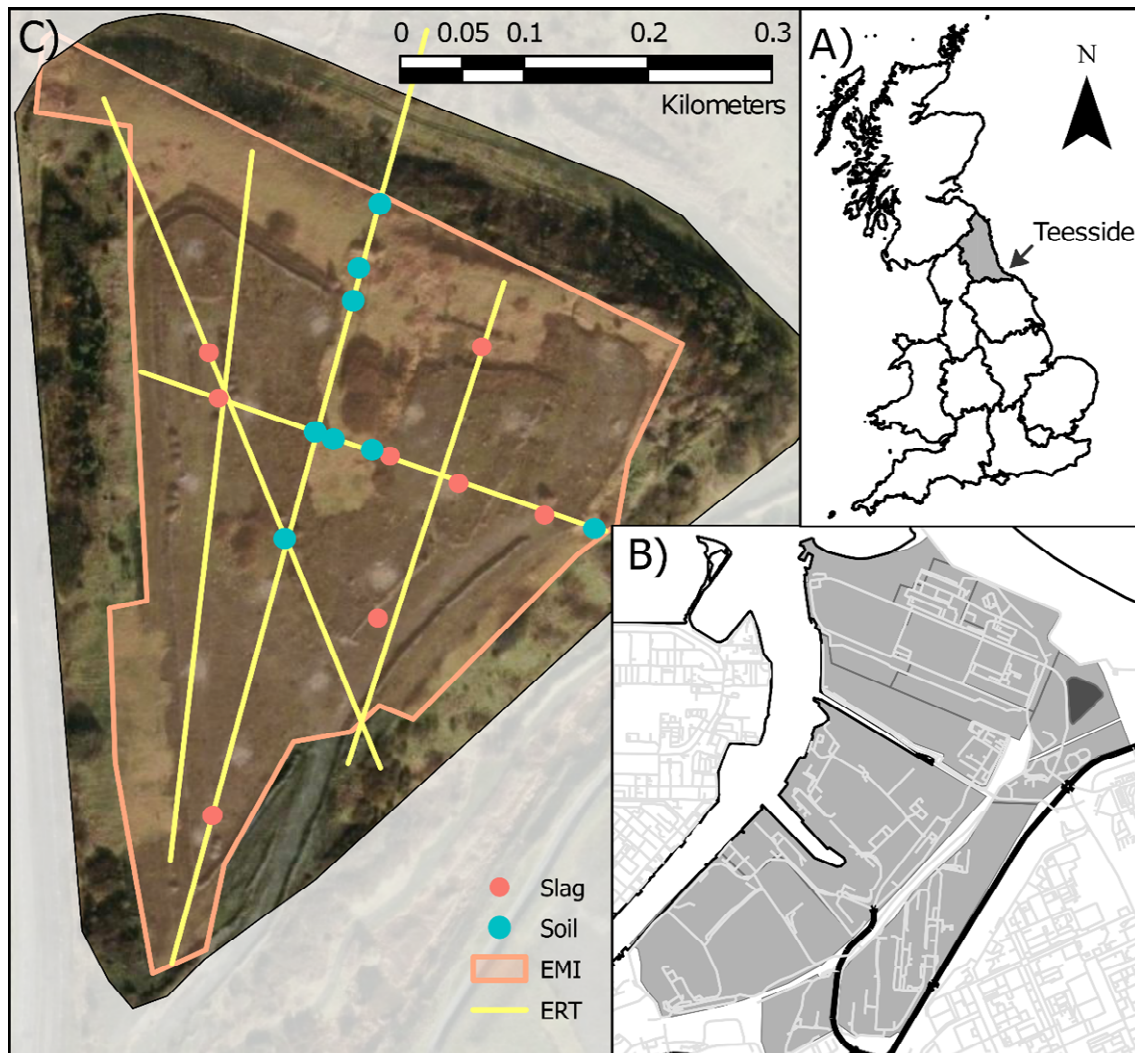


Figure 3.1 A) Teesside (UK), and the B) Long Acres study location (dark grey) located within the larger Teesworks former industrial area (light grey). C) shows the area surveyed by electromagnetic induction (EMI) (orange), electrical resistivity tomography (ERT) cross-sections (yellow lines), and sample locations, which were selected to overlap with geophysical measurements and captured the full range of conditions observed on-site (blue and red points representing slag and soil matrix respectively).

3.3.2 Geophysical methods

Geophysical measurements were carried out by partners at the French Geological Survey (BRGM) and the University of Liège (Belgium). The full methodologies and results can be found in Gourry et al. [24].

Briefly, an EMI survey was carried out (Figure 3.1) with a DUALEM-421S (Duallem, Canada) containing a horizontal coil transmitter creating a vertical magnetic field at 9 kHz and 3 horizontal and vertical receiver coils located at 1, 2 and 4 m from the transmitter. Recording electrical conductivity magnetic susceptibility in horizontal-coplanar mode at 1.5, 3, and 6 m deep and perpendicular mode at 0.5, 1, and 2 m deep for a total of 12 measurements per second, which were located using a Trimble GEO7X GPS with Zephyr III antenna.

Five ERT profiles were carried out with 96 electrodes at intervals of 2.5 m linked to a Syscal Terra (Iris Instruments, France). Brine water was added to each electrode to lower contact resistance. Measurements were collected for all five profiles in two different modes which were, resistivity, (2000 ms signal period, Dipole-Dipole configuration) and resistivity (250 ms signal period, Wenner-Schlumberger configuration).

3.3.3 Geochemical methods

Samples were transported to Cranfield University for analysis by pXRF and ICP-MS as described in section 2.3.3. Briefly, pXRF measurements of 26 elements were taken with a Delta Premium (Olympus USA). The analyser's Rh X-ray tubes were operated in soil mode by using the steel suitcase accessory; beams 1 and 2 were active for 10 s each and beam 3 for 30 s for a total scanning time of 50 s. Samples were scanned five times through their polypropylene sample bags with shaking between each scan. A Steel 316 Alloy coin was used to perform twice daily calibration checks. Factory LODs are listed in Appendix B.1. Following pXRF analysis, samples were sequentially sieved, dried, ground, and ignited before undergoing Aqua Regia acid digestion following ISO 11047:1998 [8]. Finally, a NexION 350D ICP-MS (PerkinElmer, USA) with uranium (U) internal standard was used with twenty-two individual element standards (1000 mg kg^{-1} ,

PerkinElmer, USA) to create a 5-point linear calibration curve (see Appendix B.1 for LODs). Full ICP-MS results can be found in section 2.4.

3.3.4 Data Analysis

Resistivity and chargeability from ERT and conductivity/in-phase signal from EMI were extracted for each sample location by using the data closest to the surface collected by our partners at the University of Liège and BRGM.

Violin plots were used to show the distribution of pXRF measurements. Linear regression of pXRF and geophysical measurements was carried out in R v2023.09.1 by applying the ordinary least squares (OLS) method under the “stats::lm()” function.

Data analysis and visualisation was carried out using R and the following packages: tidyverse, tidymodels, scales, cowplot, patchwork, Ggaly, and RColorBrewer [25–31]. All code is available in our CORD repository (doi.org/10.57996/cran.ceres-2636).

3.4 Results

The accuracy and precision of pXRF results was assessed with ICP-MS; the full results of which can be found in section 2.4. Of the 26 elements analysed by pXRF on raw samples, only four met the EPA’s quantitative or qualitative screening data quality level ($r^2 > 0.7$) [14] (see 2.3.4). These elements were Cr, Mn, Ca, and Fe and thus were selected for correlation with geophysical measurements.

In raw samples, Ca and Fe showed the highest concentrations whose respective mean values were 198,878 mg kg⁻¹ (19% w/w) and 92,584 mg kg⁻¹ (9.2% w/w) (Figure 3.2). All four elements showed a bimodal distribution in concentrations which was attributed to the two matrixes found on site. Higher concentrations of elements were found in slag matrix samples and lower concentrations were found in soil matrix samples, as the soil was believed to have been added to the site as a cap to stabilise slopes after waste deposition [32].

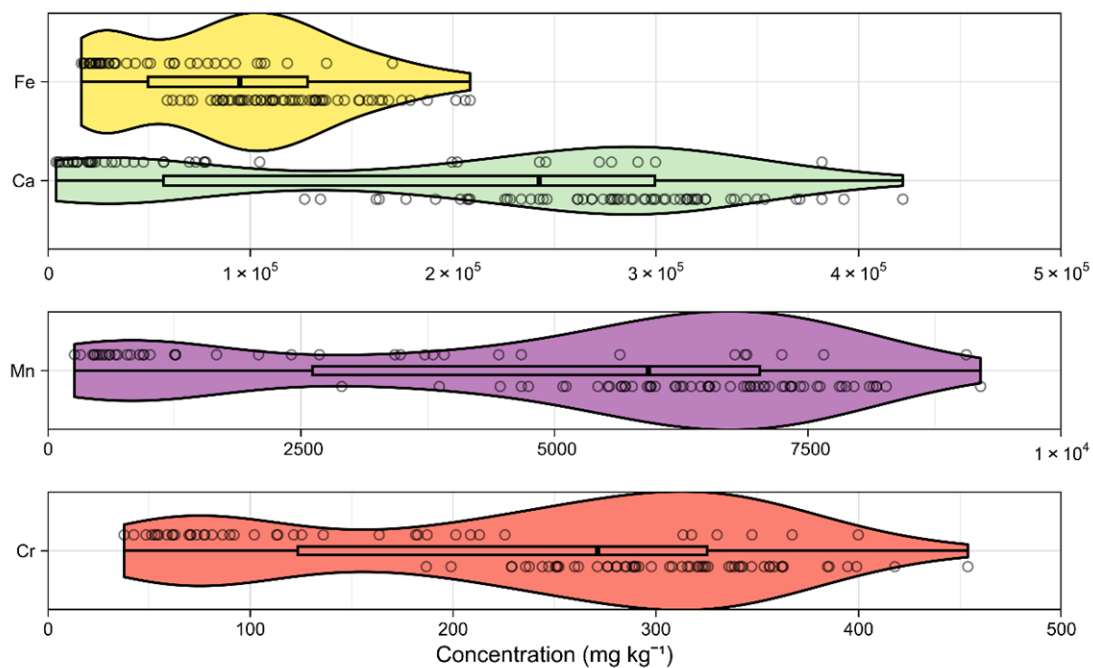


Figure 3.2 Range and distribution of Fe, Ca, Mn, and Cr detected by pXRF in raw samples (n=102) collected from an iron slag heap in Teesside (UK). Circles below box plot indicate slag matrix and circles above box plot indicate soil matrix tabulated values can be found in Appendix B.2.

To assess the viability of using EMI and ERT to predict concentrations of the metals, their corresponding readings were plotted against the pXRF

measurements at the same location in Figure 3.3

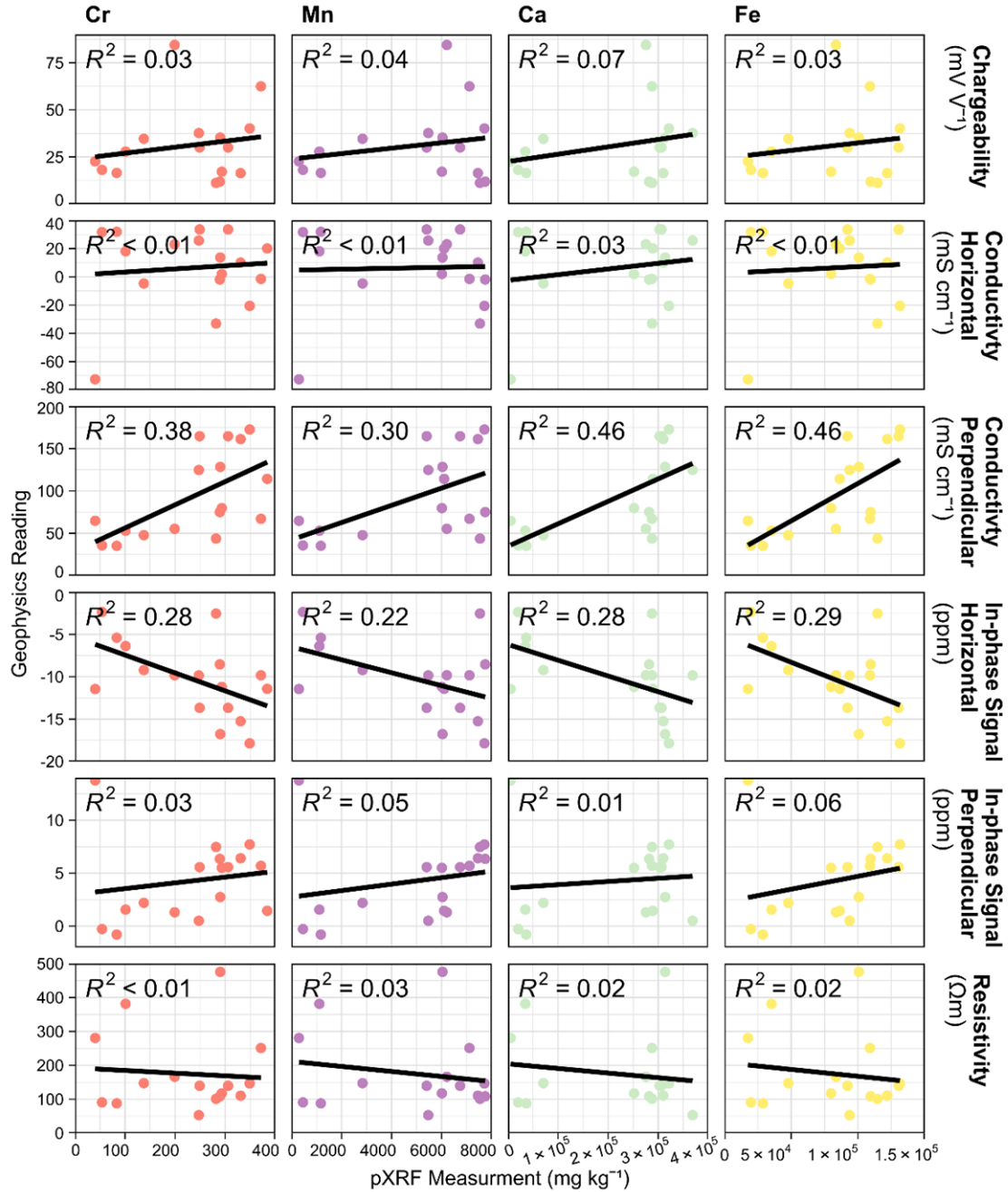


Figure 3.3. ERT's two readings, chargeability and resistivity, showed no correlation with an r^2 of <0.07 . EMI showed limited improvement with horizontal coplanar in-phase signal achieving an r^2 of 0.29 and perpendicular conductivity achieved the highest r^2 of 0.46. Hence no correlation was identified between any geophysical method employed and pXRF. To ensure pXRF was not the reason for poor correlation, ICP-MS data was also plotted against EMI and ERT (Appendix B.3), which showed a similar lack of correlation ($r^2 = 0 - 0.58$).

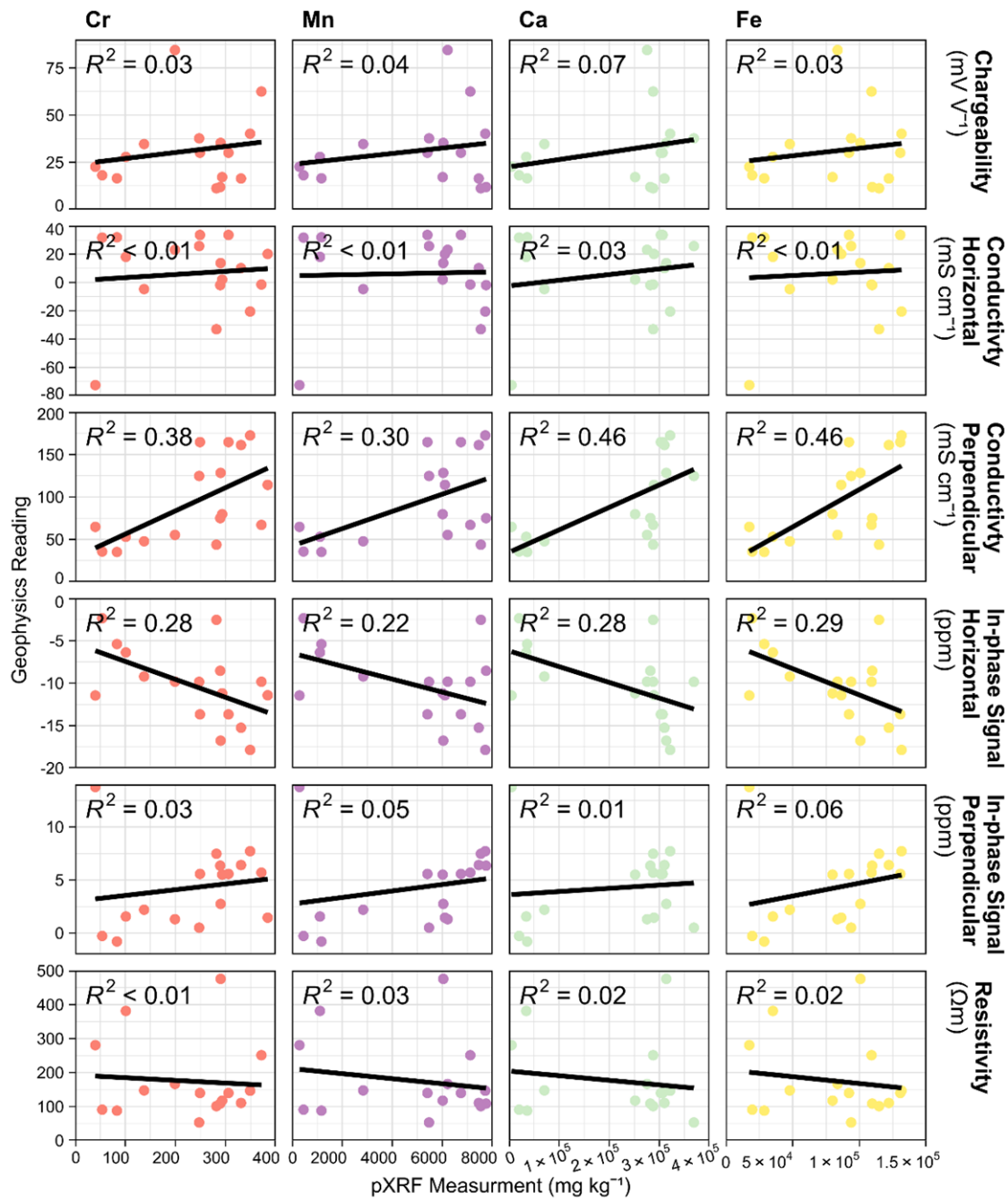


Figure 3.3 Regression of samples ($n=102$) collected from an iron slag heap in Teesside (UK), showing Fe Ca, Mn, and Cr concentrations measured by pXRF (x-axis) against geophysical measurements, (y-axis) of electrical resistivity tomography (chargeability, resistivity), and electromagnetic induction (conductivity and in-phase signal in both horizontal coplanar and perpendicular modes) with a OLS regression (black solid line).

3.5 Discussion

Previously researchers have utilised geophysics to identify layers of the same material which was then given an elemental concentration based on the analysis of borehole samples [11]. This approach is effective for tailing ponds where clear strata are likely to be present [11]. But waste dumps often contain a mixture of materials with limited structure to its deposition [33]. In the case of our study, no clear areas of homogeneous material could be identified by either ERT or EMI as shown in the separate geophysical report [24]. Hence, correlating geophysical signals directly with geochemical measurements was necessary as previously done by Barago et al. (2021) who reported r of -0.975 between inverted resistivity and summed metal concentrations [20]. While Gonzales et al. (2011) found a r^2 of 0.88 for ERT and Fe as well as an r^2 of 0.62 between ERT and (Pb + Zn) [34].

Despite previous success correlating ICP-MS and geophysics [20,34], our study found no correlation ($r^2 < 0.46$) between pXRF, and any geophysical method employed here (Figure 3.3). Inaccuracies in pXRF were considered as the cause but when geophysics measurements were plotted against ICP-MS (Appendix B.3) the same lack of correlation was found ($r^2 < 0.58$). This lack of correlation was primarily attributed to the differences in methodologies. Previous studies [20,34] collected borehole samples, which covered the same depths as geophysical methods (0 – 30m) [20]. However, due to unfavourable ground conditions, borehole sampling was not feasible and as such sample depths for pXRF were not the same as measured by geophysics. The pXRF samples were taken from ~0.2 m depth, while the shallowest geophysical measurements were at a depth of ~1 m. No previous literature could be identified that employed similar methodologies and, given the high heterogeneity observed in geophysical measurements [24], it is unlikely that subsurface samples would be representative of measurements at greater depth. Hence, future studies will require borehole sampling to collect representative samples.

However, depth was not the only limitation of our sampling method. Geophysical measurements generally make measurements over a large cross-section or volume. In the case of ERT, the resolution is approximately half of the electrode

spacing [35], meaning in our study ERT would provide a single value for 1.25 m² of cross-section. Whereas traditional geochemical sample analysis would require only 0.2 g for a single ICP-MS measurement [36] and even less for pXRF [10]. This scale difference implies that normal geochemical sample volumes are unlikely to provide the same values as the average over the larger volume that geophysical methods measure. Particularly at sites with high heterogeneity like waste sites [33].

Different strategies have been implemented to account for this problem. Gonzalez et al. (2011) maintained small geochemical sample sizes of 7 cm core sections, but reduced the distance between electrodes to 0.5 m, which increased ERT's resolution to 0.25 m² resulting in an r^2 of 0.62 – 0.88 [34]. Whereas another strategy by Barago et al. (2021) used 2 m electrode spacing and 1 m length of core sample, which were homogenised before analysis by ICP-MS and achieved an r^2 of 0.98 between ERT and elemental concentrations [20].

The method employed by Barago et al. (2021) would require samples to be returned to the lab for homogenisation, reducing the benefits of rapid analysis with pXRF. In addition, this method also risks not providing a high enough resolution at high heterogeneity waste sites. For example, Gonzalez et al. (2011) found a higher-resolution ERT cross-section was required for identification of a thin layer 0.0 – 1.5 m deep. Yet the latter method would require more time on site to measure the same length of transect. In addition, shorter electrode spacing decreases the maximum depth of measurement [37] and limits the utility of any survey implementing this method.

The results of this study cast doubt on the viability of geophysical measurements on high heterogeneity sites such as post-metallurgical sites as a tool to accelerate the surveying of metal concentrations. This uncertainty is ultimately due to the larger volumes and depths measured by geophysics that cannot be practically matched with traditional sampling for pXRF or ICP-MS analysis without significantly increased workload and costs.

3.6 Conclusion

This study set out to correlate geophysical information (EMI and ERT) with geochemical data measured by pXRF for the first time. The intention was to rapidly generate geochemical maps to aid in the recovery and remediation of waste resources in post-metallurgical waste sites.

Across 17 sample points located in a BOS slag heap in Teesside (UK), Fe, Ca, Mn, and Cr were measured with pXRF yielding mean concentrations of 94,946, 242,545, 4,960, and 238 mg kg⁻¹, respectively. However, no correlation was found between the four element concentrations and either EMI or ERT (r^2 0.00 – 0.46). This result was primarily due to the limitations of the sampling program employed, which did not include borehole sampling as that proved to be beyond the financial scope of the project. As such, generating geochemical maps of the site by using fewer samples than needed under a traditional sampling program was not possible.

The findings of this study highlight the challenges in carrying out surveys on post-metallurgical sites due to their high heterogeneity. Matrix heterogeneity and the significant sample size differences required for geophysical and chemical methods yielded an unviable correlation between these data acquisition approaches. Different sampling strategies and higher-resolution geophysical measurements may help to overcome said issues but at significantly increased cost and time. Rapid, cost-effective methods of surveying post-metallurgical sites are much needed for recovering PVE resources and supporting the transition to a greener economy. Research should be directed towards optimising geophysical survey methods to achieve the higher resolution required to overcome the matrix heterogeneity present at such sites.

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4 An Innovative Data Fusion Framework of pXRF and Vis-NIR to Address Sample Interferences and Reduce the Need for Sample preparation in Soil Analysis

4.1 Abstract

Portable X-ray fluorescence (pXRF) is widely used to rapidly measure metal concentrations however interferences caused by moisture and soil organic matter (SOM) require time consuming sample preparation to achieve accurate measurements. Therefore, this study developed a novel data fusion framework combining pXRF and visible-near infrared (Vis-NIR) spectroscopy to improve measurements of metals by accounting for interferences caused by moisture and SOM. A synthetic soil sample set with varying moisture, SOM, and elemental concentrations (Ca, Cl, Cu, Fe, K, Sn, Ti, Zn) was produced and measured using pXRF and Vis-NIR. Moisture had a suppressive, non-linear effect on pXRF measurements, with pXRF recovery as low as 50% at 15% moisture, whereas SOM exhibited negligible impact. Raw pXRF performance was high for $\text{Sn} > \text{Zn} > \text{Cu}$, ($r^2 > 0.90$) and lower for $\text{Ti} > \text{Cl} > \text{K} > \text{Fe} > \text{Ca}$ ($r^2 = 0.89 - 0.34$). The data fusion framework increased prediction accuracy for all elements with Zn, Sn, Cu, Ti increasing r^2 to >0.96 and Ca showing the largest increase to $r^2 = 0.65$. When compared to previous data fusion implementations the data fusion framework outperformed both model averaging and spectral concatenation. These findings demonstrate the potential of the novel data fusion framework to account for interference, mitigating the need for sample pre-processing and enabling rapid data collection. This method has the potential to significantly reduce the time and costs required to complete containment land surveys, facilitating the remediation of such sites.

4.2 Introduction

Heavy metal contamination makes up 35% of 342,000 contaminated sites identified in the European Economic Area [1] causing ecosystem deterioration and risk to human health [2]. However, novel recovery methods mean the once

economically unviable resources at these sites may now be profitable, funding their remediation [3]. To accurately control the risk and extract the potential resources at such sites, precision measurements are needed on a large scale. However, current methods of heavy metal detection in soil are destructive requiring complex pre-treatment at significant cost and time [4,5]. These limitations make the surveying stage a bottleneck in the remediation of contaminated sites. To address these challenges and enhance the economic feasibility of site remediation, innovative analytical methods are required.

Portable X-ray fluorescence spectroscopy (pXRF) is a handheld instrument that can be used in-situ or ex-situ to measure elemental concentrations [6]. Previous studies have achieved high accuracy ($r^2 > 0.98$) when measuring certified reference materials [7]. But accuracy drops when applying to real world samples with one study only achieving r^2 values of ~ 0.65 for V, Co, and Mo [8]; and another failing to find any correlation for As, Ni, Ti, Zn, P, and K [Chapter 2]. These differing accuracies have been attributed to several interferences such as moisture content [9], soil organic matter (SOM) content [10], and soil particle size [11]. The most common way to improve pXRF accuracy is ex-situ sample preparation such as drying and grinding [6] [Chapter 2], but this adds time and cost mitigating pXRF's benefits. Hence, researchers have developed different methods to incorporate SOM and moisture measurements to increase accuracy [10,12,13]. Furthermore, there has been recent research questioning the impact of SOM warranting further investigation [Chapter 2].

Visible near-infrared diffuse reflectance spectroscopy (Vis-NIR) has been successfully utilised to predict several soil properties such as SOM/moisture content [14], and minerals containing Al or Fe [15]. It has also successfully been used for the prediction of elemental metals such as Cd [16,17]. However, Vis-NIR cannot directly detect heavy metals at moderate or low concentrations ($< 4000 \text{ mg kg}^{-1}$ for Cd) [15]. Instead, heavy metals are indirectly correlated to the Vis-NIR spectrum via other soil characteristics such as SOM to which heavy metals are often bound [17]. But this limits any model created, to samples similar to those

on which a model was developed, as the indirect correlation they rely on may not be the same in differing sample sets [18].

While both Vis-NIR and pXRF have limitations, when their datasets are combined via data fusion the accuracies of elemental measurements can be improved [19]. Research into the data fusion of Vis-NIR and pXRF for the measurement of elemental metals, herein referred to as data fusion, is relatively novel with the first study being published in 2015 [19]. Previous methods of data fusion can be categorised into four groups: i) the simple concatenation of the Vis-NIR spectrum and the pXRF spectrum [20–23] or the concatenation of the Vis-NIR spectrum pXRF predicted metal concentration [19,24], sometimes referred to as equal weight fusion; ii) the use of spectral feature selection algorithms on concatenated spectrums to reduce redundant variables before modelling [20]; iii) matrix combinations which include outer-product analysis (OPA) [20,23,25] and co-addition fusion [23]; iv) model ensemble, or model averaging where the results of separate models are averaged together with different weightings based on their respective accuracy [20–22,25,26]

These methodologies have proven to be an effective approach producing r^2 as high as 0.95 [27] but their use of full or partial spectrum data is a limiting factor in their utility. The internal calibration of the pXRF utilises the K and L peaks defined by Moseley's law whose response is directly related to an element's concentration [23]. However, all previous data fusion methods utilised full or partial spectrums that include variables that do not directly correlate to the element in question. Instead, the multivariate model will identify correlations with other variables that happen to correlate with the element in question [25,26]. However, these correlations are not universal and will be specific to the sample set in question. Hence, new models will need to be created whenever measuring a new sample set, thus, mitigating the benefits of rapid methods.

To avoid this limitation, data fusion methods could look to leverage the knowledge of pXRF's specific interferences such as moisture [9] and SOM [10]. Chen et al [12] developed a general framework for improving pXRF accuracy by integrating moisture and SOM content. Across all six elements, the general framework

improved r^2 on average by 0.1, increasing Pb and Zn to 0.95 and 0.97 respectively. However, the general framework relied upon returning samples to the lab for oven drying and incineration, mitigating the benefits of in-situ rapid analyses.

As such, the overall aim of this study is to develop a data fusion framework to increase the accuracy of rapid elemental measurements in soil. This framework will be achieved by using portable Vis-NIR to predict moisture and SOM values that will be fed into Chen's general framework to correct pXRF measurements, enabling the accurate in-situ measurement of elemental metals without the need for laboratory work. Furthermore, given the contradicting literature on SOM interference [Chapter 2], this study aims to investigate the effects of moisture and SOM over a wide range of concentrations on accuracy pXRF measurements by using artificially spiked topsoil.

The hypotheses that will be tested are as follow:

- (i) That pXRF measurements will decrease when either moisture concentration increases, or SOM concentration increases.
- (ii) pXRF elemental concentration predictions will show stronger correlations with true elemental concentrations. When adjusted for true SOM and moisture concentrations.
- (iii) pXRF elemental concentration predictions will show stronger correlations with true elemental concentrations. When adjusted for SOM and moisture concentrations that are predicted by Vis-NIR spectroscopy.

4.3 Methods

4.3.1 Materials

Chemicals, consumables and instruments used in this work are in Table 4.1.

Table 4.1: Chemicals, consumables, and instruments used within this study.

Chemicals	Manufacturer
Calcium Carbonate (CaCO ₃) 99+%	Thermo Scientific, USA
Potassium Chloride (KCl) 99+%	Thermo Scientific, USA
Copper (II) oxide (CuO) 99+%	Thermo Scientific, USA
Iron (III) oxide (Fe ₂ O ₃) 98%	Thermo Scientific, USA
Tin (II) oxide (SnO) 99%	Thermo Scientific, USA
Titanium (IV) oxide (TiO ₂) 98.0 – 100.5%	Thermo Scientific, USA
Zinc oxide (ZnO) 99.9%	Thermo Scientific, USA
Levington Peat Free Topsoil	Evergreen Garden Care, UK
Consumables	
Prolene®, Precut Circles, 4.0 µm, Ø 63.5 mm	Chemplex USA
XRF sample cup, 1500 series	Chemplex USA
Nalgene™ Wide-Mouth LDPE Bottles 250 ml	Thermo Scientific, USA
Instruments	
Cubis® II Advanced Mass Scale	Sartorius, DEU
Olympus Delta premium pXRF	Evident, JPN
ASD Fieldspec 4 VNIR	Malvern Panalytical, NLD
KS 501 digital orbital shaker	IKA-Werke, DEU

4.3.2 Design of experiment and sample creation

To develop a data fusion framework that can accurately predict elemental metal concentrations by adjusting pXRF measurements to account for SOM, and moisture interference, a suitably large and wide-ranging sample set was required. Additionally, to assess instrument performance the true concentration of metal, SOM, and moisture had to be known. Therefore, a synthetic sample set was created by mixing varying metal (Ca, Cl, Cu, Fe, K, Sn, Ti, Zn), SOM, and moisture concentrations, with the measured weights of each variable used to calculate the true concentrations.

To ensure that an unbiased and wide range of values was measured, a full-factorial experimental design was employed [28], wherein each level (concentration) of the independent variables (moisture, SOM, and elemental concentration) was systematically combined to evaluate all possible interactions whilst minimising cost and optimising time (Table 4.2). Moisture had five levels while SOM and elemental concentration had six, levels resulting in a total of 180 combinations (Table 4.2). To minimise workload the seven elements included in this study, were treated as one independent variable for the purposes of the full-factorial experimental design, i.e. at level 2 all elements were at 100 mg kg⁻¹.

Table 4.2: Three-factor six-level full-factorial experiment to generate a wide range of values in each independent variable needed to develop a data fusion framework.

Levels	Independent Variables		
	Moisture concentration (%)	SOM concentration (%)	Elemental concentration (mg kg ⁻¹)
1	0.00	0.00	0.00
2	6.00	3.20	100.00
3	12.00	6.40	1000.00
4	18.00	9.60	4000.00
5	24.00	12.80	7000.00
6	-	16.00	10000.00

After oven drying (105 °C) and grinding (<2 mm), Levington peat free topsoil (17.19% loss on ignition, Evergreen Garden Care, UK) was used as the source of organic matter and background matrix. To achieve the various levels of organic matter half the topsoil was heated to 405 °C to ignite all organic matter. The incinerated topsoil was then mixed with the fresh topsoil in varying proportions to create the various levels of SOM concentration. For elemental concentrations, compound forms of (Table 4.1) of seven elements (CaCO₃, KCl, CuO, FeO₃, SnO, TiO₂, ZnO) were selected due to their prevalence in post metallurgical sites [2] and to provide a wide range of atomic numbers. Other elements were

considered for inclusion but were not available in non-toxic compounds. Finally, deionised water (Pruer LAB ultra, Elga, UK) was used for moisture concentrations.

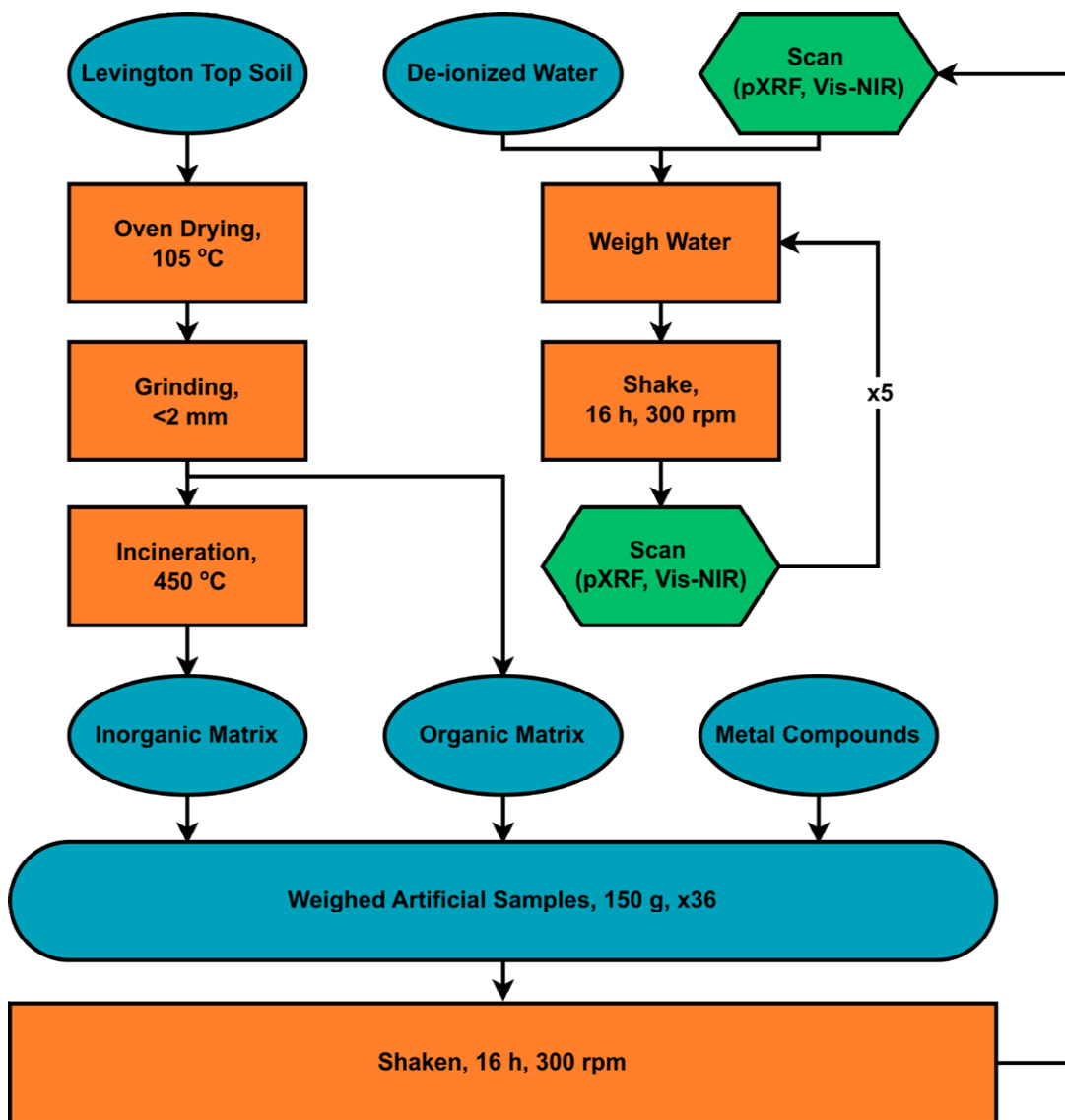


Figure 4.1 Preparation and analysis of synthetic samples for orthogonal experiment. The soil was oven dried at 105 °C and ground to <2 mm, half of the soil was then ignited at 450 °C making an inorganic matrix. The inorganic matrix, soil, and metal compounds were mixed in varying proportions to make thirty-six samples which were then shaken at 300rpm for 16h and scanned by pXRF and Vis-NIR. Finally in stages deionised water was added then samples were shaken and scanned again until all levels of moisture were measured. Blue circle = matrix, orange rectangle = process, green hexagon = analysis.

To create and scan the full sample range (Figure 4.1) 36 samples (150 g) were produced. Initially dried topsoil and ignited topsoil were weighed (Appendix C.2) into Nalgene bottles (250 ml, Thermo Scientific, USA) on a Cubis® II Advanced Mass Scale (Sartorius, DEU) to produce six replicates of the six levels SOM concentrations (Table 4.2). Secondly the eight compounds (CaCO_3 , KCl, CuO, FeO_3 , SnO, TiO_2 , ZnO) were weighed into the bottles to produce the six elemental concentrations (Table 4.2) ensuring differences between compound and elemental mass were accounted for. After weighing, samples bottles were secured horizontally on a KS 501 digital orbital shaker (16 h, 300 rpm, IKA-Werke, Staufen, DEU). Samples were then scanned as described below. After scanning deionised water was weighed into the sample to achieve the next level of moisture followed by a further 16 h of shaking and scanning. These steps were repeated a further three times until all five levels of moisture (Table 4.2) had been recorded. Actual weighed masses were recorded to four decimal places for later calculation of true elemental, moisture, and SOM concentrations. To ensure samples were sufficiently homogeneous test samples were prepared with different mixing protocols and scanned 30 times. It was determined that the method described above in combination with 15 scans of the sample would produce a homogeneous sample and result in a measured mean concentration having an error of $\pm 5\%$ of the true mean concentration for a 95% confidence interval.

4.3.3 Instrumentation pXRF and IR measurement

pXRF measurements were taken with an Olympus Delta Premium (Evident, JPN). The analyser's Rh X-ray tubes were operated in soil mode using the steel suitcase accessory; beams 1 and 2 were active for 10 s each and beam 3 for 30 s for a total scanning time of 50 s. approximately 15 g of the sample was decanted into XRF sample cups with Proleen® windows (Chemplex USA) and scanned through the Proleen® window before being returned to the bottle, shaken and decanted again. This procedure was repeated for a total of fifteen scans. A Steel 316 Alloy coin was used to perform twice daily calibration checks [29]. Factory limits of detection (LOD) are listed in Appendix C.1.

Vis-NIR measurements were collected using an ASD Fieldspec 4 (Malvern Panalytical, NLD) following modifications to Noctia et al. method [14]. In parallel with pXRF measurements approximately 15 g of sample was decanted into an XRF sample cup with Proleen® window (Chemplex USA) and measured from the top of the cup before being returned to the bottle, shaken and decanted again. This procedure was repeated for a total of fifteen measurements. The Vis-NIR was powered on 20 minutes before use and had its background set using a Spectralon standard (Labsphere, UK) every fifteen measurements. Measurements (10 mm diameter) of all samples were collected by placing the sample in direct contact with the Vis-NIR handheld probe containing a built-in quartz-halogen bulb of 3000 °K, at a 20° angle to the detection fibre. For each measurement, fifty successive scans were taken and internally averaged by the Fieldspec 4 to produce one final spectrum (350 – 2500 nm) per measurement.

4.3.4 Data analysis

The data fusion framework (Figure 4.2) developed in this study builds on previous work by Chen et al (2021) who created a general framework for improving pXRF measurements by integrating moisture and SOM concentrations [12]. Each step is outlined in detail below but in brief, this data fusion framework takes Chen's general framework and after optimal regression models have been identified replaces the moisture and SOM values with values predicted from Vis-NIR spectroscopy.

All data processing analysis and visualisation was completed with the following packages in R studio v2023.09.1: tidyverse, tidymodels, scales, cowplot, corr, rlang, ggpmisc, patchwork and RColorBrewer [30–38] except for preprocessing and modelling of IR spectra which was completed in Aspen Unscrambler v12.2 (Aspentech, USA).

Before data analysis, data was split into training (75%) and validation (25%) datasets. Preprocessing was applied to all data; modelling and variable selection were completed using training data; and the final comparison of data fusion, pXRF model and no model was completed with validation data (Figure 4.2).

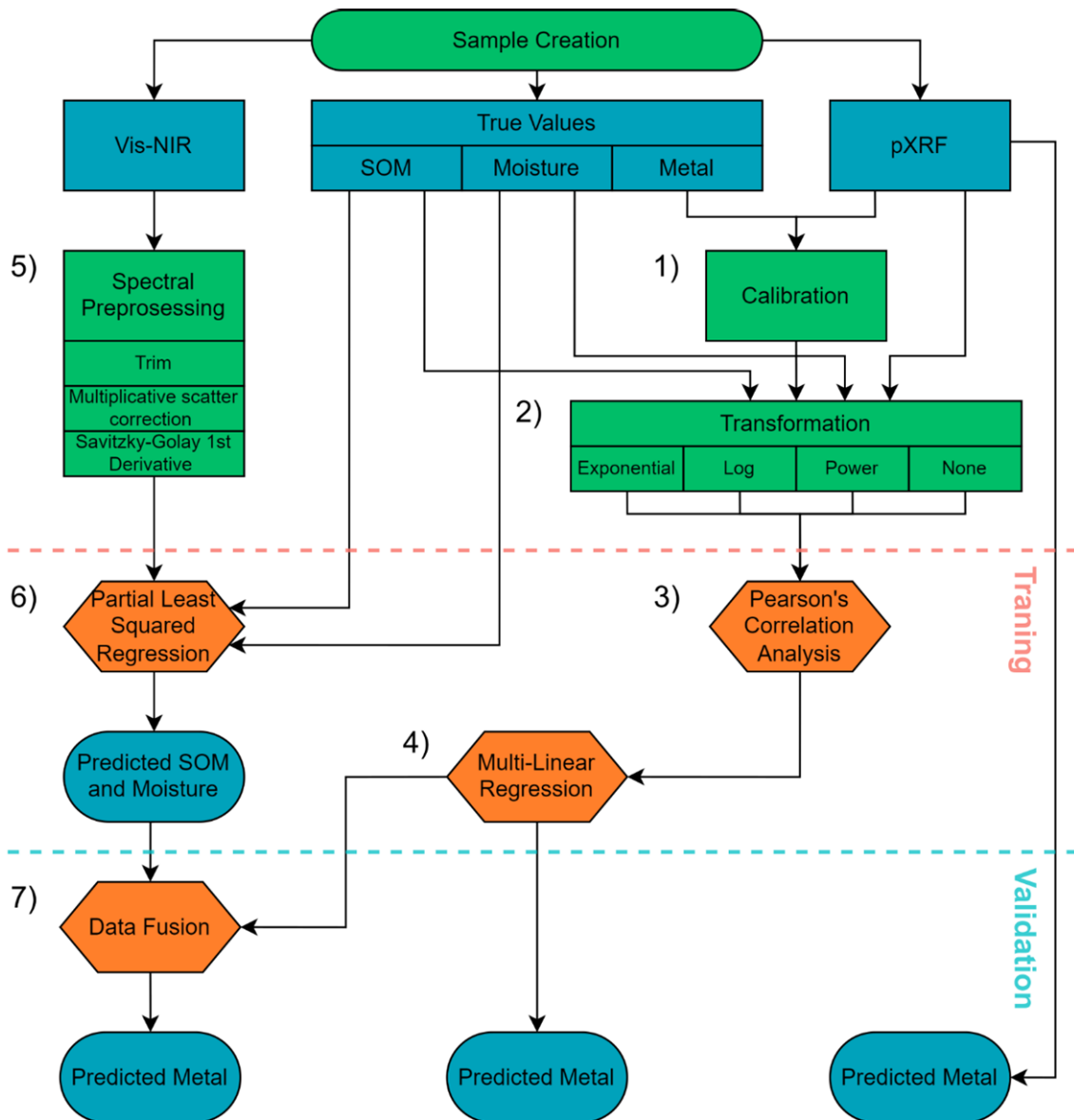


Figure 4.2: Data fusion framework to account for moisture and soil organic matter (SOM) effect on portable X-ray fluorescence spectrometry (pXRF) measurements; 1) True values (weighed elemental concentrations) were calibrated to account for background; 2) moisture SOM pXRF and calibrated true values were transformed; 3) Pearsons correlation analysis identified the most important factors; 4) the most important factors were regressed against each other generating the pXRF model; 5) Visible-near infrared (Vis-NIR) spectrums underwent spectral preprocessing; 6) pre-processed spectrums underwent partial least squared regression to predict moisture and SOM; 7) predicted moisture and SOM were fed into pXRF model to create data fusion model.

4.3.4.1.1 PxrF modelling

Step 1) True values (weighed elemental concentrations) required calibration to account for the background concentrations present in ignited topsoil. As such samples with zero moisture or SOM were used to regress true values against pXRF measurements. The regression equation from this was then applied to the entire dataset to calibrate true values (Appendix C.3).

Step 2) After calibrated true values were generated, calibrated true values, moisture and SOM values were naturally logged, squared, and cubed while pXRF measurements, were only naturally logged.

Step 3) Pearson's correlation analysis was used to correlate pXRF and Ln(pXRF) measurements for each element against calibrated true values, Moisture, SOM concentrations and their naturally logged, squared and cubed transformations (Appendix C.9). The highest correlating transformations of each variable were selected for multi-linear regression.

Step 4) Multilinear regression was carried out in R by applying the ordinary least squares (OLS) method using the "stats::lm()" function. After all models were fit Pearson's squared correlation coefficient (r^2) Lin's coordination correlation coefficient (r_c or ccc), ratio of performance to interquartile range (RPIQ), and root mean squared error (RMSE), were calculated on the calibration dataset and used to determine the best models for each element.

4.3.4.1.2 Vis-NIR modelling

Step 5) The raw spectra were extracted using the prospector package [39] in R studio v2023.09.1, wavelengths 999 – 1000 and 1799 – 1800 nm were removed due the artefactual steps occurring at the interface between the 3 detectors covering the instrument spectral range. All spectrums were then exported to Aspen Unscrambler v12.2 (Aspentech, USA). Multiplicative scatter correction (MSC) was applied followed by Savitzky-Golay 1st Derivative Transform using second order polynomial and a symmetrical smoothing width of 7 nm.

Step 6) Following Noctia et al method [14] Partial Least Square Regression (PLSR) was used to generate separate predictive models for moisture and SOM

from training data. The Nonlinear Iterative Partial Least Squares (NIPLS) algorithm was used, and seven latent factors were tested with 6 and 7 factors being identified as the optimal number for moisture and SOM respectively. Models were then used to predict moisture and SOM values for validation data (Appendix C.8).

4.3.4.1.3 Data fusion and pXRF recovery

Step 7) After optimal pXRF and Vis-NIR models were identified, moisture and SOM values in pXRF models were substituted for predicted SOM and moisture values predicted by the Vis-NIR models to create the data fusion model. Finally using validation data calibrated true metal concentrations were regressed against raw pXRF measurements, pXRF model predictions and data fusion model predictions.

In addition to the data fusion framework the effects of moisture and organic matter on pXRF measurements were directly investigated by plotting moisture and SOM against pXRF Recovery (Equation 4-1). In cases where the 95% confidence intervals of the slope and intercept overlapped with the hypothesised trend, no significant difference would be identified. However, a significant difference would be observed when the confidence intervals did not overlap, indicating that the relationship between pXRF recovery and either moisture or SOM deviated from the expected trend.

$$\frac{pXRF \text{ measurment}}{Calibrated \text{ True value}} \times 100$$

**Equation
4-1**

4.4 Results

4.4.1 Descriptive statistics.

Target concentrations for each element ranged between 0 and 10,000 mg kg⁻¹. However, practical limitations led to varying weighed concentrations: Ca, Cl, and K had maximum concentrations of ~5000 mg kg⁻¹; Ti, and Zn had ~ 8000 mg kg⁻¹; Cu, Fe and Sn exceeded 10,000 mg kg⁻¹; and moisture and SOM had ~30% and ~16% respectively (see Appendix C.4).

Furthermore, due to background concentrations within the topsoil the weighed concentrations required adjusting. As hydrofluoric (HF) acid digestion was not available to measure total elemental concentrations, pXRF measurements of mixtures with zero SOM and moisture were used to generate a calibration curve, which then adjusted all measurements.

After calibration Cl, Cu, Sn, and Zn showed minimal change in their concentrations $\pm$ ~1000 mg kg⁻¹ while Ca, Fe K, and Ti showed significant increases to maximums of 48,610, 42,629, 26,936, and 18,690 mg kg⁻¹ respectively (Figure 4.3 and Appendix C.5). Both positive and negative shifts in the slope of pXRF against true were observed for all elements (Appendix C.4). However, no change in r^2 was observed for any element (Appendix C.3). As such calibrated true values were used for all further data analysis and will be referred to as true values from now on.

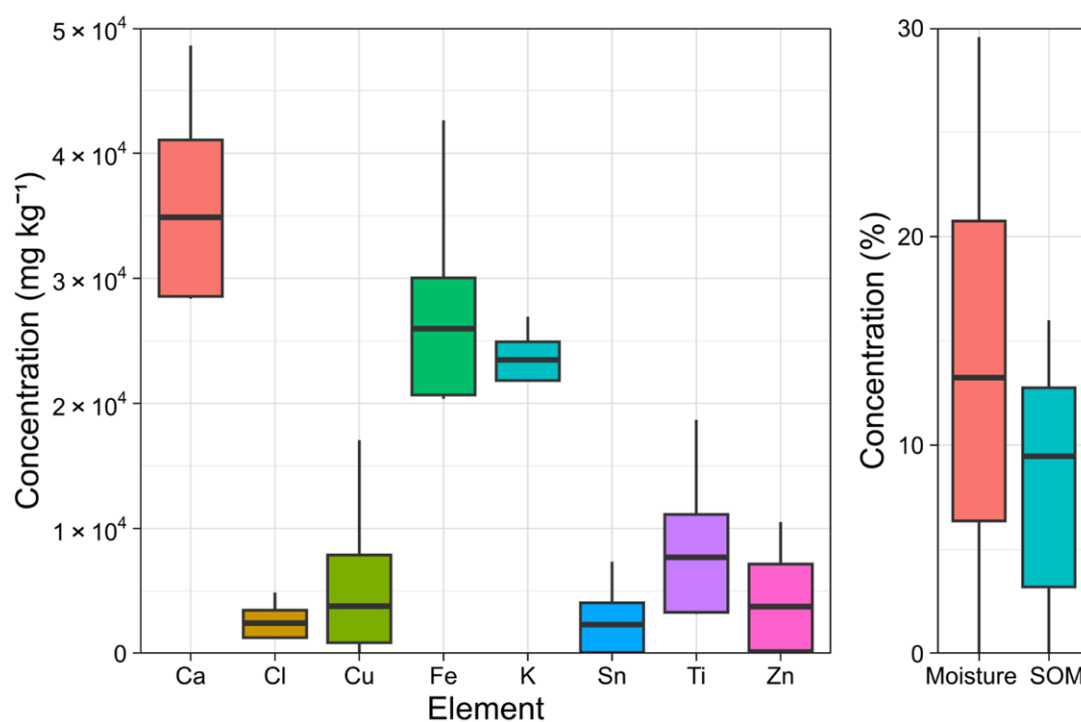


Figure 4.3 Box plot showing distribution of elements, moisture, and SOM within the synthetic samples after the calibration of elements using pXRF results where moisture and SOM were not present. A tabular form of this data can be found in Appendix C.5.

4.4.2 Moisture and SOM interference effects

4.4.2.1 SOM

To investigate the effects of increasing percentages of SOM and moisture on pXRF accuracy, the differing masses of SOM and elements added to each mixture had to be accounted for. Therefore, percentage recovery of pXRF was calculated (Equation 4-1), where a value of 100% would indicate pXRF returned the same measurement as the true value of the mixture as previously done by Rouillon et al (2016) [7]. Standard methods do not remove organic matter before acid digestion [40] hence SOM mass was included in the total mass of the sample. As such pXRF recovery will remain at 100% if SOM's only influence on pXRF measurements is due to simple dilution of analyte (slope = 0, intercept = 100% Figure 4.4).

Zn did not show a significant difference with a slope of -0.201 and 95% confidence intervals of 0.077, and -0.479 (Figure 4.4, Appendix C.6). But all other elements showed significant differences. Ti showed the smallest difference followed by Cl < Fe < Ca < Cu < Sn < K indicating that SOM had more than a dilution effect on pXRF measurements for these elements. Despite the significant difference only K and Sn showed substantial differences from the hypothesised slope with slopes of -1.433 and -1.258 respectively. Furthermore, only K had a high r^2 of 0.830 compared to the next highest at 0.205 for Ca indicating that SOM concentration was not the largest factor in the determination of pXRF recovery for most elements. Finally while most elements showed similar correlations for all six element levels Ti showed diverging trends with higher element levels having a pXRF recovery over 100% at high SOM concentrations and low element levels having a recovery under 100% at high SOM concentrations.

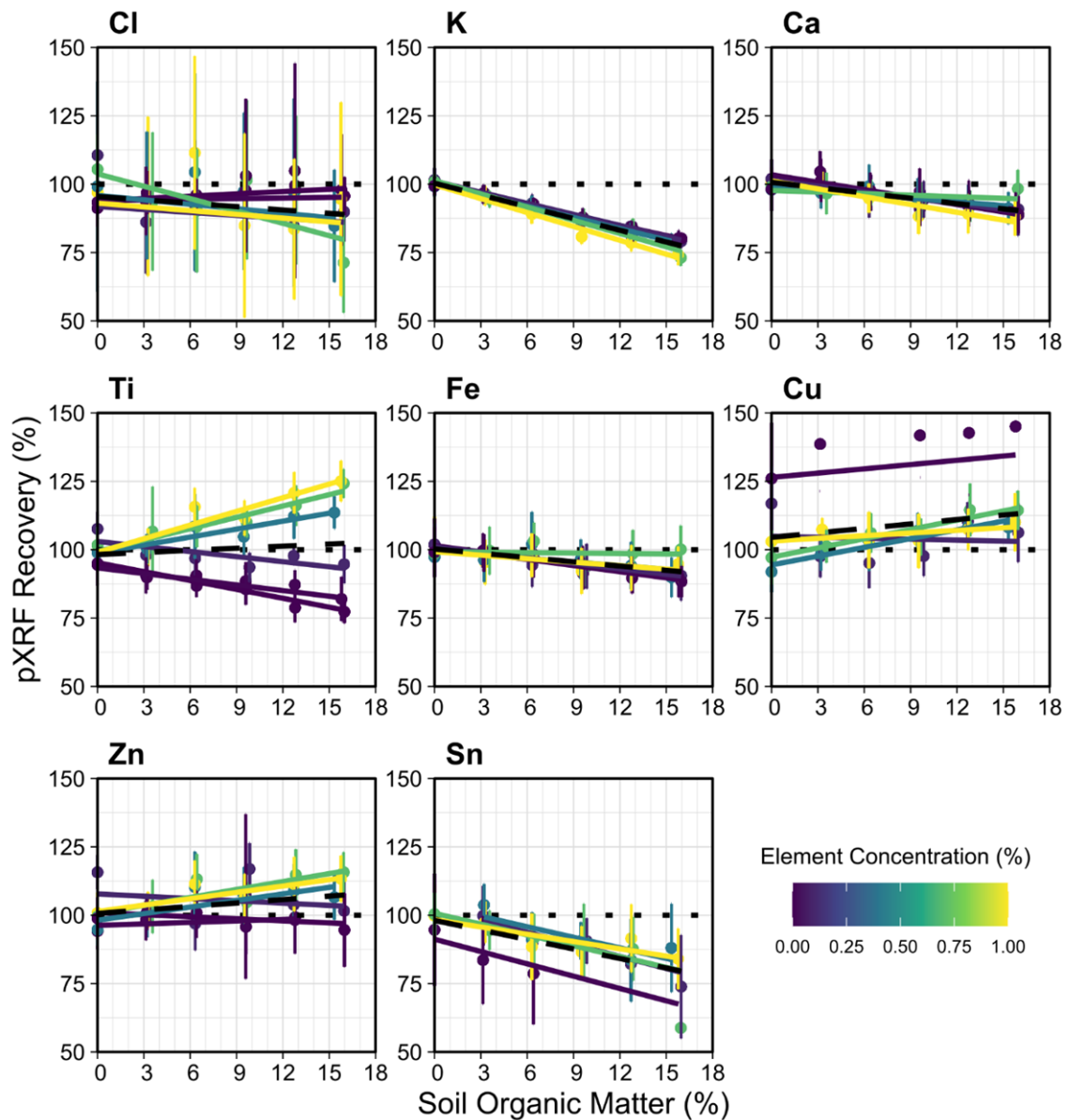


Figure 4.4 A comparison of the effects of soil organic matter (SOM) on elemental pXRF recoveries. Coloured solid lines indicate the trend of different element levels (starting concentrations Table 4.2) with lower concentrations in blue and higher concentrations in yellow. Black dashed line indicates the overall trend for each element. Black dotted line indicates the null hypothesis ($y = 0x + 100$) that SOM only has a simple diluting effect on pXRF measurements. Regression statistics can be found in Appendix C.7.

4.4.2.2 Moisture

Unlike SOM, moisture is removed from samples before undergoing acid digestion [40]. As such moisture was not included in the total mass of the sample used to calculate true concentrations. Meaning, the null hypothesis that moisture has only a simple dilution effect on pXRF measurement is shown as $y = -1x + 100$ in Figure 4.5.

Unlike SOM, moisture showed a non-linear trend for all eight elements which was substantially different from the null hypothesis. For Ca Ti, Fe, and Zn this presented itself as an initial sharp decrease in recovery percentage with the lowest mean recoveries being observed at ~15% moisture. The depth of decrease appeared to correlate with the atomic number of each element with Ca showing the lowest recovery at ~50% followed by Ti ~55%, Fe ~60%, and Zn, ~70%. After the steep decrease in recovery Ca and Ti showed increases in recovery while Fe, and Zn showed plateaus with all four elements converging at ~70% recovery when moisture reached ~30% which matched the predicted recovery expected from the simple dilution effect of moisture. Cu and Sn may have followed similar trends to the other four elements but increased variation between element levels and fewer data points limit interpretation.

Cl and K did not show similar trends to the other elements with Cl showing recovery increase above 100% as moisture increased and a peak in mean recovery at ~20% moisture. However, K showed two peaks in recovery at ~6 and ~ 20% moisture. Furthermore, unlike the other elements Cl and K showed divergences in their trends due to element level, with higher starting concentrations showing increases while lower starting concentrations showed decreases.

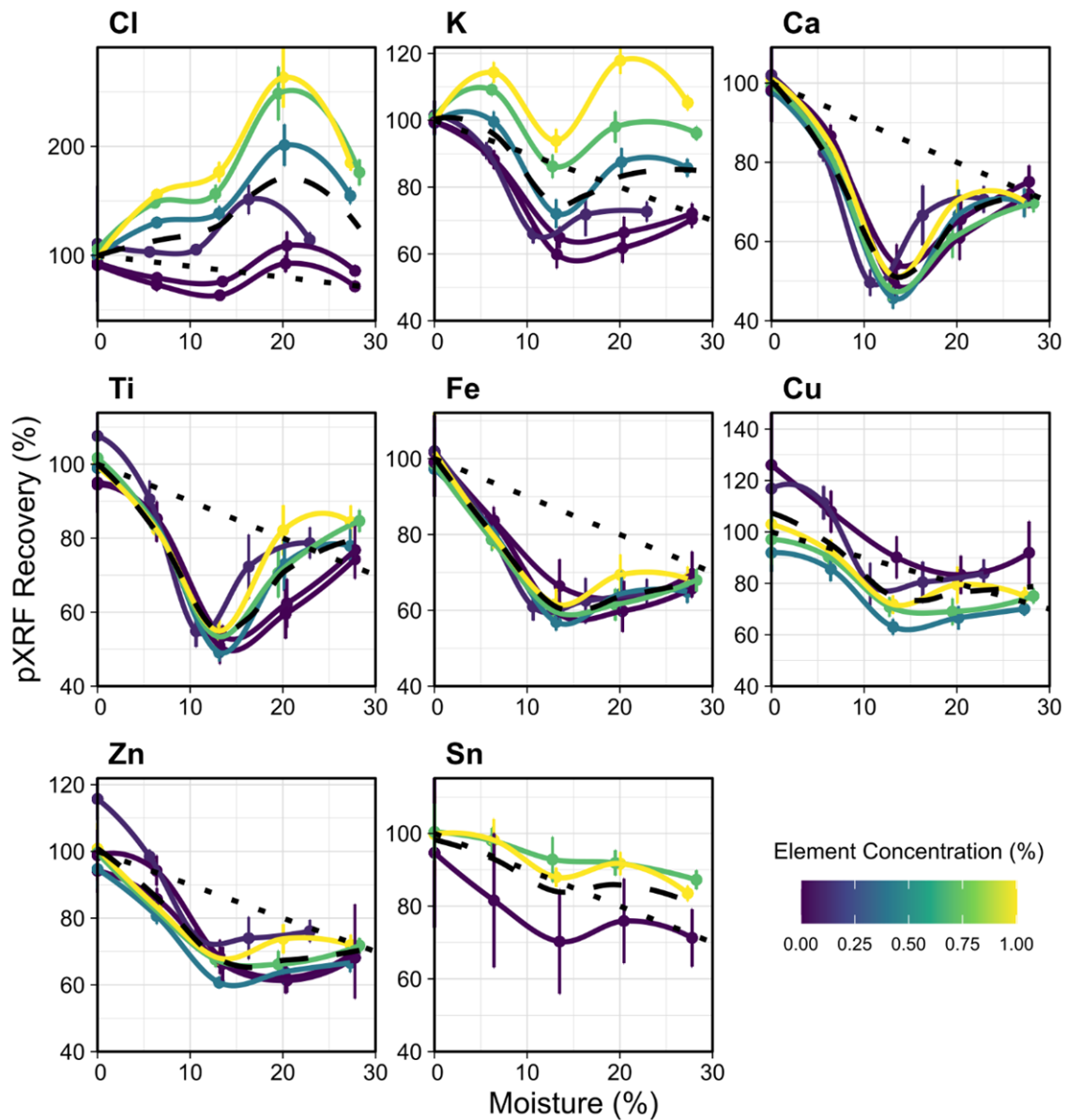


Figure 4.5 A comparison of the effects of moisture on elemental pXRF recoveries. Coloured solid lines indicate the trend of different element levels (starting concentrations Table 4.2) with lower concentrations in blue and higher concentrations in yellow. Black dashed line indicates the overall trend for each element. Black dotted line indicates the null hypothesis ($y = -1x + 100$) that moisture only has a simple diluting effect on pXRF measurements.

4.4.3 Data fusion

Raw pXRF measurements showed the best prediction for, Sn, followed by Cu>Zn>Ti (r^2 0.97 – 0.89) (Figure 4.6, Table 4.3). while Cl>K>Fe>Ca (r^2 0.79 – 0.34) had worse predictions. But Ca>Fe>K showed the greatest improvements after the framework was applied to account for moisture and SOM's effects increasing their r^2 by 0.38, 0.32, and 0.15 respectively. Whereas the other elements showed less than 0.084 increase in r^2 Cl>Ti>Zn>Cu after the framework model was applied, while Sn showed no change in r^2 . However, Cl, Ti, Zn, Cu, and Sn did show substantial decreases in RMSE (222 – 1560) and increases RPIQ (3.85 – 11.57) indicating random error had been removed from the predictions by the framework model. As such Zn>Sn>Cu>Ti>Fe>Cl were considered excellent framework models with $r^2 > 0.85$ and K>Ca good framework models with $r^2 > 0.7$.

Despite Ca, Cl, Cu, Fe, K and Sn's best framework models incorporating both moisture and SOM (Appendix C.10), there was little difference between these models and the best models that did not incorporate SOM with less than 0.05 increase in r^2 after incorporating SOM (Appendix C.10). Furthermore, Ti and Zn's best models did not incorporate SOM.

After the Vis-NIR predicted values for SOM and moisture were fed into the framework model (Step 7 Figure 4.2) to create the data fusion model Sn showed no change in performance with r^2 , r_c , RPIQ and RMSE remaining the same. However, all other elements showed a decrease in prediction quality although this was not substantial for any goodness of fit measure (change in r^2 0.07 – 0.00; r_c 0.04 – 0.00; RPIQ 0.34 – 14; RMSE 430 – 0, Table 4.3). Meaning Zn>Sn>Cu>Ti>Fe>Cl were still considered excellent models with $r^2 > 0.85$ and K a good model with $r^2 > 0.7$. However, Ca's r^2 dropped to 0.65 making it ill-advised for use.

Table 4.3: Goodness of fit measures for raw pXRF predictions, framework model, and fusion model.

Element	Method	r ²	r _c	RPIQ	RMSE	Intercept	slope	Intercept 95% CI	Slope 95% CI
Cl	Raw	0.792	0.608	1.097	2004	-1484	1.968	(-1696, -1273)	(1.893, 2.043)
Cl	Framework	0.877	0.933	4.949	444	300	0.865	(232, 368)	(0.841, 0.889)
Cl	Fusion	0.876	0.933	4.612	444	296	0.866	(227, 365)	(0.841, 0.89)
K	Raw	0.645	0.314	0.568	5456	-31675	2.166	(-34502, -28849)	(2.046, 2.285)
K	Framework	0.791	0.883	3.821	811	4972	0.788	(4259, 5684)	(0.758, 0.819)
K	Fusion	0.783	0.877	3.501	825	5368	0.772	(4645, 6090)	(0.741, 0.803)
Ca	Raw	0.338	0.271	0.953	12857	2789	0.608	(551, 5028)	(0.546, 0.671)
Ca	Framework	0.714	0.831	3.216	3810	9943	0.709	(8762, 11124)	(0.676, 0.741)
Ca	Fusion	0.646	0.791	3.073	4240	11324	0.675	(9994, 12654)	(0.638, 0.712)
Ti	Raw	0.885	0.899	3.447	2252	-731	0.906	(-956, -506)	(0.882, 0.93)
Ti	Framework	0.967	0.983	8.479	916	242	0.960	(120, 365)	(0.947, 0.973)
Ti	Fusion	0.965	0.982	8.192	940	310	0.952	(184, 436)	(0.938, 0.965)
Cu	Raw	0.952	0.962	6.742	1109	-72	0.877	(-153, 9)	(0.863, 0.892)
Cu	Framework	0.968	0.984	9.967	750	111	0.971	(38, 184)	(0.958, 0.983)
Cu	Fusion	0.967	0.983	10.173	764	139	0.968	(65, 214)	(0.955, 0.981)
Fe	Raw	0.566	0.454	1.111	8434	644	0.704	(-585, 1872)	(0.659, 0.749)
Fe	Framework	0.882	0.936	4.188	2237	3297	0.868	(2663, 3931)	(0.845, 0.892)
Fe	Fusion	0.862	0.925	3.950	2389	3859	0.851	(3175, 4543)	(0.826, 0.877)
Zn	Raw	0.936	0.943	5.757	1199	-103	0.852	(-190, -17)	(0.836, 0.868)
Zn	Framework	0.989	0.994	17.327	398	-25	0.995	(-66, 17)	(0.987, 1.003)
Zn	Fusion	0.989	0.994	17.151	401	-6	0.990	(-48, 36)	(0.982, 0.997)
Sn	Raw	0.969	0.960	6.001	648	-27	0.868	(-77, 23)	(0.855, 0.881)
Sn	Framework	0.969	0.984	9.119	426	83	0.974	(27, 139)	(0.959, 0.988)
Sn	Fusion	0.969	0.984	9.119	426	83	0.974	(27, 139)	(0.959, 0.988)

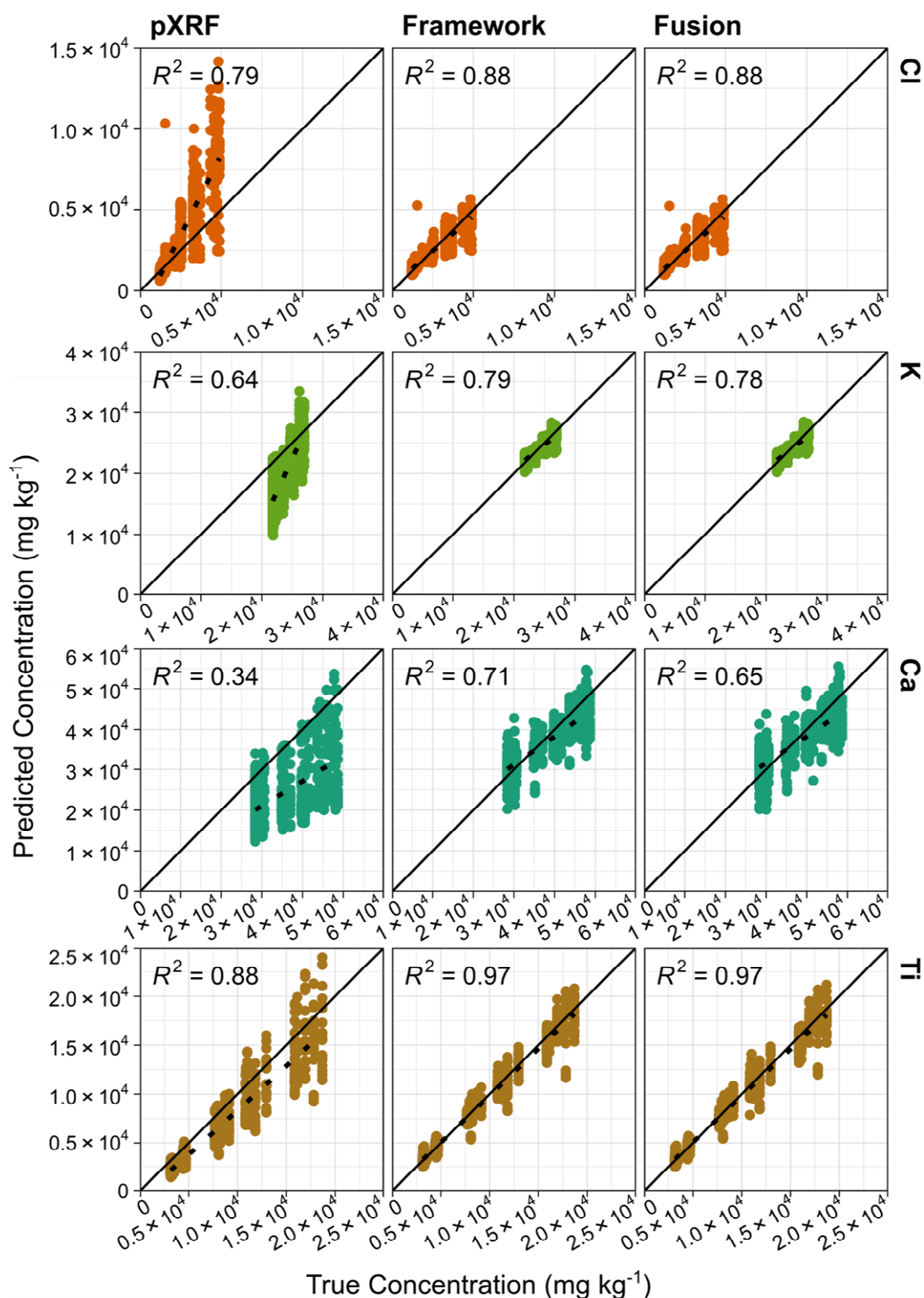


Figure 4.6 Predicted vs actual plots of raw pXRF, framework and fusion model predictions for four elements (Cl, K, Ca, Ti) in a synthetic soil sample set (n=180). The solid black line indicated the one-to-one relationship, dashed line indicates the regression of true and predicted concentrations.

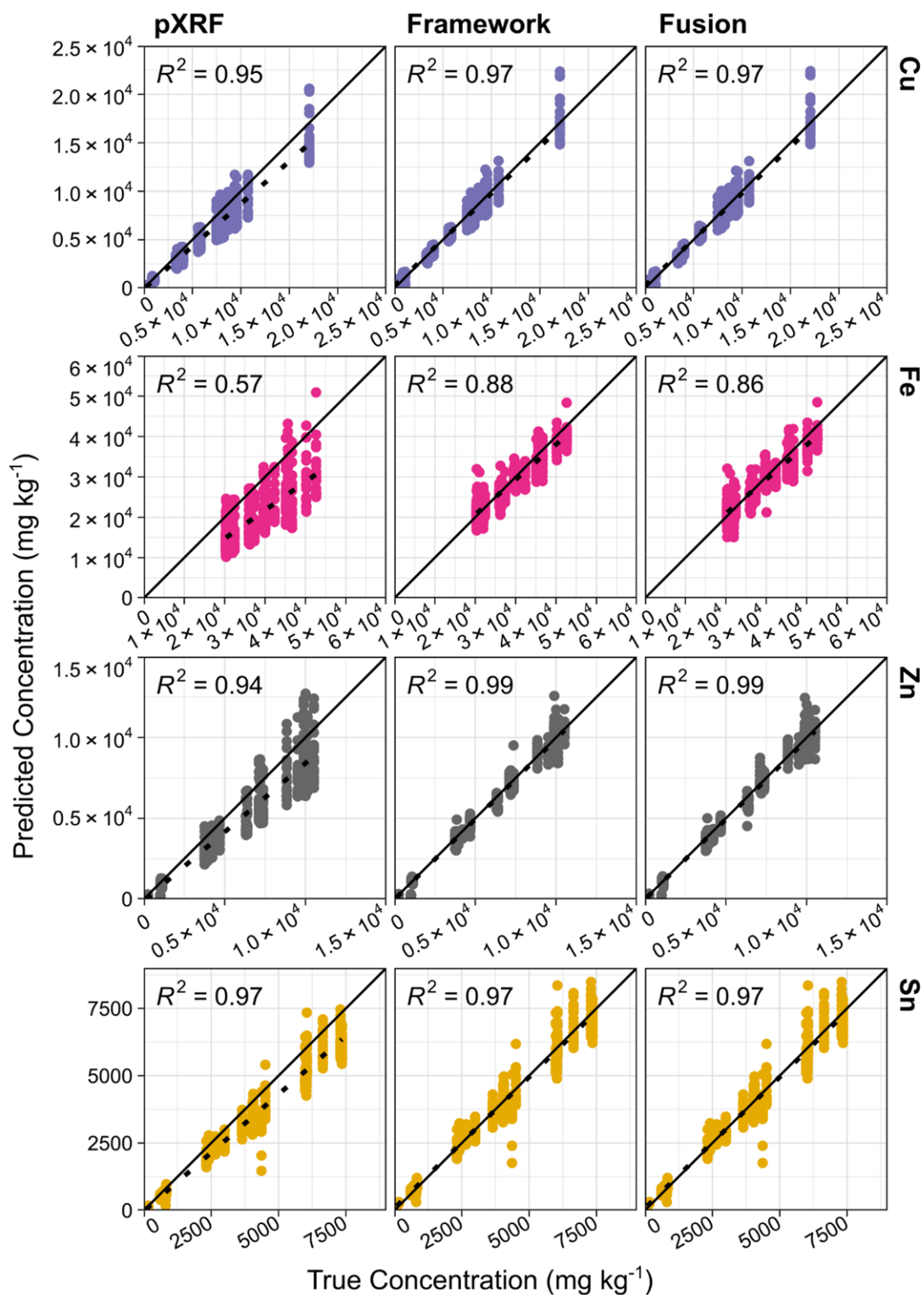


Figure 4.7 Predicted vs actual plots of raw pXRF, framework and fusion model predictions for four elements (Cu, Fe, Zn, Sn) in a synthetic soil sample set (n=180). The solid black line indicated the one-to-one relationship, dashed line indicates the regression of true and predicted concentrations.

4.5 Discussion

4.5.1 SOM effects

Previous studies have shown that both moisture and SOM significantly interfere with pXRF measurements [10,13]; however, results have been limited by relatively small samples that were site specific or unrepresentative [10,12]. As such this research has, for the first time, used a representative synthetic sample set to investigate both SOM and moisture's effects on pXRF without the complication of site-specific soil matrix chemistry. Hence this study hypothesised that pXRF measurements will decrease when either moisture concentration increases, or SOM concentration increases; and that this decrease would be significantly and substantially different to just the dilution effect of these two factors.

In the case of SOM all elements except for Zn showed a significant difference (slope 95% confidence interval did not include zero) from the null hypothesis that SOM would have a simple dilution effect (Figure 4.4). This corroborates with research by Ravansari et al (2018) who found a significant difference ($p < 0.01$) between the slopes of the theoretical dilution effect of cellulose (an organic matter surrogate) and the observed response for Ti, Zn, Cu, and Fe. However, in the present study, while these differences were significant for most elements, only K and Sn showed substantial differences from the hypothesised slope with slopes of -1.433 and -1.258 respectively. A factor which Ravansari et al (2018) did not investigate.

Furthermore, when the present study implemented the data fusion framework, models for Ca, Cl, Cu, Fe, K and Sn incorporating SOM and moisture were only marginally better than the best models that incorporated only moisture (Δr^2 difference of < 0.05) (Appendix C.10) This was corroborated by previous research [Chapter 2] that demonstrated that igniting samples as part of sample preparation to remove SOM made no substantial difference to pXRF predictions with slopes of ~ 1 and $r^2 \sim 1$ for the regression of pre and post ignited samples. Ravansari et al (2018) also developed a model which they claimed overcame the interference of cellulose on pXRF, however their use of paired t-tests is unable to confirm this

as t-tests are used to identify statistical differences not the correlation of a prediction and true values like r^2 or RPIQ making their conclusion of an improved prediction invalid.

A possible explanation for this significant but not substantial trend seen in most elements is the Compton normalisation used by the Olympus Delta Premium pXRF. The Compton peak is generated by incoherent backscattering of X-ray radiation, and its intensity is a product of the sample matrix. Hence normalizing to the Compton peak helps mitigate the matrix effects on the response peaks used to calculate elemental concentration by pXRF, and as such is recognised in United States Environmental Protection Agency (EPA) method 6200 [29,41].

However, the results of the present study are limited by the range of SOM% used (0 – 16%) which while representative of typical soil is substantially lower than the higher values that can be found in wetlands (90%) [42]. Additionally, the present study is limited by the use of only one instrument as different manufacturers use different calibration methods. For example, Shand et al (2014) used a Bruker S-1 Turbo^{SD} with an empirical calibration method based on a SiO₂ matrix and found substantial over prediction by pXRF for Fe, Mn (pXRF recovery >200%) when SOM was >20% [43].

The results herein cast further doubt on the need for measuring and incorporating SOM into pXRF models due to the limited gains in model performance. Meaning, where SOM is not required for other reasons, this measurement can be ignored streamlining site surveys. However, caution should be taken as this conclusion can only be made when SOM is less than 16% and for instruments that use Compton normalisation within the internal calibration.

4.5.2 Moisture effects

It was hypothesised that pXRF recovery percentage would decrease at the same rate as percentage moisture increased. However, for the first time the results of this study showed that moisture had a nonlinear trend (Figure 4.1). In the case of Ca, Ti, Fe, and Zn, there was an initial sharp decline in recovery percentages, with the lowest average recoveries occurring at around 15% moisture before

pXRF recovery either plateaued (Fe, Zn) or increased (Ca, Ti) with all four elements converging at 70% pXRF recovery and 30% moisture.

These results are contrary to that of Shuttleworth et al (2014) who successfully used Equation 4-2 to account for the simple dilution effect of moisture, adjusting the in-situ Pb pXRF measurement linear regression slope and intercept from 0.79 to 0.96 and -1.71 to -0.48 respectively [13]. Meaning a linear trend must have been present between pXRF recovery and moisture percentages.

$$\text{corrected conc.} = \frac{(\text{raw conc.} \times \text{wet sample mass})}{\text{dry sample mass}} \quad \text{Equation 4-2}$$

Unlike this study, Shuttleworth's et al (2014) samples were collected from peat bogs with very high moisture content ranging from 43 – 85%. This may in part explain their linear trend as the results presented herein showed a return to the hypothesised simple dilution effect at 30% moisture. Another difference was the element investigated, in these results the nonlinear trend appeared to decrease in size as atomic number increased. This is due to the higher energy X-rays released by higher atomic number elements, meaning a higher maximum egressing X-ray escape path length [6]. Hence Pb may have an atomic number high enough that its relationship with moisture is just the simple dilution effect.

However, neither of these differences explains the presence of the present study's non-linear trend. Given the apparent reduction in the non-linear trend as the atomic number increases it can be inferred that the effect moisture has on the samples occurs in the same distances as the maximum egressing X-ray escape path length of the lighter elements. This distance is not known for the samples used in this study, but can be assumed to be <2mm based on previous literature [6]. Furthermore, as pXRF recovery was below the dilution effects slope of -1, water must be doing more than simply displacing the sample and analyte from the maximum egressing X-ray escape path length.

Due to the nature of the experimental design, metal compounds were significantly finer <10 µm than the soil matrix <2 mm. Therefore, the effect of capillary action was considered as a mechanism which could transport the added metal

compounds from the surface of the soil particles, to within the soil particles and beyond the maximum egressing X-ray escape path length of lighter elements. But this theory was dismissed as in the case of Fe and Ca only ~10% of the true metal concentration was added by Fe_2O_3 and CaCO_3 with ~90% present as background in the soil matrix.

One final theory is that the soil matrix in use may have shown shrink swell characteristics. Wilson et al (2013) showed that a Vertisol sample expanded >19% when exposed to water [44]. This may shift analyte beyond the maximum egressing X-ray escape path length, but at the same time the density of the soil will be reduced and as such increase the maximum egressing x-ray escape path length [6]. This effect may reduce pXRF recovery more than the simple dilution effect, however this theory cannot be validated with the data available from this study.

While Ca, Ti, Fe, and Zn, showed non-linear trends below the theoretical dilution effect, Cl and K showed nonlinear trends with pXRF recovery above 100% at higher spike concentrations. This was primarily attributed to the compound KCl used to spike K and Cl in this study. KCl is soluble in water meaning its distribution would be dictated by the location of water within the mixture. Therefore, it is likely to be more prevalent on the surface of particles, leading to higher a percentage of analyte within the maximum egressing X-ray escape path length. However, as water soluble compounds are likely to be mobilised at sites before surveying is conducted, this is unlikely to affect pXRF measurements of field samples.

The findings from this study suggest that the effects of moisture particularly at concentrations below 30% are substantially more complex than previously thought. As a result, simple correction equations such as proposed by Shuttleworth et al (2014) are unlikely to be effective across the full range of moisture percentages. Further research should be undertaken to investigate if the trends seen herein can be replicated in field samples. Furthermore, modelling should be undertaken to understand the effects of shrink swell soils on the maximum egressing X-ray escape path length. Such research may benefit from utilising XMI-MSIM software developed by Schoonjans et al. (2012) [45].

4.5.3 Data fusion framework

4.5.3.1 Prediction improvement compared to factory inbuilt calibration framework

Previous studies evaluating pXRF's raw predictions observed substantial differences between different elements. This study found that raw pXRF predicted Sn, Cu and Zn to a very high quality with r^2 of >0.90 (Table 4.3). Ti and Cl also had a strong correlation coefficient ($r^2 > 0.7$), while K Fe and Ca were lower ($r^2 < 0.70$). These results achieved improved prediction over previous data fusion studies for Zn, and Cu which achieved lower r^2 of 0.04 to 0.88 [12,21], while other elements showed similarly low r^2 of 0.18 – 0.63 for Fe Ca and Ti [12,21] although S.M. O'Rourke et al (2014) reported a higher r^2 of 0.83 for Fe. However, results from the present study are consistent with other pXRF studies that were not attempting data fusion with r^2 between 0.81 and 0.99 for Cu, Fe, Ti and Zn [8,46,47]. The high r^2 for Cu Sn, and Zn in this study were believed to be due to the calibration of true values needed to account for background concentrations in the soil matrix. However, inspection of correlations before and after calibration showed no change in r^2 (Appendix C.4). Instead, high r^2 were due to their higher atomic numbers which are less affected by SOM and moisture interference [11].

Upon implementing Chen et al (2021) general framework to improve pXRF measurement the greatest improvements in r^2 were by Ca, Fe, and K, with increases of 0.38 – 0.15. In contrast, the other elements, Cl, Ti, Zn, and Cu, showed lesser increases (<0.084), while Sn exhibited no change in r^2 . After the framework was implemented all eight elements had high or very high r^2 and would be suitable for quantitative screening or definitive measurement according to the EPA [48]. These results differ from Chen et al (2021) who only achieved high $r^2 > 0.70$ for three of the five elements investigated. However, the average increase in that study was similar to this study at ~ 0.135 . This study's implementation of Chen's framework was more effective in part by controlling heterogeneity. Soil was ground to <2 mm and mixed for over 12 h whereas Chen et al performed measurements on unprocessed samples through polypropylene sample bags.

4.5.3.2 Prediction changes before and after Vis-NIR introduction to model.

Despite a number of recent studies combining pXRF and Vis-NIR data to improve elemental predictions [20,21,25,26] there has yet to be a study trialling data fusion on samples containing varying levels of moisture, a well recorded interference of pXRF measurements [13]. Although all goodness of fit statistics deteriorated when true SOM and moisture values were replaced with predicted values from Vis-NIR models, Zn, Sn, Cu, Ti, Fe, Cl were still considered excellent models with $r^2 > 0.85$ and K a good model with $r^2 > 0.7$ (Table 4.3). However, Ca's r^2 dropped from 0.71 to 0.65 meaning its accuracy was only suitable for qualitative screening according to the EPA [48].

In general, the data fusion framework implemented in this study outperformed previous studies. S.M. O'Rourke et al (2014) measured 322 different samples from the Irish National Soil Database with mid-infrared spectroscopy (MIR), pXRF and utilised Granger-Ramanathan averaging (GRA) to combine the Cubist models of each instruments full spectra [21] (Appendix C.10). Their highest RPIQ was Cu ((RPIQ 2.47, R^2 0.83) followed by Ti (RPIQ 1.11, R^2 0.73) Fe (RPIQ 0.86, R^2 0.75) Ca (RPIQ 0.76, R^2 0.97) and Zn (RPIQ 0.60 R^2 0.33). In all cases, in the present studies substantially higher RPIQs were observed indicating lower levels of random and systematic error. However, Ca achieved a higher R^2 of 0.97 compared to our r^2 of 0.65. However, caution should be taken comparing these two statistics, as S.M. O'Rourke (2014) uses the less common R^2 the coefficient of determination (Equation 4-3) [15] while this study uses the universally known r^2 Pearson's squared correlation coefficient (Equation 4-4) [49]. The former of which measures both systematic and random error while the latter only measures random error. It is important to select goodness of fit metrics that are appropriate, in wide use, and can be compared across studies such as r^2 , RPIQ, slope or r_c .

$$R^2 = 1 - \frac{\sum_{i=1}^n (x_i - y_i)^2}{\sum_{i=1}^n (x_i - \bar{x})^2} \quad \text{Equation 4-3}$$

$$r^2 = \left(\frac{\sum (x_i - \bar{x}) (y_i - \bar{y})}{\sqrt{\sum (x_i - \bar{x})^2 \sum (y_i - \bar{y})^2}} \right)^2 \quad \text{Equation 4-4}$$

Where x_i , y_i , $\bar{x}$, and $\bar{y}$ are the true, predicted, mean of true, and mean of predicted value respectively.

Shrestha et al (2021) also implemented GRA and spectral concatenation over 612 samples from the regional geochemical baseline soil survey of southern New Zealand [26] (Appendix C.10). They found partial least square support vector machine (PLS-SVM) of individual spectrums across eight elements consistently outperformed PLSR models. This was primarily attributed to SVM ability to handle non-linear trends. However, their implementation of GRA on Vis-NIR/MIR and pXRF models was ineffective. Fusion models performed similar or the same as pXRF models which produced r^2 of 0.93 and 0.96 for Cu and Zn respectively. Both these models performed worse than the present studies data fusion framework which achieved r^2 of 0.97 and 0.99 for Cu and Zn respectively. The same was also true of G Shrestha et al (2021) spectral concatenation for Zn which achieved a r^2 of 0.96. However, Shrestha et al. (2021) spectral concatenation for Cu improved on their pXRF model achieving a r^2 of 0.97 and was the same as our studies r^2 . Yet, their r_c and RPIQ were lower at 0.980 and 6.38, respectively, compared to this study (r^2 0.967 r_c 0.983, RPIQ 10.17).

A common theme across previous data fusion studies is the use of full spectrum models. This method ignores the values output by the pXRF instead opting to run PLSR, Cubist or PLS-SVG on the full spectrum collected by the pXRF. This method was chosen to overcome the relatively high LOD of factory calibrations [25] which exists due to the overlap of low-intensity L-line by the stronger K-lines of more prevalent elements [50]. Utilising the full pXRF spectrum has the advantage that spectral co-evolutions can be identified, that are not directly caused by the element of interest but are instead a result of correlations between different elements. For example, G. Shrestha et al (2021) found a correlation between Ni and Cr (r 0.72) and Zn and Cu (r 0.69) [26]. But relying on the full spectrum creates a limitation in any model generated as the co-evolving correlations will be specific to the sample set [18]. In the case of both G Shrestha et al (2021) and S.M. O'Rourke (2014) their sample sets were from rural land with no locations containing polluted land [21,26]. As such the site-specific soil

matrix chemistry and co-evolved correlations will be lithogenic in origin and hence unrelated to anthropogenic pollution. As such new models will need to be made at every new site minimising the benefit of rapid portable instruments. Furthermore, the full spectrum methodologies implemented do not use the Compton normalisation included within factory pXRF models, that help mitigate the site specific soil matrix chemistry [41]. This can be seen in S.M. O'Rourke (2014) prediction of Zn with a full spectrum Cubest pXRF model which achieved a r^2 of 0.03 compared to the instrument prediction of r^2 0.76 [21].

4.5.3.3 Benefits and limitations of data fusion framework

In contrast to previous studies, our study seeks to utilise portable instruments for the identification and recovery of resources to feed into the circular economy. Hence the concentrations of interest are substantially higher than the current LODs of pXRF (Appendix C.1) [3]. Instead, this study sought to leverage the knowledge of specific interference and intentionally incorporate them into the model. For this reason, our method has several strengths over previous data fusion methods. Firstly, the data fusion framework used fewer latent variables and/or variables (7 Vis-NIR, 1 pXRF) than previous full spectrum data fusion methods (10 Vis-NIR, 15 pXRF) [22] and as such less samples are needed to generate models [51].

Secondly previous studies used air-dried samples that were ground to <2 mm [21,26]. a methodology that is widely used to reduce the interference from heterogeneity, and moisture [6] [Chapter 2]. Yet these sample pre-processing steps largely negate the benefits of rapid portable spectrometers by requiring samples to be returned to the laboratory. Instead, our method successfully predicted moisture concentrations with Vis-NIR and then successfully corrected the elemental prediction of pXRF, negating the need for drying of samples. However, our study utilised ground <2mm soil to mitigate the effects of heterogeneity. To some extent heterogeneity can be overcome by repeated measurements [10] or using variable beam size to quantify heterogeneity [52]. But further work is needed to incorporate heterogeneity into the data fusion framework.

Despite the strengths of this studies data fusion framework, caution should be applied to its interpretation. While the range of SOM and moisture (SOM 0 – 16%, moisture 0 – 30%) are wider than previous work by Chen et al (2021) (SOM 0.3 – 3.3%, Moisture 1.5 – 8.5%) they still do not cover the full range that can be encountered in soil. Furthermore, the non-linear trend of moisture was successfully accounted for by the data fusion framework. But purpose-built non-linear models such as support vector machine (SVM) may better incorporate such trends. Finally this study utilised a synthetic sample matrix which while representative will deviate from field studies. Therefore, future research should aim to build upon this study by testing other nonlinear models within the framework, utilising field samples and widening the range of moisture and SOM included in the sample set.

Despite these limitations, a final strength of this study is its utilisation of Compton normalisation. As Compton normalisation can reduce the effects of site-specific soil matrix chemistry there is the potential to generate a high accuracy universal model. Such a model would not require calibration for each new site significantly simplifying site surveys and creating a truly rapid and low-cost tool. However, there are several knowledge gaps that will have to be overcome before such a model can be created. Firstly, a universal Vis-NIR model for SOM and moisture will have to be developed. Such a model may be possible with the growth of the global Vis-NIR spectral library [53]. Secondly as this study showed, moisture's relationship with pXRF signal is inconsistent across the literature which may be a result of soil texture and the presence of shrink swell clays [6]. Therefore, further studies should investigate the effects of increasing moisture content in different soil textures. And if clear relationships can be identified, the soil textures predicted by Vis-NIR [54] should be incorporated into the data fusion framework.

4.6 Conclusion

This study set out to understand the effect of SOM, and moisture's suppression of elemental (Ca, Cl, Cu, Fe, K, Sn, Ti, Zn) measurements by pXRF. Moisture had an elementally dependent nonlinear trend causing pXRF to substantially underpredict all eight elements more than hypothesised; whilst SOM caused a significant but not substantial difference in elemental prediction. This insubstantial difference translated into minimal improvement in data fusion models when SOM was incorporated. Therefore, SOM can be ignored in future modelling attempts if SOM measurements are not otherwise required and increasing survey speeds are the priority. In contrast, our results for moisture's influence on pXRF complicate the optimisation of pXRF. These results show that simple linear calibrations such as those developed by Shuttleworth et al (2014) [13] are inappropriate for moisture concentrations <30%. A key novelty of our study was the synthetic sample matrix which allowed for the investigation of SOM and moisture without the interference of site-specific soil matrix chemistry. However, future work should be undertaken to investigate if moisture's non-linear trends can be identified in field samples.

This study also set out to develop a novel data fusion framework to increase the accuracy of rapid elemental measurements in soil. This framework used portable Vis-NIR to predict moisture and SOM values that then corrected pXRF measurements. Across all eight elements, the data fusion framework produced more accurate predictions than raw pXRF results, and successfully accounted for moisture and SOM within the samples. When compared to previous studies, the data fusion framework outperformed both GRA and spectral concatenation methods. The main strength of the data fusion framework is its ability to account for the suppression of pXRF results by moisture, enabling more accurate in-situ measurements. Furthermore, its use of the Compton normalisation to account for site specific soil matrix chemistry opens the possibility of creating a high accuracy universal in-situ measurement method. However, this study is limited by the relatively narrow range of variables included in the synthetic sample matrix. Future studies should test the data fusion framework on field samples and widen the range of moisture, SOM and soil textures included in the sample set.

4.7 References

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5 Rapid Prediction of Iron Speciation in a solid matrix via the data fusion of pXRF and Vis-NIR spectroscopy

5.1 Abstract

Total elemental analysis is widely implemented as part of metal/metalloid contaminated site surveys. However, the speciation of heavy metals plays an important role in its risk to the environment and human health. Yet, sequential extraction, the only method currently able to provide fractionated elemental concentrations, is a slow and inaccurate method with significant limitations. Therefore, this scoping study set out to determine the feasibility of predicting metal speciation in a simplified heterogeneous synthetic sample set using data fusion of portable X-ray fluorescence (pXRF) and visible near-infrared spectroscopy (Vis-NIR). Results showed that Vis-NIR was able to predict Fe_2O_3 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with good accuracy ($r^2 > 0.85$) when predictions were assessed across the full range of concentrations but was inaccurate when higher concentrations predictions were excluded $< 5000 \text{ mg kg}^{-1}$ ($r^2 < 0.08$). Whereas data fusion of pXRF and Vis-NIR reported higher accuracy ($r^2 = 0.96$ full range, $r^2 > 0.71$ low range) across all concentration ranges. These findings suggest that data fusions has the potential to predict speciation in solid environmental samples. Therefore, data fusion of pXRF and Vis-NIR could significantly improve the risk assessment of contaminated sites, and its potential for effective resource recovery by providing speciated metal concentrations.

5.2 Introduction

Over 119,000 sites in Europe are contaminated with heavy metals [1], causing the deterioration of ecosystems and presenting a risk to human health [2]. However, novel bio- or chemical-leaching offer a promising approach to reduce the cost of remediating these sites via the recovery and utilisation of such metals [3,4]. Nevertheless, to determine the availability of potentially toxic or valuable elements (PTE, PVE), elemental concentration and speciation of metals must be identified. At present, the only method to determine the speciation of elements in

multiple solid environmental samples is sequential extraction, which has been applied to mine tailings, soils [5], organic fertilisers [6] and slag [7]. The method requires between five and seven laborious extraction steps, followed by induction coupled plasma (ICP) analysis of each phase. While effective, sequential extraction is an order of magnitude more time consuming and labour intensive than traditional elemental analysis. As such, there is a need for a rapid method to predict both the elemental and speciated concentrations of heavy metals in environmental matrixes to enable more accurate risk analysis and effective resource recovery.

Elemental analysis of metals is traditionally carried out by extraction and ICP [8], however, in recent years, portable X-ray fluorescence spectroscopy (pXRF) has demonstrated a potential for rapid measurement, without the need for laborious extraction steps [9]. Nevertheless, achieving high accuracy results in complex matrixes requires careful sample preparation [Chapter 2] to remove heterogeneity [10] and moisture [11] or the incorporation of other measurements to account for the interference [12] [Chapter 4].

Spectroscopic methods such as Raman, Fourier transform infrared, and ultraviolet–visible spectroscopies have long been used to detect compounds in solution [13]. More recently, portable visible near-infrared diffuse reflectance spectroscopy (Vis-NIR) has been successfully utilised to measure soil, and predict soil organic material (SOM) and moisture [14] [Chapter 4] and mineral concentrations [15]. However, Vis-NIR cannot directly detect heavy metals at low concentrations due to the dominating effects of the matrix [15,16] instead relying on indirect co-evolving correlations present within the sample set [17,18].

Separately, neither Vis-NIR nor pXRF can predict both the elemental and speciated concentrations of metals in soil, however, the fusion of their data sets ('data fusion' approaches) is a growing area of research that has led to improvements in rapid elemental prediction [19,20]. Two approaches of data fusion have been trialled: Firstly, top-down data fusion which uses field samples and a reference method such as ICP. The full spectrums of pXRF, and Vis-NIR are combined to construct models which are trained using the reference methods

results [19,20]. Secondly, bottom-up data fusion which uses a synthetic sample set as the basis for the construction of a data fusion framework where pXRF predicts elemental concentrations and Vis-NIR predicts specific variables such as SOM or moisture. These variables are then combined in a model equation to provide an accurate elemental concentration [Chapter 4]. Yet, there has to date been no study investigating the potential of data fusion to predict the speciation of heavy metals within a solid matrix. Therefore, this study aims to demonstrate the potential to measure metal speciation in environmental matrices using bottom-up data fusion, by predicting the concentrations of two iron compounds in a solid matrix via the data fusion of pXRF and Vis-NIR. As such, we hypothesize that combined pXRF and Vis-NIR data can accurately predict the concentration of Iron Oxide and Iron Sulphate in a sand matrix.

5.3 Methods

5.3.1 Sample Creation

To predict concentration and speciation of Fe in a solid matrix, a synthetic sample set ($n=46$) was created by combining Sand, (Extra Pure, SLR, Low Iron, 40 – 100 Mesh, Fisher Chemical, USA), Iron (III) oxide (Fe_2O_3 98% ,Thermo Scientific, USA) and Iron (II) sulphate heptahydrate, ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 99.5% ,Thermo Scientific, USA (referred to as FeSO_4)) in varying proportions to create ranges of elemental Fe 0 – 100,000 mg kg^{-1} , Fe_2O_3 0 – 142,107 mg kg^{-1} , FeSO_4 0 – 499,971 mg kg^{-1} , and a ratio of elemental Fe attributed to Fe_2O_3 and FeSO_4 (referred to as $\text{Fe}_2\text{O}_3:\text{FeSO}_4$) ranging from 1:0 to 0:1. Samples were then mixed on an orbital shaker (16 h at 300 rpm) to homogenise, before measurement with Olympus Delta Premium pXRF (Evident, JPN) and ASD Fieldspec 4 Vis-NIR Spectrometer (Malvern Panalytical, NLD).

5.3.2 Instrument measurement.

Instruments were operated as described in [Chapter 4]. In brief, fifteen measurements were taken by both pXRF and Vis-NIR on 15 g of sample held within a XRF sample cup and shaken in between each measurement. The Vis-NIR had its background set using a Spectralon standard (Labsphere, UK) every

fifteen measurements. For each measurement, an average of fifty successive scans were collected by placing the sample in direct contact with the Vis-NIR handheld probe. The pXRF was calibrated twice a day with a 316 Alloy coin. Using the soil mode and suitcase accessory, one 50 s scan was taken through Proleen® windows (Chemplex USA) of the pXRF sample cup per measurement.

5.3.3 Data analysis

The fifteen measurements of elemental Fe obtained with the pXRF were averaged for each sample using R studio v2023.09.1 (Figure 5.1). Whereas Vis-NIR spectra were exported to Aspen Unscrambler v12.2 (Aspentech, USA) for preprocessing and modelling (Figure 5.1). Vis-NIR preprocessing included averaging the fifteen scans from each sample to one spectrum; smoothing by Savitzky-Golay; and standard normal variate (SNV). The Vis-NIR spectra were then separated into calibration (75%) and validation (25%) sets before partial least square regression (PLSR) predicted the ratio of Fe₂O₃:FeSO₄, as well as the concentrations of Fe₂O₃ and FeSO₄.

Data fusion of the Fe₂O₃:FeSO₄ ratio and true elemental concentration, and pXRF measurements (Figure 5.1) were carried out in R studio v2023.09.1 by Equation 5-1 and Equation 5-2. Final regression of data and goodness of fit statistics were calculated on the full (0-100,000 mg kg⁻¹) and lower range of the dataset (0-5000 mg kg⁻¹) of elemental Fe.

$$\text{Fe}_2\text{O}_3 = \text{Fe elemental} \times \frac{\text{Fe}_2\text{O}_3:\text{FeSO}_4 \text{ ratio}}{\text{percentage of Fe in Fe}_2\text{O}_3} \quad \text{Equation 5-1}$$

$$\text{Fe}_2\text{O}_3 = \text{Fe elemental} \times \frac{\text{Fe}_2\text{O}_3:\text{FeSO}_4 \text{ ratio} - 1}{\text{percentage of Fe in FeSO}_4} \quad \text{Equation 5-2}$$

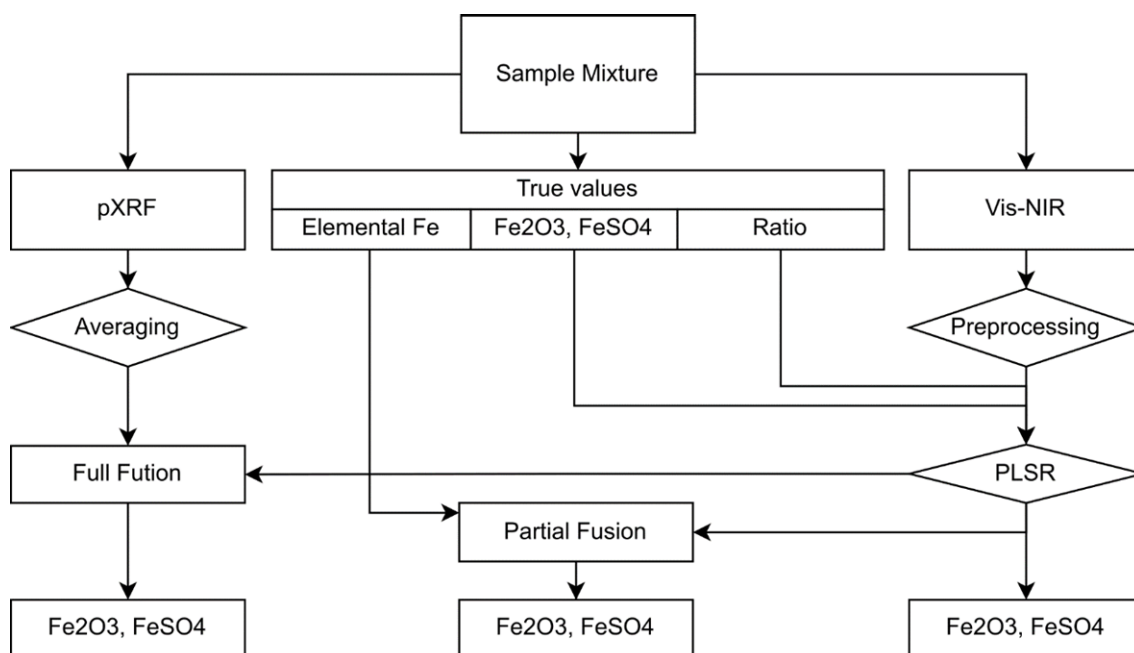


Figure 5.1 Data fusion framework for the prediction of Fe_2O_3 and FeSO_4 with pXRF and Vis-NIR in a synthetic sample set ($n=47$) containing low Fe sand, Fe_2O_3 and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in varying proportions.

5.4 Results and Discussion

5.4.1 Assessment of a novel data fusion framework's ability to predict Fe speciation.

This study aims to demonstrate the potential to measure metal speciation in environmental matrices using a synthetic sample set. While the matrix used is unrepresentative of typical environmental samples due to its simplicity, its heterogeneous and fine particulate nature mimics that of processed soil samples [9]. Hence, it was deemed a suitable compromise to determine the feasibility of this study's aim and should be followed up with more complex samples.

Within the Vis-NIR spectra (Figure 5.2) several peaks of importance were identified. Firstly, two peaks at $\sim 750 - 1000 \text{ nm}$ and $350 - 600 \text{ nm}$ were identified and increased in absorbance as the ratio of $\text{Fe}_2\text{O}_3:\text{FeSO}_4$ reached 1:0; both peaks have been previously attributed to Iron oxides [21] in soil matrixes. Secondly, peaks at $\sim 1375 - 1750 \text{ nm}$ and $\sim 1875 - 2125 \text{ nm}$ showed increasing absorbance as the $\text{Fe}_2\text{O}_3:\text{FeSO}_4$ approached 0:1. These peaks have previously been attributed the O-H bond [22,23] and, hence, in this study they were

attributed to the heptahydrate portion of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Finally, a broad peak from $\sim 350 - 875 \text{ nm}$ showed an increased reflectance above $200,000 \text{ mg kg}^{-1}$ of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Due to its occurrence only happening at high concentrations, and a lack of literature on this peak, it was attributed to the FeSO_4 part of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

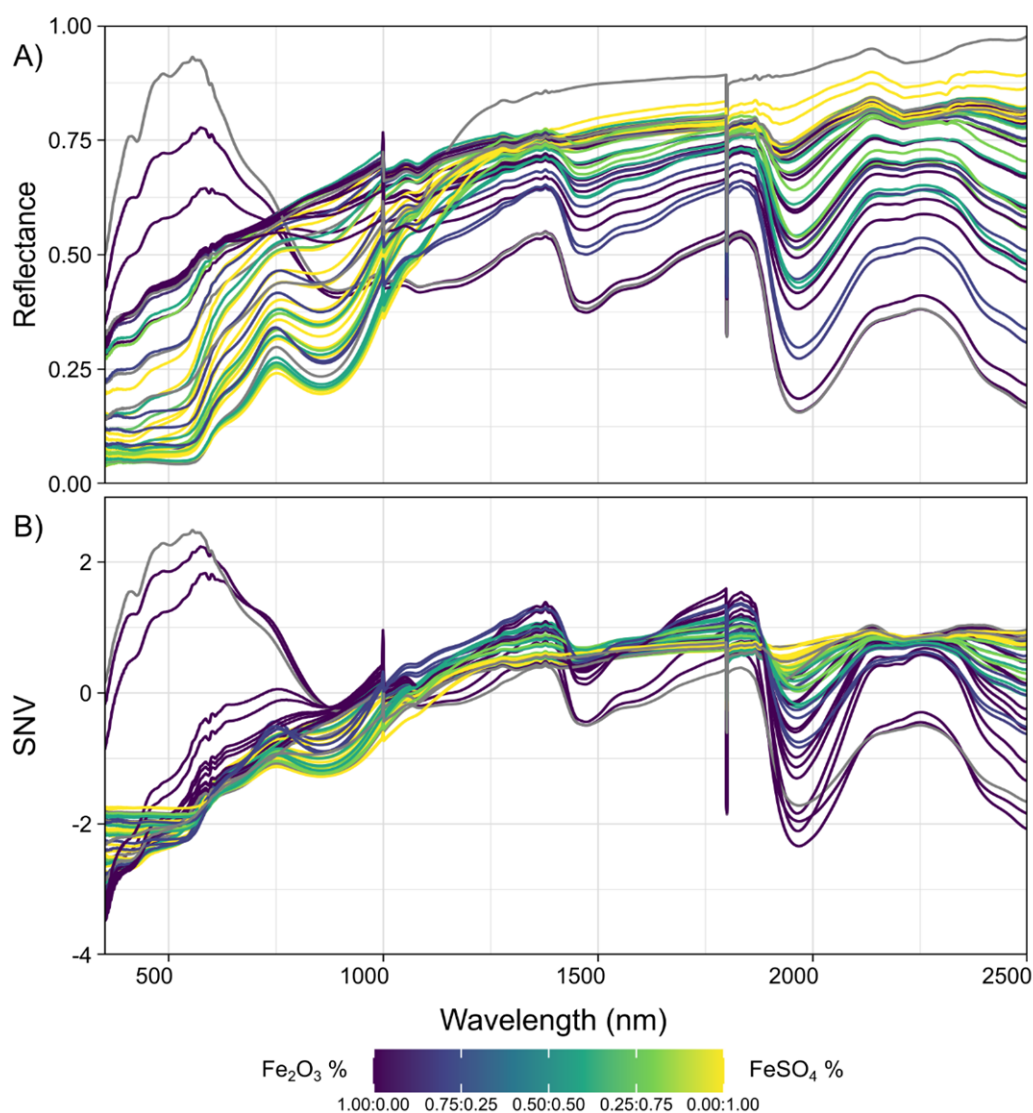


Figure 5.2 Vis-NIR reflectance spectra from 350 – 2500 nm of a synthetic sample set ($n=47$) containing low Fe sand, Fe_2O_3 and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in varying proportions. The colour scale indicates the ratio of elemental Fe held within Fe_2O_3 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. a) smoothed spectra, b) spectra after standard normal variate (SNV) preprocessing.

Utilizing the full Vis-NIR spectrum, PLSR was carried out to predict the ratio of $\text{Fe}_2\text{O}_3:\text{FeSO}_4$ (Figure 5.3, Table 5.1). Across the full range of Fe concentrations Vis-NIR showed a high accuracy in predicting the $\text{Fe}_2\text{O}_3:\text{FeSO}_4$ ratio with a Pearson's squared correlation coefficient (r^2) of 0.938, Lin's concordant correlation coefficient (r_c) of 0.965, and a high ratio of performance to interquartile range (RPIQ) of 9.439. Furthermore, this high accuracy was maintained when predictions were made on the lower range of concentrations (Fe 0 – 5000 mg kg^{-1}) (Table 5.1, Appendix D.1) with a similar r^2 of 0.921 and r_c of 0.953 but a lower RPIQ of 7.710.

Despite a higher r^2 of 0.991, pXRF was less accurate than previous studies which reported slopes of 0.906 for Fe [24]. where as in the present research pXRF over predicted elemental Fe with a slope of 1.652, an effect that was reduced in the lower range (Fe 0 – 5000 mg kg^{-1}) with a slope of 1.318 (target slope 1.000) (Figure 5.3.A, Table 5.1). The overprediction by pXRF was in part attributed to the density of the sand matrix and the finer fraction of analyte. Ravansari et al. (2020) calculated that the maximum egressing X-ray path length in solid SiO_2 is 273 μm , which is shorter than the particle size of the sand matrix (<420 μm) used in this study [9]. Consequently, the finer particles of Fe_2O_3 and FeSO_4 are likely to be unevenly distributed, concentrating more within the X-ray path length. As a result, pXRF overestimates the actual concentration of Fe.

Previous studies have demonstrated the viability of predicting contaminant concentrations with Vis-NIR achieving $r^2 > 0.90$ for Cr, Cu, Fe_2O_3 and Al_2O_3 [25]. Therefore, in this study it was hypothesised that Vis-NIR would be able to predict the concentration of Fe_2O_3 and FeSO_4 to a high accuracy without the need for data fusion. As hypothesised, Vis-NIR accurately predicted the full range of FeSO_4 (r^2 0.952, RPIQ 1.044), while Fe_2O_3 predictions were slightly poorer (r^2 0.879, RPIQ 0.776) (Table 5.1, Figure 5.3.C). However, when just the lower concentration range (Fe 0 – 5000 mg kg^{-1}) was regressed no correlation could be found with r^2 , r_c and RPIQ all <0.400 for both compounds (Appendix D.1).

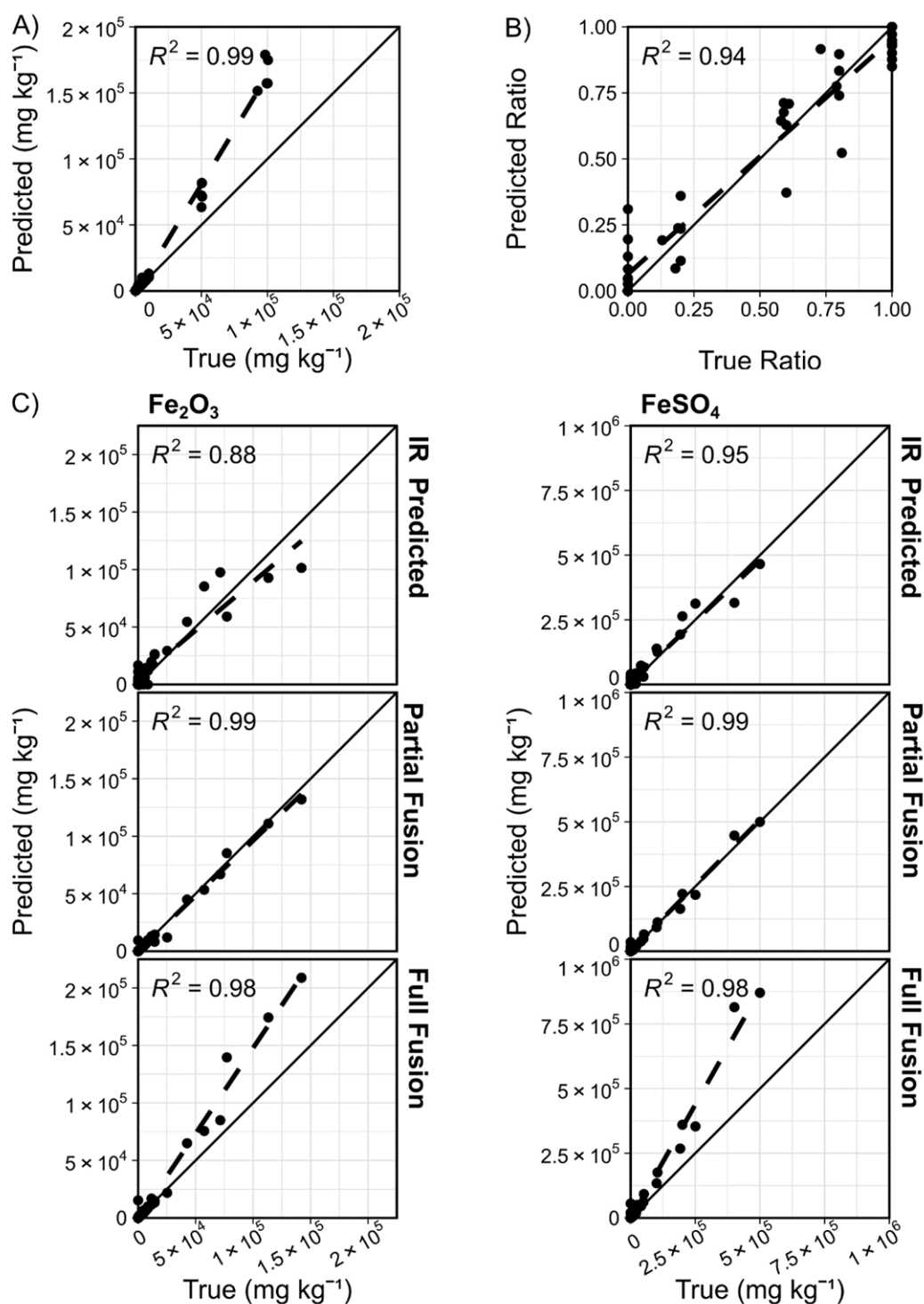


Figure 5.3 Predicted vs actual plots for the full range of a synthetic sample set (n=47) containing sand, Fe_2O_3 and FeSO_4 . True values were regressed against a) elemental Fe prediction by pXRF; b) ratio Fe_2O_3 and FeSO_4 predicted by Vis-NIR; c) Fe_2O_3 and FeSO_4 predictions by Vis-NIR, partial fusion of Vis-NIR ratio and true elemental Fe, and full fusion of Vis-NIR ratio and pXRF elemental Fe.

Table 5.1 Goodness of fit statistics for the regression of true values against the predictions of pXRF, Vis-NIR, partial and full fusion, for a synthetic sample set (n=47) containing low Fe sand, Fe₂O₃ and FeSO₄ in varying proportions. Goodness of fit statistics include Pearson's squared correlation coefficient (r^2), Lin's concordant correlation coefficient (r_c) ratio of performance to interquartile range (RPIQ), root mean square error (RMSE), intercept, slope and 95% confidence intervals (CI).

Method	Compound	r^2	r_c	RPIQ	RMSE	Intercept	Slope	Intercept 95% CI	Slope 95% CI
Full Range									
pXRF	Fe	0.991	0.856	0.387	23457	-1962	1.652	(-3732, -193)	(1.604, 1.7)
Vis-NIR	Ratio	0.939	0.965	9.439	0	0	0.890	(0, 0)	(0.82, 0.96)
Vis-NIR	Fe ₂ O ₃	0.879	0.929	0.776	10980	4812	0.844	(1567, 8057)	(0.748, 0.941)
partial fusion	Fe ₂ O ₃	0.988	0.994	2.502	3406	223	0.959	(-847, 1293)	(0.927, 0.991)
full fusion	Fe ₂ O ₃	0.980	0.903	0.494	17242	-976	1.487	(-3158, 1206)	(1.423, 1.552)
Vis-NIR	FeSO ₄	0.952	0.973	1.044	23813	9627	0.940	(2222, 17033)	(0.875, 1.005)
partial fusion	FeSO ₄	0.988	0.994	2.097	11860	579	1.014	(-3368, 4525)	(0.98, 1.049)
full fusion	FeSO ₄	0.979	0.825	0.277	89828	-3836	1.767	(-12819, 5146)	(1.688, 1.846)
Low range									
pXRF	Fe	0.835	0.822	1.925	1266	46	1.318	(-554, 646)	(1.071, 1.565)
Vis-NIR	Ratio	0.921	0.953	7.710	0	0	0.848	(0, 0)	(0.741, 0.955)
Vis-NIR	Fe ₂ O ₃	0.278	0.251	0.237	5800	3346	1.318	(1097, 5594)	(0.402, 2.235)
partial fusion	Fe ₂ O ₃	0.994	0.996	7.291	189	44	0.949	(-36, 124)	(0.916, 0.982)
full fusion	Fe ₂ O ₃	0.972	0.985	3.924	351	119	0.956	(-53, 292)	(0.886, 1.026)
Vis-NIR	FeSO ₄	0.321	0.365	0.360	13945	7700	1.097	(1942, 13458)	(0.409, 1.785)
partial fusion	FeSO ₄	0.992	0.996	7.627	657	169	0.982	(-156, 494)	(0.943, 1.02)
full fusion	FeSO ₄	0.941	0.808	0.788	6359	-111	1.678	(-1631, 1409)	(1.496, 1.859)

Despite a substantial body of research, pXRF should not be assumed to provide definitive total metal concentrations (Chapter 2). Instead, traditional methods such as ICP should be relied upon where definitive predictions are required. As such a partial data fusion method was tested where true elemental Fe concentrations (calculated from the mass added to the samples) were combined with the $\text{Fe}_2\text{O}_3:\text{FeSO}_4$ ratio predicted by Vis-NIR (Figure 5.3.C, Table 5.1). Partial fusion showed a higher accuracy prediction than just Vis-NIR for both Fe_2O_3 and FeSO_4 with r^2 of 0.988, r_c of 0.994 and RPIQ's of >2.000; and unlike Vis-NIR alone this accuracy increased on the lower range (Fe 0 – 5000 mg kg^{-1}) with r^2 / r_c increasing to >0.990 and RPIQ >7.000, (Table 5.1, Appendix D.1).

Finally, the combination of pXRF elemental Fe and Vis-NIR $\text{Fe}_2\text{O}_3:\text{FeSO}_4$ ratio predictions produced lower accuracies than partial fusion but higher r^2 (>0.970) than Vis-NIR predictions. However, due to pXRF's over prediction of elemental Fe, full fusion also overpredicted Fe_2O_3 and FeSO_4 resulting in lower r_c (<0.903) and RPIQ (<0.500). Furthermore, as with full fusion, a similar quality of predictions was also maintained in the low range of concentrations (Fe 0 – 5000 mg kg^{-1}) with r^2/r_c >0.940 and RPIQ's increasing to 3.924 and 0.788, respectively (Table 5.1, Appendix D.1). The performance of full and partial fusion at lower concentrations is particularly important for current site investigators who are primarily interested in PTE which can still present risks at low concentrations. For example, the UK Environment Agency recommends a soil screening value of 35.1, 28.2, and 35.6 mg kg^{-1} for Cu, Ni, and Zn respectively [26].

5.4.2 Fe speciation: faster and cleaner analysis through data fusion.

For the first time it has been demonstrated that both elemental and speciated concentrations of Fe can be predicted in heterogeneous solid matrixes by the data fusion of Vis-NIR and pXRF. Furthermore, the data fusion proved to be more accurate than Vis-NIR alone when elemental Fe concentrations were <5000 mg kg^{-1} , a factor that is particularly important for identifying PTE which can pose a risk at low concentrations [27]. However, the full data fusion method overpredicted both Fe_2O_3 and FeSO_4 due to the overprediction of elemental Fe by pXRF, a limitation that was not present in the partial fusion method. This was

attributed to the nature of the synthetic sample matrix having a higher density than typical soils thus reducing the volume of sample measured by pXRF and hence should present less of a problem in future studies on more representative samples. However, where high density samples are encountered, future studies could instead use ICP, albeit incurring a penalty in the speed of analysis [8]. Alternatively, future studies could account for over predictions by adjusting the regression coefficient within the instrument's software before exporting data for further analysis [28].

Despite the limitation in accuracy and narrow scope of this study, the potential benefits of the data fusion method presented in this study, are significant. Principally, measuring each sample took ~30 minutes which could be further reduced if fewer than the 15 replicate measurements taken here were collected, as has been done in previous studies [29]. The time-saving advantage of data fusion represents a significant improvement over sequential extraction, which, despite being the most viable method for speciation analysis, requires up to 50 hours for extraction [30]. This extended processing time limits the number of samples that can be analysed, often leading site surveyors to overestimate the risk of contaminated land due to insufficient understanding of the pathways through which PTE could be mobilised.

Whilst the steps involved in sequential extractions differ depending on the exact matrix of interest and the interests of the researcher, the general principles are to in sequential order: extract the fractions that are water soluble; adsorbed weakly with the complex; bound to carbonates; oxides; organic complexes; sulphides; and the metals bound within the SiO₂ matrix [5]. Sequential extraction offers the distinct advantages that each fraction is associated with a specific pathway in which PTE could be mobilised in the environment allowing for detailed risk assessment of sites [5]. Furthermore, by their nature, extraction processes, provide estimates of the effectiveness of novel bio and chemical leaching methods used to recover PVE [3,4]. However, due to the multiple wet chemistry steps, sequential extraction has several significant limitations, such as: (i) earlier extraction steps may induce reactions that bind the analyte to the wrong fraction

in subsequent steps; (ii) precipitates may be formed that are then not removed with their correct fraction; (iii) error introduced by sample handling during repeated centrifuging, decanting and washing; and (iv) the matrix structure can block leachate access to the analyte [30].

In comparison, data fusion can negate the wet chemistry related limitations of sequential extraction. Furthermore, data fusion has several other potential benefits; (i) once a model is created, the technical skills required for analysis are reduced; (ii) there is less risk to health and the environment by not requiring hazardous chemicals; (iii) non-destructive *in-situ* sampling may be possible depending on the accuracy required; (iv) rather than fractionation, full speciation may be predicted; and (v) could enable the identification of anthropogenic and lithogenic metals allowing for more accurate identification of pollution due to the differing chemicals found in the environment and anthropogenic pollution [31].

However, there are potential limitations that could prevent further progression of the data fusion method for field samples. Firstly, in this study a highly simplified matrix was used, but real-world samples are substantially more complex. Therefore, preprocessing and modelling may not be able to resolve the overlapping peaks in the Vis-NIR spectrum. Secondly, our methodology multiplied the ratio of speciation with elemental Fe concentrations (Equation 5-1, Equation 5-2) to predict speciated metal concentrations, however when multiple elements are present their ratios of speciation may not be equal. As such the accuracy of bottom-up data fusion may be substantially reduced when multiple elements are present.

5.4.3 Future work

To expand upon this scoping study's novel data fusion methodology, top-down and bottom-up data fusion approaches have been identified. Bottom-up data fusion, used in this study and [Chapter 4] would iteratively improve the data fusion framework by increasing the complexity and representativeness of the synthetic sample set, until sufficient variables have been incorporated to allow accurate measurement of field samples. This approach would require significantly larger synthetic sample numbers and may never be able to factor in all the variables

present within inherently complex environmental samples. That said, if successful, a universal model could predict elemental and speciation concentrations in any sample set.

The second approach, top-down data fusion, would be similar to previous studies which improved pXRF's elemental predictions [19,20]. By using sequential extraction data collected on a real environmental sample set to train machine learning models, built on the full spectra obtained from pXRF and Vis-NIR [20]. Previous work has shown this approach can produce accurate results with just one sample set [19]. Furthermore, adjustments of the sequential extraction method would allow for the fractions reported by the data fusion model to be changed as required [30]. However, full spectrum methods are inherently sample set specific due to co-evolving correlations which may not be present in other sample sets [32]. Furthermore, the accuracy of such a model would be dependent on the accuracy of the sequential extraction method employed.

Top-down data fusion may also benefit from the inclusion of x-ray absorbance fine structure spectroscopy (XAFS). This method has been previously used to study the oxidation states of metals [33], and the distribution of contaminants at the microscale [34]. However, XAFS requires a prior knowledge of the expected contaminant species; highly skilled analysis; and the use of synchrotron facilities with lead times of at least six months [35]. Therefore, at present it is impractical for the generation of large datasets needed for contaminated site surveys. However, the incorporation of limited but highly accurate data regarding contaminant speciation and sample microstructure in top-down data fusion may be worth further research. For example, Vis-NIR and pXRF are only able to measure the first μm to mm of a sample which can introduce significant errors [9]. But knowledge of the microstructure of a sample provided by XAFS may allow for model corrections improving the overall model accuracy.

5.5 Conclusion

This scoping study establishes that, for the first time, both elemental and speciated concentrations of Fe can be accurately predicted in a heterogeneous solid matrix through the combined use of Vis-NIR and pXRF data. Furthermore,

this data fusion method maintained its accuracy in low concentrations (0 – 5000 mg kg⁻¹) with direct implications for PTE surveys which remains toxic to humans and the environment at low concentrations. To build on this initial investigation further work is required to apply this method to more representative samples with multiple elements and more complex matrices. A data fusion of pXRF and Vis-NIR to rapidly predict speciated metal concentrations would significantly reduce the cost and time burden of collecting the data necessary for site surveyor to determine the pathways through which PTE could be mobilised. Hence allowing siter surveyor to more accurately assess the risk of a contaminated site, and the potential of novel resource recovery methods to recover PVE further increasing the economic viability of remediation.

5.6 References

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6 Overall Discussion

6.1 Introduction

Previous chapters have highlighted the potential of recovering resources from post-metallurgical sites to feed into the circular economy [1]. Furthermore, recent research has identified the potential of portable X-ray fluorescence spectrometry (pXRF) to reduce the cost and time needed to survey such sites [2]. However, despite the significant resources present at such sites current research has focused on the identification of potentially toxic elements (PTE) leaving potentially valuable elements (PVE) unapprised [2]. Furthermore, the potential of pXRF is limited by moisture [3], soil organic matter (SOM) [4], heterogeneity [5], and the reference method or material used [6]. Therefore, there is a need to appraise pXRF on post-metallurgical sites and develop methods to overcome pXRF's limitations. As such, the overall aim of this PhD was to further develop an innovative rapid, non-invasive method for quantifying elemental and speciated metal contaminated soils using pXRF and visible near-infrared spectroscopy (Vis-NIR). The research investigated the applicability of these methods and evaluated the influence of sample preparation and inter-sample interferences. To address this aim four objectives were developed (Figure 6.1).

The first objective was to determine the effects of pre-treatment on the accuracy of pXRF measurements of weathered slag. Of the five pre-treatments assessed, sieving and grinding increased precision while drying and grinding increased accuracy. However, igniting samples made no substantial difference.

Using the same samples from the above study, objective two investigated if pXRF and geophysical data correlated in post-metallurgical waste sites. with the goal of developing a method to generate higher spatial resolution maps than would be practically possible with pXRF alone. Across six different geophysical measurements no correlation was identified with pXRF therefore the novel mapping method was not possible.

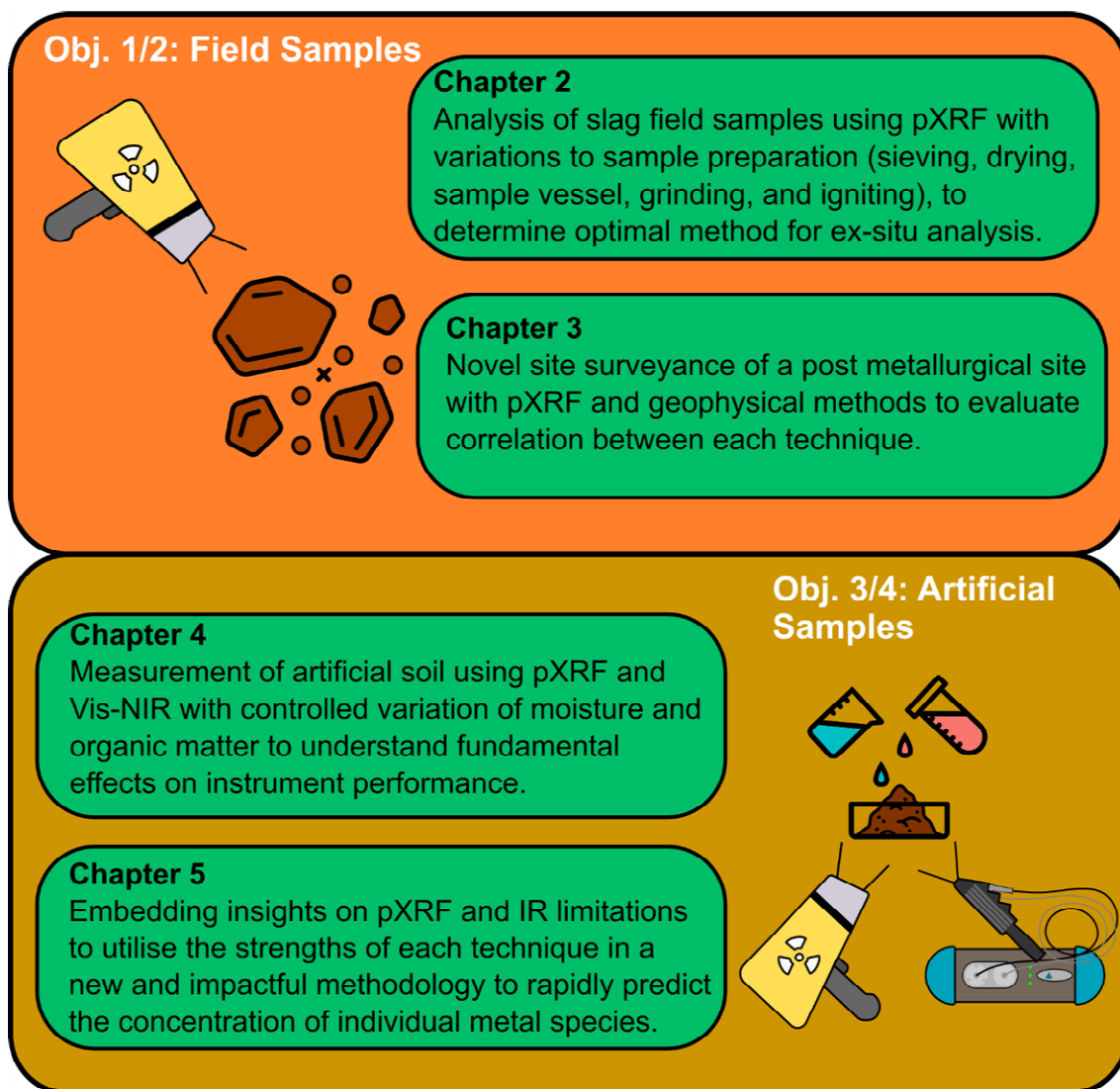


Figure 6.1 A Summary of thesis structure and links between objectives and chapters.

Objective three developed a data fusion framework using pXRF and visible near-infrared spectroscopy (Vis-NIR), to increase the accuracy of pXRF measurements of heavy metals in environmental matrixes. Across all eight elements analysed, data fusion produced more accurate results than pXRF. Furthermore, the data fusion framework outperformed data fusion methods implemented by previous studies [7,8].

Finally objective four developed a data fusion framework using pXRF and Vis-NIR spectroscopy to predict speciated metal concentrations. Within a simplified

heterogeneous solid matrix, both elemental and speciated iron concentrations were predicted to a high degree of accuracy.

6.2 Key findings and scientific contribution

To meet the aim of this thesis and the further development of rapid quantification methods, a deeper understanding of the interference and challenges limiting pXRF was required. Chapters 2, and 4 set out to advance the understanding of SOM and moisture, while heterogeneity was discussed in Chapters 2, 3, and 5, and reference materials/methods were discussed in Chapter 2.

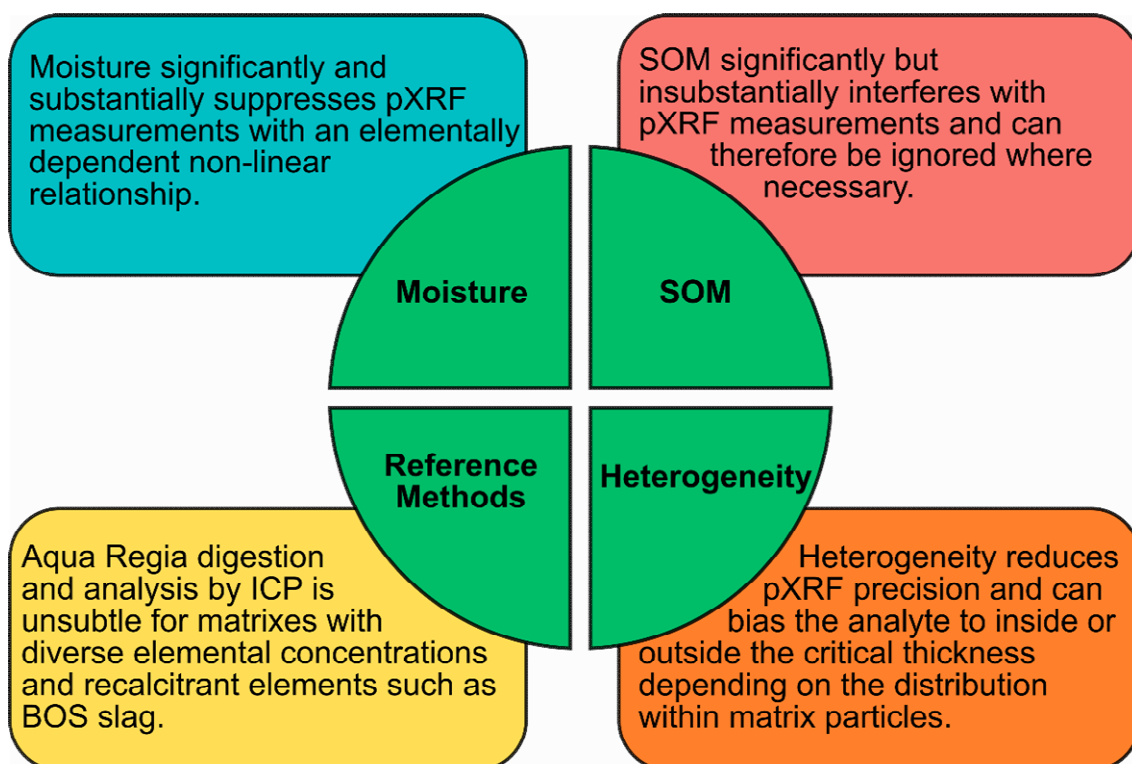


Figure 6.2 The key interference limiting pXRF and the key findings within this study.

6.2.1 The insignificance of SOM in pXRF analysis.

For the first time, no substantial difference was found before and after igniting samples to remove SOM (Figure 2.5). This result was corroborated by Chapter 4 which found a significant but unsubstantial difference in the pXRF recovery percentage as SOM percentages increased (Figure 4.4). The limited impact of SOM was further shown by the limited increase in accuracy of the data fusion

framework models after SOM was incorporated as a variable (appendix C.10). These results were contrary to a previous literature review [2] that emphasized the importance of SOM. However, upon reviewing the literature it was identified that only two papers [4,9] had investigated SOM, the former of which had identified a significant difference but had used unrepresentative sources of organic matter including graphite cellulose and sugar [4]. Furthermore, they had not assessed the magnitude of said difference [4]. while the second study by Chen et al. (2021), incorporated SOM in only two of the six models generated to improve pXRF predictions. Furthermore, their range of SOM concentrations was extremely low (0.3 – 3.3%).

Two theories were put forward to explain SOM's unsubstantial interference. Firstly, pXRF algorithms often use Compton normalisation to account for sample specific soil matrix chemistry [10]. Hence, the internal algorithms are likely to account for some or all of SOM's effects. The second theory proposes that when SOM percentage increases in a sample, the density of both the analyte and matrix will decrease, and as such the egressing X-ray path length will increase. This results in the concentration of analyte decreasing in a sample, but the mass of analyte within the pXRF's critical thickness remaining the same, and hence little to no change is detected as SOM percentages increase. However, further work is needed to test these theories.

In light of the results presented within this thesis and a review of previous literature [2,4,9] it can be concluded that moderate SOM concentrations do not interfere with pXRF measurements in a meaningful way. And hence SOM does not require accounting for when collecting accurate pXRF measurements if SOM is <16%.

6.2.2 The influence of sample heterogeneity on pXRF accuracy: the impact of particle distribution and size.

In Chapter 2, heterogeneity was removed from samples via sieving and grinding, which as hypothesised substantially reduced relative standard deviation of pXRF measurements (Figure 2.4). However, in contrast to previous literature [5], grinding caused pXRF measurements to increase for three out of six elements

(Figure 2.5). While In Chapter 5, fine powder chemicals and 80-100 mesh sand were mixed to generate what should have been a low heterogeneity mixture, however pXRF substantially over reported elemental concentrations (Figure 5.3). The increase in pXRF measurement reported in chapter 2, and overprediction observed in chapter 5, were attributed to the egressing X-ray's path length. This path length can be <2 mm [2], and hence shorter than the diameter of matrix particles. Therefore, it is likely that when samples were ground in Chapter 2, analyte outside the pXRF's critical thickness was released from within the matrix particles. Hence increasing the mass of analyte within the critical thickness. This same effect would explain Chapter 5's over prediction of Fe, as the analyte was added into the mixture, and therefor would be distributed in between the sand particles. As a result, this would place the analyte disproportionately within the critical thickness of the pXRF.

In chapter 3, the failure to correlate pXRF and geophysics was partly attributed to the large-scale heterogeneity present in the post-metallurgical waste site. This heterogeneity combined with the significantly different sizes of sample measured by geophysics ~ 1 m² [11], compared to pXRF <0.5 g [2] means that unless an impractical number of measurements were taken with pXRF it is unlikely that a correlation between there results could be identified.

Heterogeneity effects on the precision of pXRF have been well documented [4,5]. However, within this thesis it has been identified that heterogeneity can also reduce pXRF accuracy by biasing the distribution of analyte to within or beyond the critical thickness of pXRF. This discovery is particularly important for future studies which use synthetic samples where metals are not evenly distributed within the matrix particles and hence will be overpredicted by pXRF.

6.2.3 Reevaluating reference materials and ICP reliability for pXRF calibration: the need for accurate reference data.

In Chapter 2, induction-coupled plasma (ICP) was used as the reference method against which pXRF's ability to measure basic oxygen steelmaking (BOS) slag was assessed. However, despite ICP's use in the wider literature for this purpose [3,12] our results showed that ICP as was not a suitable reference method for

BOS slag for several reasons. Firstly, unlike samples whose elements are primarily lithogenic in origin, BOS slag contains a disparate abundance of elements. Therefore, low abundance elements are either diluted below ICP's LOD, or their spectral lines are masked by high abundance elements [13]. Secondly, in Chapter 2, pXRF reported higher concentrations of several elements than ICP. This difference was attributed the aqua regia method used. As a partial digestion method aqua regia cannot digest recalcitrant compounds such as iron spirals found in BOS slag [14]. Therefore, it is believed that ICP underreported the true metal concentration in the samples, however this was not validated due to a third challenge. Certified reference materials (CRM) have been used previously to calibrate pXRF and validate both pXRF and ICP [6]. However, at present only two BOS slag CRMs are available for purchase [15,16], furthermore these CRMs are unweathered and hence unlikely to be fully representative of field weathered BOS slag. Therefore, for further validation and optimisation of BOS slag analysis, representative CRMs will need to be produced using total extraction methods such as HF acid digestion.

In chapters 4 and 5, synthetic environmental sample sets were produced via the mixing of fine soil/sand with different metal compounds. While efforts were taken to homogenise samples, including grinding of the matrix, and extended mixing times, homogeneity could not be achieved on the scale needed for pXRF. This was due to the particle size of the matrix being larger than that of the analyte (as discussed above) resulting in pXRF's overprediction in Chapter 5 (Figure 5.3). Future studies may be able to overcome this limitation by ensuring both matrix and analyte particles are of equal size.

Contrary to previous literature [2,6], this study has shown that ICP cannot be assumed to provide a reliable reference method for pXRF when recalcitrant compounds may be present within samples. Furthermore, it has been identified that the lack of representative CRMs for unconventional matrices such as BOS slag limits the validation and optimisation of both pXRF and ICP. And finally, the small-scale heterogeneity that affects pXRF makes the creation of homogeneous

synthetic sample sets challenging, therefore further improvement to the methodology is needed.

6.2.4 The complex effects of moisture on pXRF measurements.

Moisture has previously been reported to interfere with pXRF measurements [3], in part because reference ICP derived concentrations are determined on dry samples [17]. This was corroborated In Chapter 2 were removing moisture substantially increased pXRF concentration for all six elements (Table 2.4). However, when comparing pXRF measurements from before and after drying, against ICP measurements, only three of the six elements showed substantial changes relative to ICP (Table 2.3). Furthermore, the increase in predicted concentration did not always result in an increase in accuracy, due to limitations of ICP as a reference method (as discussed above).

Due to these inconsistent results, further work was carried out in Chapter 4. Where the moisture was systematically increased in a synthetic sample set, which is a novel approach. It was theorised that as percentage moisture increased, pXRF recovery percentage would linearly decrease at a 1 to 1 rate. However, this theory was disproven with all eight elements showing a non-linear trend. This trend was found to be elementally dependent with higher atomic number elements showing a reduced non-linear trend (Figure 4.5). This result was suspected to be due to the presence of shrink swell clays within the matrix which expand when wet, hence shifting analyte to beyond the pXRF critical thickness. However, such an effect would also reduce the density of the sample and hence increase the critical thickness.

The results contained within this thesis reveal a more complex interaction between moisture and pXRF measurements than previously thought, particularly at concentrations <30%. As a result, simple correction equations such as put forward by Shuttleworth et al. (2014) are not appropriate for compensating for moisture. In light of this, data fusion frameworks may be a better method of compensation as tested in chapter 4.

6.3 Novel methodologies

In parallel to the investigation of the four key limitations of pXRF, four novel methodologies were developed to improve pXRF measurements: sample preparation for optimal ex situ measurements (Chapter 2); data-fusion framework for improved in situ measurements (Chapter 4); data-fusion framework for speciated metal quantification (Chapter 5); and the data-fusion of geophysics and pXRF to generate spatial maps, however due to limitations in sampling equipment and large scale heterogeneity at the field site this final method was unsuccessful (Chapter 3).

6.3.1 Evaluating preprocessing methods for optimal ex situ pXRF measurement.

Many studies [18,19] using pXRF ex situ, and assume their sample preprocessing methods to be appropriate, despite the lack of evidence available in the literature as to the optimal method. Therefore, in Chapter 2, this research aimed to determine the preprocessing steps necessary to achieve the highest performance from pXRF possible.

As a result of the effects discussed in section 6.2, the optimal methodologies require sieving or grinding samples to reduce heterogeneity and drying to remove the interference caused by moisture. However, the results of this study showed that preprocessing samples will only improve pXRF results if in situ measurements already showed a correlation with the reference method (Table 2.3). Finally due to the inconsistency in the effects of preprocessing on elemental prediction in our study, it was determined that ex situ pXRF has not reached maturity measuring environmental samples. Therefore, it is necessary to validate pXRF using a suitable reference method for every new sample set or site studied. Furthermore, the results in Chapter 2 and discussed in section 6.2.3, suggest aqua regia-ICP is not a suitable reference method when recalcitrant elements are present. Instead, total digestion by HF acid or calibration via representative CRM's are recommended as suitable alternatives.

6.3.2 Overcoming moisture and SOM interference with a novel data fusion framework, for accurate in situ measurements.

In situ pXRF measurements are consistently less accurate than ex situ measurements throughout the literature [2] due to the interferences discussed in section 6.2. Therefore, in Chapter 4, this thesis set out to use a novel data fusion framework to account for the effects of moisture and SOM on in situ pXRF measurements. To test this method on a wide range of SOM, moisture, and elemental concentrations, and to reduce heterogeneity a synthetic sample set was constructed (Figure 4.1). This sample set was measured by pXRF and Vis-NIR, the latter of which was used to predict moisture and SOM concentration, which were in turn used to correct pXRF measurements (Figure 4.2).

Across all eight elements the data fusion framework improved the accuracy of elemental predictions by an average of 0.11 r^2 compared to raw pXRF predictions, successfully accounting for moisture and SOMs effects (Table 4.3). Furthermore, our methodology outperformed Chen et al. general framework [9] and other full spectrum fusion methods such as Granger-Ramanathan averaging [7] and spectral concatenation [8] (appendix C.10). The data fusion framework has two specific strengths over previously implemented data fusion methods. Firstly, previous methods were implemented on dried samples and hence would not provide the same prediction accuracy in situ. Secondly, this study utilised the Compton normalisation included within the pXRF to overcome site-specific soil matrix chemistry. Whereas previous studies used full spectrum fusion methods which depend on co-evolving correlations that are unique to a sample set/site. As a result, our method has the potential to become a universal method that does not require calibration for each new site or sample set.

6.3.3 Demonstrating the potential for data fusion to rapidly measure speciated metals in heterogeneous solid matrixes.

The final method tested in Chapter 5 of this thesis set out to predict the speciated concentrations of Fe in a heterogeneous solid matrix. Due to the limited scope of this chapter a simplified matrix was needed, hence a synthetic sample set containing sand, Fe_2O_3 , and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in varying proportions was produced.

Using pXRF to predict elemental Fe and Vis-NIR to predict the ratio of Fe compounds a data fusion framework was created, which successfully predicted the concentration of Fe_2O_3 , and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Figure 5.3). Furthermore, this data fusion method maintained its accuracy in low concentrations ($<5000 \text{ mg kg}^{-1}$) which is of particular importance when surveying for PTE which can pose risks at low concentrations [12].

Despite the narrow scope of this study, the potential benefits of this method are significant. Principally, measuring each sample took ~30 minutes, a vast improvement over the alternative method, sequential extraction which requires up to 50 hours for extraction [14]. Furthermore, our method does not require hazardous chemicals; provides fully speciated concentrations as opposed to fractionation; and does not require the destruction of the sample. However, there may be limitations to this method that prevent its application to field samples. Firstly, this study used a simplified matrix, but real-world samples are far more complex. As a result, the Vis-NIR spectrum may contain too many overlapping peaks which cannot be resolved to predict speciation. Secondly this data fusion framework multiplied the speciation ratio by elemental Fe concentrations. However, when multiple elements are involved, their speciation ratios may differ, making the average ratio unsuitable for data fusion. Yet the results from this chapter warrant further research due to the significant potential of this methodology.

6.4 Impact

The overall aim of this thesis was chosen to help address the limitations of current contaminated site survey methods, as this is one of the key barriers to increasing the rate of site remediation. Currently, site investigations are designed in line with local legal frameworks, in the case of the UK this framework is Part 2a Environmental Protection Act (1990) which may determine a site to be contaminated if it poses a hazard to human health, waters, property, or ecological systems [20]. The metals typically of interest to site investigators are As, Cd, Cr, Cu, Pb, Hg, Ni, Se, and Zn, [21], which made up 98% of the identified metal/metalloid contaminated sites identified in the UK from 2000 to 2013 [20]. In

addition to the toxic nine, there is also interest in Ba, Be, V, and Br (water soluble) known as CELA suite. But other less common toxic metals are often investigated if evidence for them is found in the preliminary stages [21]. According to the international standards ISO 2136:2020 and ASTM E2531, site investigations are carried out using a conceptual site model (CSM) which is continually updated as the investigation passes through three phases (Figure 6.3).

The first phase (preliminary investigation), is primarily a desk based study gathering information about previous uses, water tables and local geology potentially combined with a brief (walk over) site survey where it can be determined if there is likely to be a risk of contamination; hypothesis are also made to inform the later stages of investigation. The second phase (exploratory investigation) will involve collecting soil samples, surface-water, and groundwater, among others, to be further analysed in the laboratory to produce a qualitative level model that can test the hypothesis. If all hypotheses have been accepted, then further investigation may not be required but it may also become apparent that contamination is more widespread than hypothesised. In that case, a third phase (detailed investigation) may be necessary, which aims to achieve a quantitative level of concentration and location of contaminants. This phase uses the same methods as in the exploratory investigation but with a wider or higher resolution sampling program; and potentially more detailed analysis depending on the needs of the site. Finally further supplementary investigations may be carried out if areas remain above acceptable uncertainty levels. [22–24] Given the high cost of laboratory analysis by ICP, the CSM's tiered approach minimises costs while avoiding the risk of overlooking potential contamination. Yet this approach can require years of work before remediation on a site can commence.

In Chapter 2, ex situ pXRF analysis was optimised to achieve quantitative screening predictions and if immediately adopted by site surveyors, could be carried out in on-site laboratories avoiding the need to transport samples off-site for ICP analysis. Hence, reducing the time taken to complete the preliminary and exploratory investigations (Figure 6.3). However, Chapter 2 did not achieve definitive predictions by pXRF and as such ICP results will still be needed,

particularly in the detailed investigation phase of the CSM which require high levels of accuracy (Table 2.3).

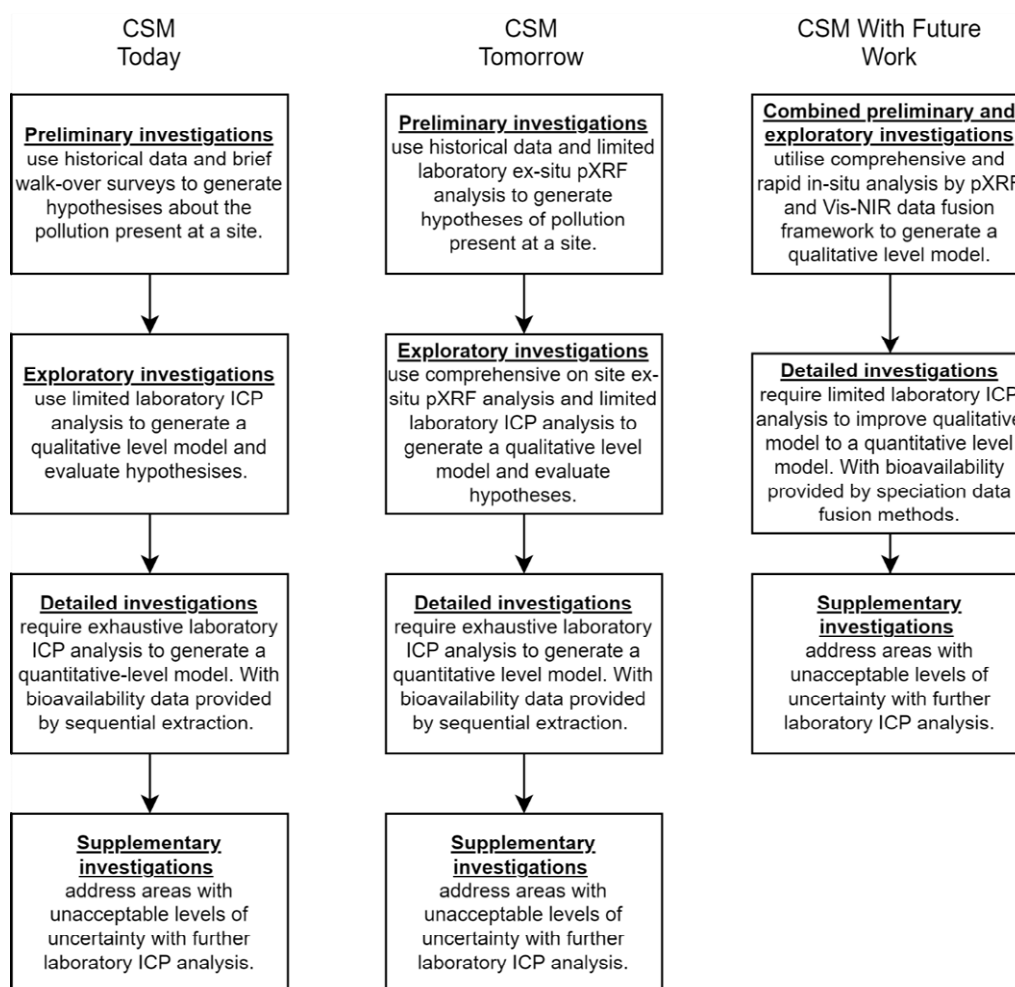


Figure 6.3 Phases of conceptual site model (CSM), at present; tomorrow with the implementation of ex situ pXRF analyses (Chapter 2); and with future work to implement data fusion frameworks for in situ (Chapter 4) and speciated analyses (chapter 5).

Site surveyors should be cautious when looking to implement pXRF on post-metallurgical sites containing BOS slag, as only six out of twelve elements investigated showed useful data quality. Furthermore, only two (Pb, Cr) of the nine elements currently of interest to site surveyors [21] were of useful data quality. Similarly, Chapter 2 showed that on post-metallurgical sites ICP can underreport concentrations due to the recalcitrant elements present, however as

site surveys are primarily interested in PTE, missing recalcitrant elements is not a concern as they are not mobile or bioavailable and hence pose little risk [14]. However robust data handling will be needed to account for the difference between pXRF and ICP results.

The method presented in Chapter 2 may provide some time and cost savings for site surveyors tomorrow. However, with further development the data fusion framework presented in Chapter 4 may justify a restructuring of the CSM, reducing the time needed to survey a site from years to months. This data fusion framework has shown the potential to achieve definitive results despite the presences of moisture within the samples analysed. Therefore, with future work there is potential to achieve qualitative screening in situ measurements. If such a method were available to site surveyors, the time and cost involved in data collection would be significantly reduced. In such a scenario, the CSM could be redesigned with preliminary and exploratory investigations happening simultaneously in a relatively short period of time producing a comprehensive qualitative model of the site. Following on from this, the detailed investigation could employ the in situ data fusion framework with supplementary ICP analysis to produce a definitive model across the entire site (Figure 6.3). Finally, in Chapter 4, a novel method to rapidly predict the speciated concentrations of metal in a solid sample. With further work this method could successfully be developed to rapidly quantify bioavailability data for CSM saving significant time compared to the current method of sequential extraction (Figure 6.3).

In addition to the many sites that need remediation [20], there is a growing need for a wider variety of resources, which could be recovered from these sites. From 2014 to 2020, renewable electricity capacity grew by 107% and the international energy agency forecasts that by 2026 95% of new global power capacity built each year will be renewable [25]. Renewable energy generators need a diverse range of metals in large quantities, for example solar photovoltaics need sizable amounts of Ga, As, Cd, Te, In, Ag, and Se, [26]. To prioritise finding sources for this diverse list of critical resources, the EU created the *Ad hoc* Working Group on Defining Critical Raw Materials which, in 2020, identified 43 critical raw

materials that are necessary for future economic growth [27] and that have a high supply risk (Table 6.1). However, many other elements have been identified as important to the economy and the green energy transition (Table 6.1) that do not have a supply risk but have economic value [26]. Hence, all of these are candidates to be included in site investigations to make there remediation more cost effective as well as contributing to the circular economy.

However, to include these extra elements in the CSM would increase data collection time and cost. While it is the case that ICP can simultaneously measure >20 elements, where elements having diverse concentrations, multiple dilutions are required [28]. Furthermore, as discussed in Chapter 2, ICP struggles to handle samples where differences in elemental concentrations are extreme. Alternatively, pXRF can simultaneously measure >20 elements without the need for sample dilutions preventing further cost or time needed to produce CSMs. Furthermore, if developed further the prediction of speciation using data fusion (Chapter 5) could predict oxidation states of elements. This data would allow for accurate assessment of the effectiveness of novel extraction methods such as bio-hydrometallurgy which relies upon the oxidation of Fe^{2+} by *Acidithiobacillus ferrooxidans* to release elements from the matrix for recovery [29].

Table 6.1 Elements currently of interest for remediation and the circular economy.

Toxic elements currently surveyed [20,21].	As, Ba, Be, B, Cd, Cr, Cu, Pb, Hg, Ni, Se, V, Zn
EU Critical Raw Materials 2020 [27].	Al, Sb, Ba, Be, Bi, B, Co, Er, Eu, F, Gd, Ga, Ge, Hf, Ho, In, La, Li, Lu, Mg, Nd, Nb, Pd, P, Pt, Pr, Rh, Ru, Sm, Sc, Si, Sr, Ta, Tb, Tm, Ti, W, V, Yb, Y
Elements directly used in energy pathways [26].	Ac, Al, Sb, As, Bi, B, Cd, Ca, Ce, Cr, Co, Cu, Dy, Eu, F, Gd, Ga, Ge, Au, Hf, Ho, In, Fe, La, Pb, Li, Mg, Mn, Hg, Mo, Nd, Ni, Nb, Pd, P, Pt, Po, K, Pr, Ra

6.5 Limitations of research

- During the investigations both field samples (Chapter 2) and synthetic samples (Chapter 4) were used to investigate the effects of SOM and moisture on pXRF. However, the ranges of both sample sets were limited to 0-16% and 0-30% for SOM and moisture respectively, therefore the relationships identified may not continue at higher concentrations. Furthermore, in Chapter 4 only one make of pXRF was trialled hence other manufacturer's internal calibrations may show different relationships.
- The limitations of BOS slag analysis by aqua regia ICP were discussed in Chapter 2. However, due to a lack of availability neither a representative BOS slag CRM, nor total digestion by HF were used to assess ICP's performance. Instead, conclusions were drawn from existing literature.
- In Chapter 3, the correlation of geophysics and pXRF was primarily limited by the lack of borehole sampling, which meant geophysics and pXRF measurements were taken on different volumes of mass. However, the collection of boreholes samples at this site would have increased the time and cost beyond the scope of a rapid analysis methodologies and this thesis.
- To generate the synthetic sample set used in chapter 4, soil, ignited soil, moisture and metal compounds were weighed and mixed. The weighed masses were also used to calculate true concentrations. However, due practical limitations, total digestion by HF was unavailable to determine the background elemental concentrations within the soil matrix. Therefore, true concentrations were calibrated using the pXRF measurements of dry inorganic samples. This calibration introduced an element of feedback loop bias; however, it did not alter the effects of moisture and SOM, or the increase in accuracy caused by the data fusion framework (appendix C.10).
- The synthetic sample set in chapter 4, was used to control variables not under investigation (i.e. heterogeneity). However, despite efforts to ensure the sample set was representative, the number of variables present in field

samples means caution should be taken in applying Chapter 4's conclusions to field samples without further studies.

- The results of Chapter 5's speciation data fusion model was achieved on a highly simplified samples set using Vis-NIR to predict speciation ratios. However, real-world samples are substantially more complex. Therefore, it may be the case that the matrix and overlapping peaks in the Vis-NIR spectrum cannot be resolved to predict speciation. Furthermore, when multiple elements are present their ratios of speciation may not be equal. Hence, the average ratio of speciation provided by Vis-NIR may not be appropriate for individual elements.

6.6 Future work

The research conducted in this thesis has significantly improved our understanding of the interferences affecting pXRF and developed novel data fusion framework approaches to improve predictions but is constrained by time and methodological limitations. Therefore, recommendations for future research include:

- In this thesis limitations in the analysis of BOS slag with partial digestion by aqua regia and ICP were identified. However, validation of the theories presented herein were beyond the scope of this thesis. Therefore, future work should undertake both total digestion by HF and ICP-MS analysis or LiBr disk creation for bench XRF analysis to assess the accuracy of aqua regia on BOS slag. A better understanding of the limitations of aqua regia on BOS slag would allow for better assessment of pXRF methods and the efficacy of novel resource recovery methods.
- The ex situ pXRF analysis of a heterogeneous waste site successfully predicted six elements to qualitative or quantitative levels. However, it was proposed that further increases in accuracy could be obtained by using multiple CRMs of differing matrixes. Therefore, future work should obtain CRM's representative of different matrices found in heterogeneous waste sites to calibrate pXRF and investigate if accuracy can be further improved.

- In this thesis it was demonstrated that SOM dose not substantially interfere with pXRF measurements. In addition, it was shown for the first time that moisture has a nonlinear relationship with pXRF recovery. However, these results were observed within limited ranges of SOM and moisture, 0 – 16% and 0 – 30%, respectively. Therefore, future studies are needed to determine if these relationships are present at higher concentrations of SOM and moisture. And to determine if moistures non-linear relationship can be replicated in field samples and differing soil textures. Furthermore, the observed relationships are not fully understood and hence work should be undertaken to model the change in maximum X-ray egression pathlengths in varying SOM and moisture conditions.

In Figure 6.3 a restructured CSM was proposed that would be able to carry out the preliminary and exploratory investigations in a combined survey phase by utilising the data-fusion of pXRF and Vis-NIR to collect accurate in-situ data and provide information on the speciation and bioavailability of contaminants. However, before such a restructured CSM could be implemented further research on the methods proposed in chapters 4 and 5 is required.

- Specifically In chapter 4 the data fusion framework presented, successfully overcame both SOM and moisture interference. However, this was achieved in a homogeneous synthetic sample set. Future work should attempt to replicate the framework results in field samples. Research should also be conducted to incorporate heterogeneity into the framework. And finally other non-linear modelling methods such as cubist should be trialled. With further work a global in situ method could be developed which would enable a restructuring of CSM phases reducing the time needed to complete site surveys.
- While in chapter 5 the potential of data fusion to predict speciation of Fe in a simplified environmental matrix was successfully demonstrated. Therefore, two approaches are proposed to develop this method further. Firstly, using real field samples and sequential extraction top-down data fusion would train machine learning models built on the full spectra

obtained from pXRF and Vis-NIR. This approach may lead to an accurate method with just one sample set. However, full spectrum models are inherently sample set specific, and as such limited sequential extraction analysis would be required for every new site or sample set. The second approach, bottom-up data fusion would use increasingly complex synthetic sample sets to build up a data fusion framework. While slower this approach may lead to a universal model that could predict speciation concentrations in any sample set. Finally, these approaches should be investigated in parallel with other speciation analysis methods such as x-ray absorption fine structure spectroscopy.

6.7 Conclusion

This PhD used a combination of synthetic and post-metallurgical site samples to understand the effects of different variables on pXRF measurements, and to develop novel methodologies that overcame said limitations. This was achieved by: i) determining the effects of pre-treatment on the accuracy of pXRF measurements of weathered BOS slag; ii) investigating if pXRF and geophysical data correlate in post-metallurgical waste sites and to develop a method to generate higher spatial resolution maps than would be practically possible with pXRF alone; iii) developing a data fusion framework using pXRF and Vis-NIR, to increase the accuracy of pXRF measurements of heavy metals in environmental matrixes; and iv) developing a data fusion framework using pXRF and Vis-NIR spectroscopy to predict metal speciation and concentration.

Objective one was addressed by measuring weathered BOS slag from a post-metallurgical site, using pXRF before and after preprocessing steps. These steps were sieving, drying, changing sample vessel, grinding, igniting, and then finally aqua regia digestion for ICP measurement (Chapter 2). Sieving and grinding improved precision, while drying and grinding enhanced accuracy. Furthermore, this study provides the first evidence that SOM does not substantially impact pXRF accuracy. However, significant challenges for both pXRF and ICP were identified in measuring heterogeneous waste sites containing BOS slag with several elements reported below ICP's LOD; a negative correlation for Ti between

ICP and pXRF; and the over reporting of concentrations by pXRF which was attributed to incomplete digestion by aqua regia of recalcitrant iron spinals in BOS slag. As a result of this study, and the best practise methodologies proposed, site investigators can gather more information at lower cost using ex situ analysis in the early stages of generating CSM. However further research is required to validate aqua regia's suitability as a reference method for measuring BOS slag. In addition, more research should investigate the potential of utilising CRMs of different matrices to construct a multi-matrix calibration that may improve pXRF's performance on complex sites.

To address Objective 2 electromagnetic induction (EMI), electrical resistivity tomography (ERT), and ex situ pXRF measurement were for the first time collected at a post-metallurgical waste site and correlated against each other (Chapter 3). However, no correlation was found between either EMI or ERT and pXRF measurements. As such, generating geochemical maps of the site by using fewer samples than needed under a traditional sampling program was not possible. Future studies may yet achieve satisfactory correlations by employing borehole sampling, however this will reduce the speed of data collection. In addition, the high heterogeneity at such sites and the significant sample size differences required for geophysical and chemical methods will also present a barrier to achieving correlations. Therefore, research should be directed towards optimising geophysical survey methods to achieve the higher resolution required to overcome the matrix heterogeneity present at such sites.

Objective three was addressed by constructing a synthetic sample set with varying SOM, moisture and elemental concentrations. Samples were then measured with pXRF and Vis-NIR and passed through a data fusion framework to account for the interference of moisture and SOM on the prediction of elemental concentrations (Chapter 4). This studies results showed that increasing SOM percentages caused a significant but insubstantial difference in pXRF measurements. It was also shown for the first time that moisture had an elementally dependent non-linear trend causing pXRF to substantially under predict five elements more than hypostasised. These results show that SOMs

effects can be ignored in future uses of pXRF where speed of data collection is the priority. However, the non-linear trend shown by moisture requires more advanced correction methods than previously proposed, such as the novel data fusion framework presented in this study. This data fusion framework produced more accurate predictions than raw pXRF results, successfully accounting for moisture and SOM within the samples. Furthermore, this method outperformed previous studies who implemented data fusion methods such as Granger-Ramanathan averaging and spectral concatenation on dried samples. As such the data fusion framework will enable more accurate in situ measurements allowing site surveyors to rapidly develop qualitative models of contaminated sites in the first phase of CSM generation. Furthermore, this method of data fusion makes use of Compton normalisation to account for site specific soil matrix chemistry which with further research may allow for an accurate universal model that does not require site specific calibrations. To achieve this, future studies are needed to test the data fusion framework on field samples and widen the range of moisture, SOM and soil textures included in the sample set.

To address the final objective, in a scoping study a synthetic sample set was constructed with sand, Fe_2O_3 , and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in varying proportions (Chapter 5). These samples were then measured with pXRF and Vis-NIR and passed through a data fusion framework to predict the concentration of Fe_2O_3 , and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. For the first time this data fusion framework successfully predicted Fe_2O_3 , and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to a high degree of accuracy. This accuracy was maintained at low concentrations $<5000 \text{ mg kg}^{-1}$ which is of particular significance for PTE which may still be toxic at low concentrations. This methodology was significantly faster at $\sim 30\text{min}$ per sample than the alternative technology sequential extraction. Furthermore, this novel methodology does not require hazardous chemicals; provides fully speciated concentrations as opposed to fractionation; and does not require the destruction of the sample. However, due to simplified matrix used, it may be the case that in real samples overlapping peaks in the Vis-NIR spectrum cannot be resolved sufficiently to predict speciation. As such further work is needed to test more complex synthetic samples using a bottom-up data fusion approach or field samples using a top-

down data fusion approach. However, if successful the reduction in speciation data acquisition costs would be significant enabling more targeted remediation and resource recovery at contaminated sites.

In conclusion, this research has examined the interferences limiting pXRF measurement of environmental samples and developed novel methodologies to overcome these interferences. It was shown that SOM does not substantially interfere with pXRF, whereas moisture's effects were more complex than previously reported. The optimal steps of pre-processing for ex situ analyses were identified and will allow site investigators to immediately take advantage of pXRFs rapid analysis and low cost to decrease the cost of data collection in the initial phase of CRM construction. For the first time the correlation of pXRF and geophysical measurements was investigated and deemed unviable with current methods available. Novel data fusion frameworks were developed that with further work may allow site surveyors to collect accurate elemental concentrations in situ and speciation data in substantially shorter times. Such methods could substantially reduce the time needed to survey contaminated land and provide the data needed for resource recovery reducing the cost of remediation.

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Appendix A

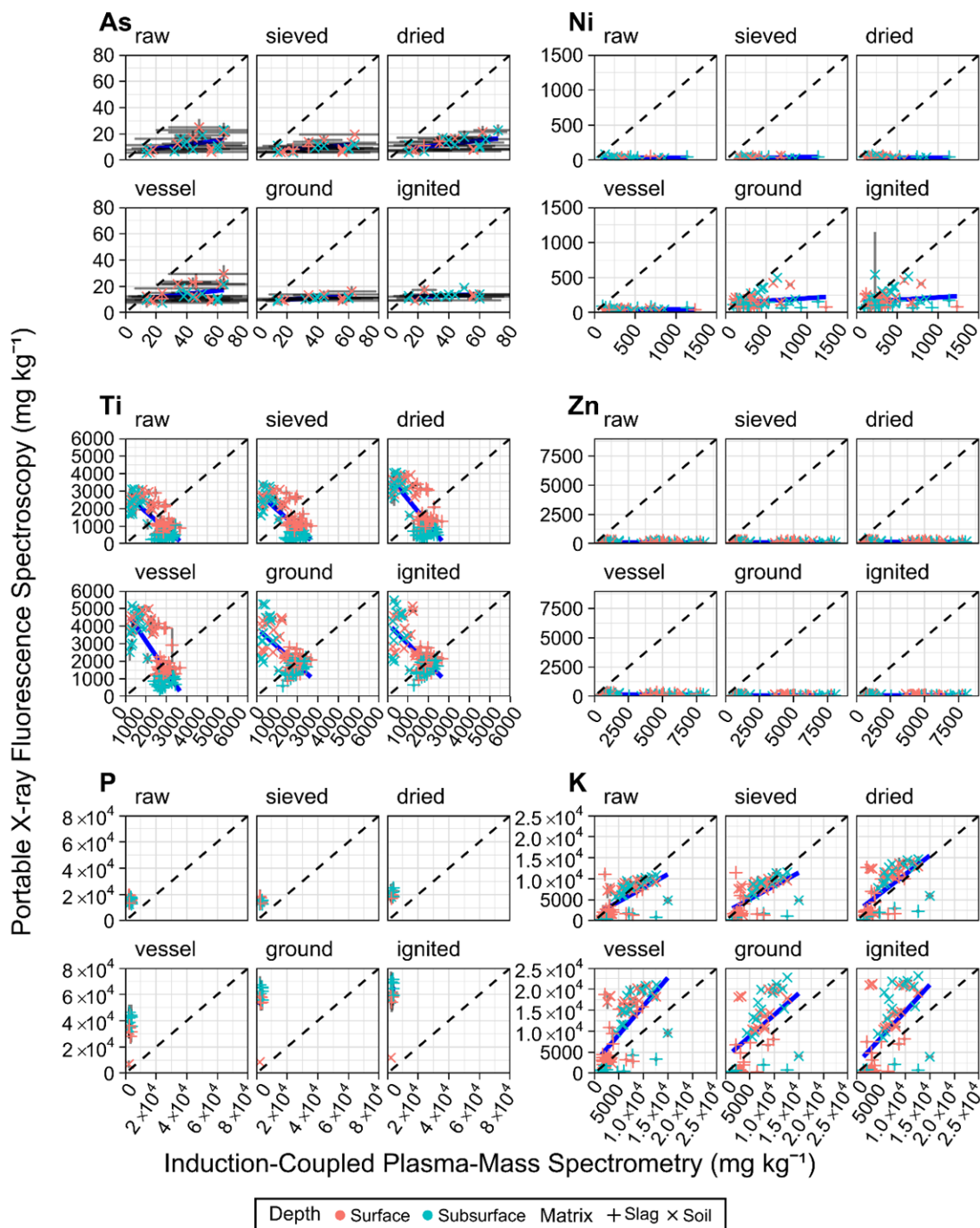
A.1 Limits of detection for ICP-MS, and pXRF. LODs were provided by instruments based on the calibration curve of ICP-MS and the factory calibration of pXRF. ICP-MS undiluted was calculated to account for the dilution of the sample during acid digestion.

Limits of Detection			
Element	ICP-MS (ug/L)	ICP-MS undiluted dilution (mg/kg)	pXRF (mg/kg)
P	0.01	2220.56	477.00
S	NA	NA	87.00
Cl	NA	NA	43.00
K	2.43	485.72	194.00
Ca	17.43	3486.87	32.00
Ti	0.13	25.84	30.00
Cr	0.06	12.43	2.30
Mn	0.06	11.70	3.70
Fe	3.02	604.86	11.00
Co	0.01	1.04	7.00
Ni	0.01	1.93	8.00
Cu	0.08	16.36	3.90
Zn	0.38	76.99	2.10
As	0.04	8.35	1.50
Se	0.72	144.21	1.00
Rb	NA	NA	1.20
Sr	0.03	6.28	0.80
Zr	NA	NA	1.60
Mo	0.02	3.70	2.30
Ag	NA	NA	11.00
Cd	0.02	4.86	13.00
Sn	0.01	2.91	20.00
Sb	0.01	2.66	22.00
Ba	0.19	38.82	4.20
Hg	0.01	2.79	3.10
Pb	0.01	2.45	2.40

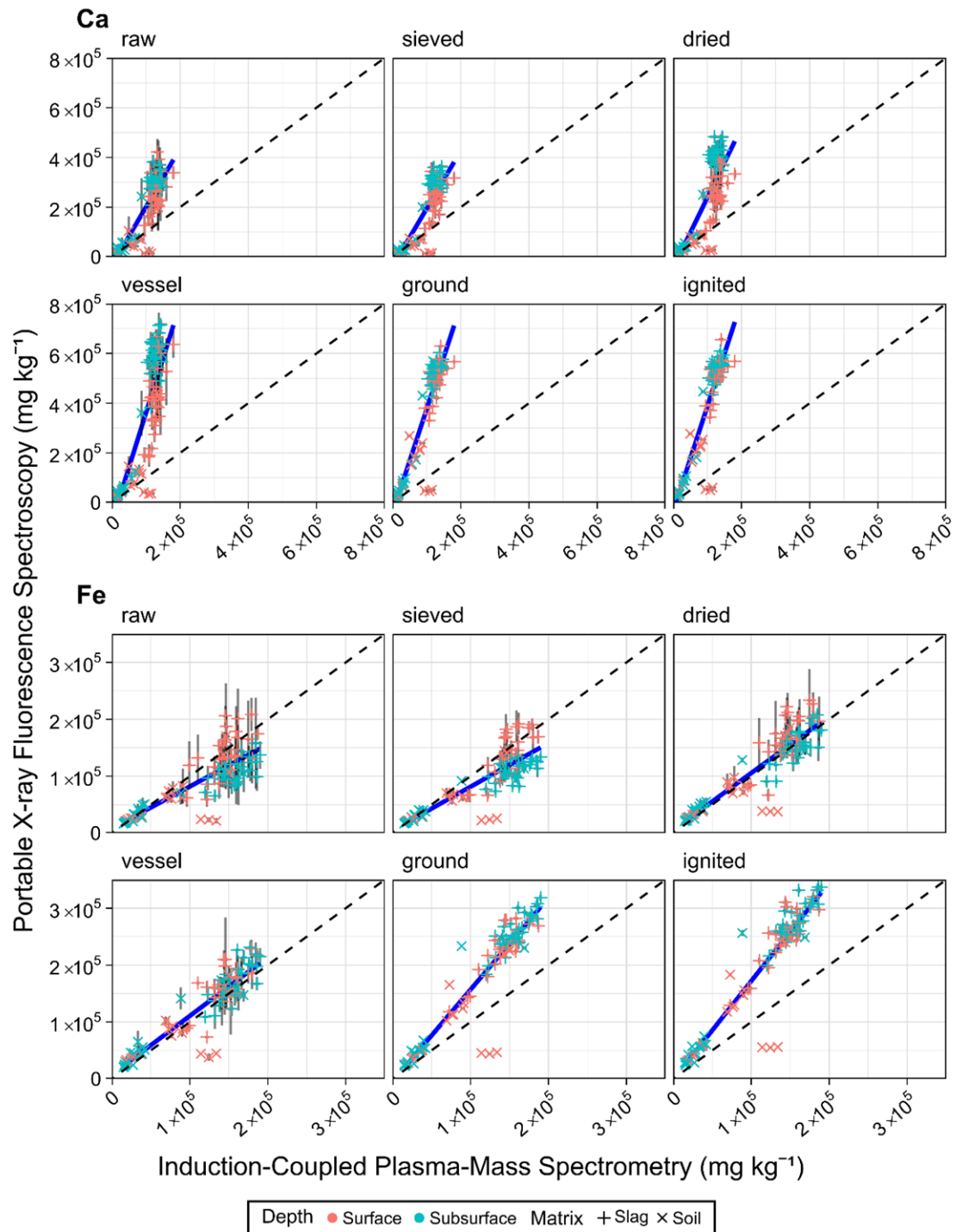
A.2 Concentrations used to calibrate ICP-MS

ICP-MS Calibration curves		
Elements	(ug l ⁻¹)	accounting for dilution (mg kg ⁻¹)
P, Ti, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag Cd, Sn, Sb, Ba, Hg, Pb	0	0
	25	5,000
	50	10,000
	75	15,000
	100	20,000
K, Ca	0	0
	250	50,000
	500	100,000
	750	150,000
	1,000	200,000
Fe	0	0
	275	55,000
	555	111,000
	825	165,000
	1,100	220,000

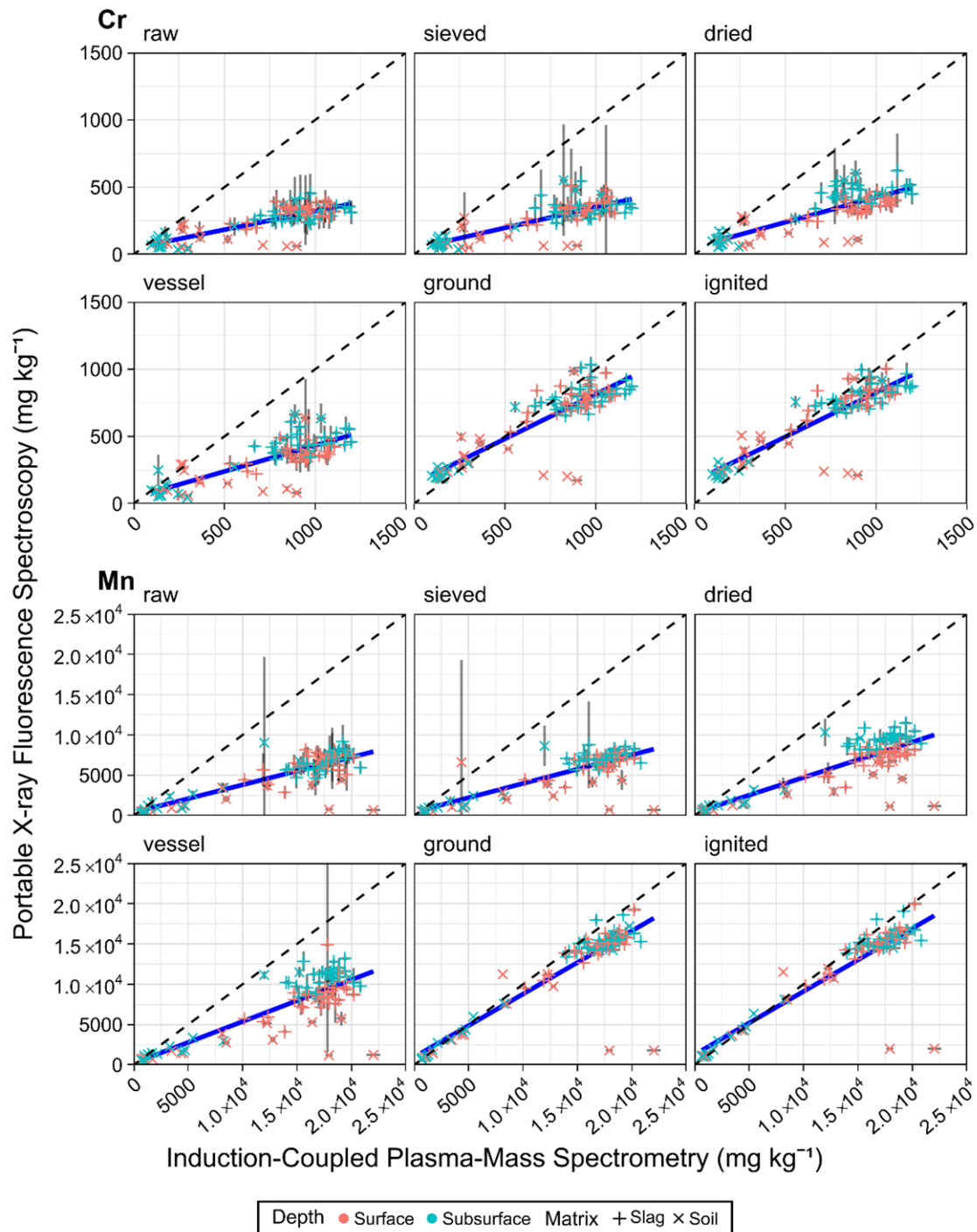
A.3 Regression of samples (n=102) collected from an iron slag heap in Teesside, UK. Showing As, Ni, Ti, Zn, P, and K concentrations measured by pXRF after each processing step (y-axis) against ICP-MS measurements (x-axis). OLS regression (blue solid line); ideal 1 to 1 relationship (black dashed line); slag matrix (horizontal cross); soil matrix (diagonal cross); surface samples (red cross); subsurface samples (blue cross) standard deviation error bars (black solid lines).



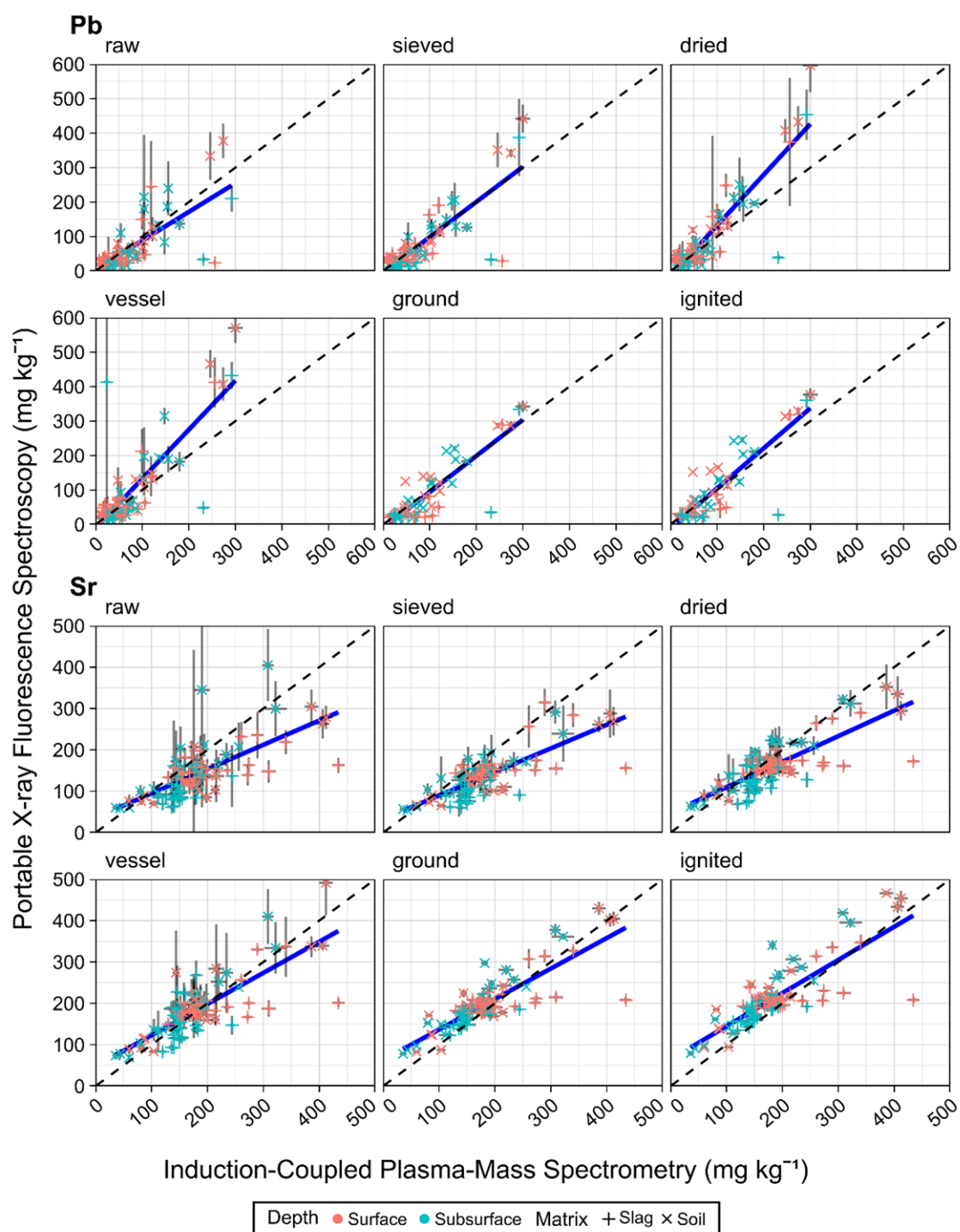
A.4 Regression of samples (n=102) collected from an iron slag heap in Teesside, UK, showing Fe and Ca concentrations measured by pXRF after each processing step (y-axis) against ICP-MS measurements (x-axis). OLS regression (blue solid line); ideal 1 to 1 relationship (black dashed line); slag matrix (horizontal cross); soil matrix (diagonal cross); surface samples (red cross); subsurface samples (blue cross). error bars (black solid lines)



A.5 Regression of samples (n=102) collected from an iron slag heap in Teesside, UK, showing Cr and Mn concentrations measured by pXRF after each processing step (y-axis) against ICP-MS measurements (x-axis). OLS regression (blue solid line); ideal 1 to 1 relationship (black dashed line); slag matrix (horizontal cross); soil matrix (diagonal cross); surface samples (red cross); subsurface samples (blue cross). error bars (black solid lines).



A.6 Regression of samples (n=102) collected from an iron slag heap in Teesside, UK, showing Pb and Sr concentrations measured by pXRF after each processing step (y-axis) against ICP-MS measurements (x-axis). OLS regression (blue solid line); ideal 1 to 1 relationship (black dashed line); slag matrix (horizontal cross); soil matrix (diagonal cross); surface samples (red cross); subsurface samples (blue cross). error bars (black solid lines).

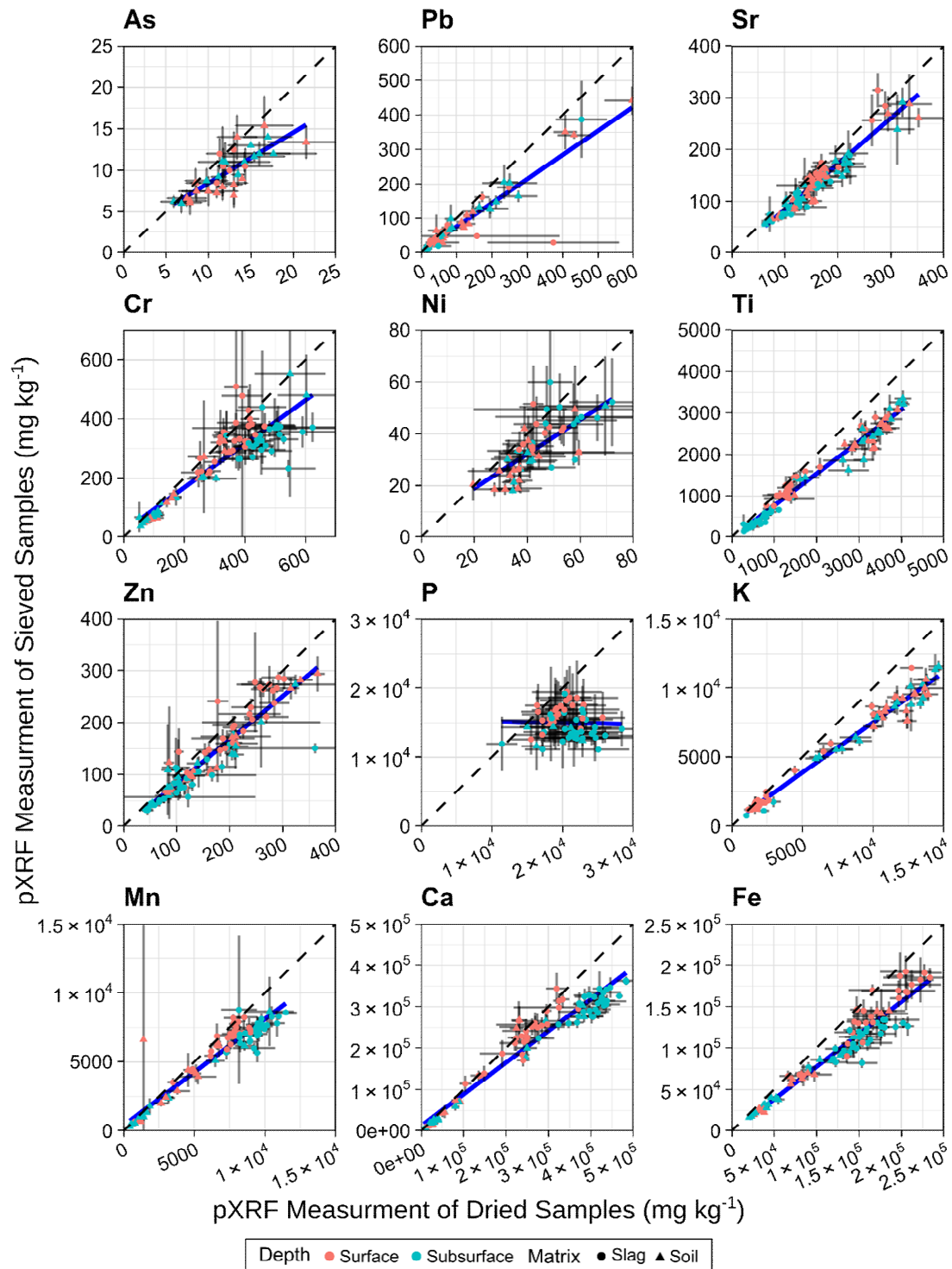


A.7 Additional summary statistics of ordinary least squared regression on pXRF and ICP-MS measurements of samples (n=102). n is the number of samples above pXRF and ICP-MS LOD; residual prediction deviation (RPD); Person's correlation coefficient squared (r^2); ratio of performance to inter-quartile Distance (RPIQ); Lin's concordance correlation coefficient (r_c); mean absolute error (MAE); coefficient of determination (R^2); relative standard deviation (RSD); data quality assessment levels as defined by EPA [31].

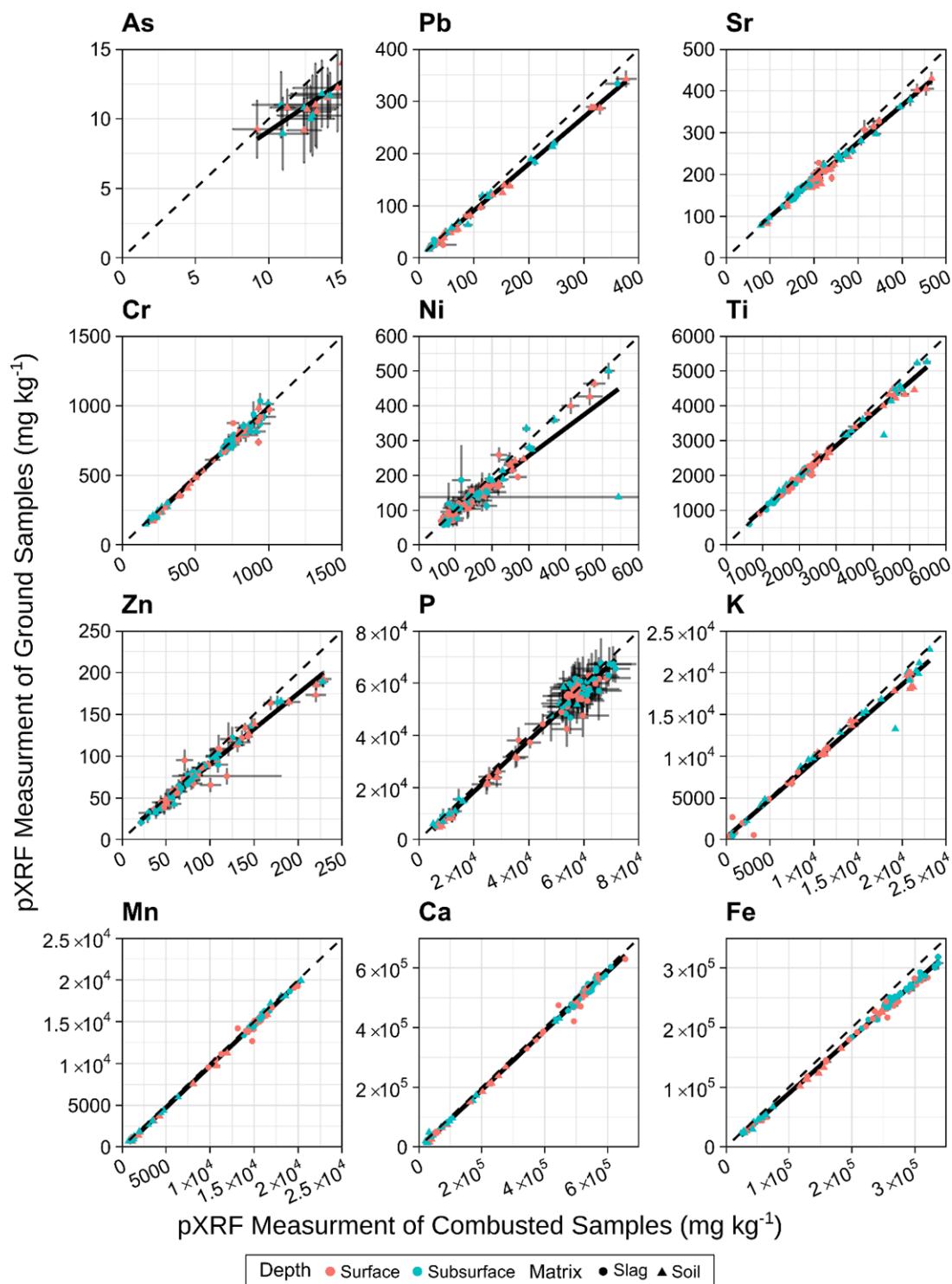
Element	Processing Step	n	RPD	r^2	RMSE	RPIQ	r_c	MAE	R^2	RSD	Intercept	Slope	Intercept 95% CI	Slope 95% CI	Data Quality
As	Raw	32	0.50	0.20	34.13	0.64	0.07	30.71	-3.27	20.46	5.80	0.15	(-1, 13)	(0.006, 0.302)	No Correlation
	Sieved	33	0.52	0.20	34.45	0.93	0.04	30.33	-2.84	15.81	6.45	0.09	(3, 10)	(0.002, 0.172)	No Correlation
	Dried	31	0.54	0.25	33.03	0.89	0.07	29.05	-2.56	17.84	7.12	0.13	(2, 12)	(0.026, 0.237)	No Correlation
	Vessel	40	0.57	0.14	30.28	1.06	0.07	25.95	-2.25	18.29	9.27	0.13	(3, 15)	(-0.006, 0.259)	No Correlation
	Ground	21	0.53	0.25	33.13	0.83	0.03	28.96	-2.82	19.80	9.06	0.06	(7, 11)	(0.001, 0.11)	No Correlation
	Ignited	20	0.56	0.09	30.48	1.05	0.03	25.97	-2.41	14.57	11.37	0.04	(8, 15)	(-0.043, 0.131)	No Correlation
Pb	Raw	86	1.24	0.53	50.53	1.24	0.72	31.27	0.34	25.14	5.13	0.83	(-12, 22)	(0.655, 1.01)	No Correlation
	Sieved	82	1.40	0.67	49.00	1.44	0.80	30.44	0.48	19.30	-3.57	1.02	(-20, 13)	(0.856, 1.185)	Qualitative
	Dried	88	1.10	0.80	61.12	1.05	0.78	36.59	0.16	22.01	-14.95	1.47	(-31, 1)	(1.31, 1.633)	Quantitative
	Vessel	88	0.89	0.67	74.98	0.81	0.69	39.88	-0.28	19.85	-10.32	1.43	(-32, 11)	(1.203, 1.649)	Qualitative
	Ground	61	1.72	0.77	41.96	1.45	0.86	27.57	0.65	9.30	-11.19	1.05	(-29, 7)	(0.895, 1.205)	Quantitative
	Ignited	56	1.47	0.75	49.76	1.47	0.83	33.61	0.53	8.89	-10.99	1.16	(-33, 11)	(0.975, 1.348)	Quantitative
Sr	Raw	102	1.11	0.49	65.56	0.79	0.59	49.80	0.19	18.17	36.23	0.59	(12, 60)	(0.465, 0.709)	No Correlation
	Sieved	99	1.14	0.60	65.16	0.81	0.59	49.39	0.22	10.04	32.55	0.57	(14, 51)	(0.474, 0.667)	No Correlation
	Dried	102	1.46	0.61	49.95	1.03	0.72	35.58	0.53	9.23	47.83	0.62	(28, 67)	(0.519, 0.718)	Qualitative
	Vessel	102	1.53	0.61	47.57	1.08	0.78	33.90	0.57	10.98	47.63	0.75	(24, 72)	(0.631, 0.876)	Qualitative
	Ground	102	1.71	0.70	42.69	1.21	0.81	30.46	0.65	3.71	62.92	0.74	(44, 82)	(0.64, 0.835)	Quantitative
	Ignited	102	1.40	0.67	51.98	0.99	0.76	39.35	0.49	3.55	64.55	0.80	(42, 87)	(0.688, 0.916)	Qualitative
Cr	Raw	99	0.65	0.69	530.72	1.24	0.19	464.87	-1.40	18.80	46.89	0.28	(17, 77)	(0.237, 0.314)	Qualitative
	Sieved	96	0.69	0.65	509.55	1.33	0.23	440.69	-1.10	15.17	43.97	0.31	(7, 81)	(0.26, 0.355)	Qualitative
	Dried	98	0.77	0.69	455.51	1.46	0.30	390.59	-0.71	12.67	55.35	0.37	(15, 96)	(0.317, 0.42)	Qualitative
	Vessel	96	0.76	0.66	453.35	1.42	0.31	393.76	-0.73	11.91	45.97	0.39	(0, 92)	(0.33, 0.447)	Qualitative
	Ground	100	1.80	0.77	192.04	3.36	0.81	144.81	0.69	3.41	150.23	0.66	(91, 210)	(0.588, 0.739)	Quantitative
	Ignited	100	1.90	0.79	182.26	3.54	0.82	139.21	0.72	3.67	167.47	0.66	(111, 224)	(0.589, 0.731)	Quantitative
Ni	Raw	40	0.55	0.00	439.61	0.50	0.00	368.57	-2.39	19.93	37.11	0.00	(26, 48)	(-0.025, 0.021)	No Correlation
	Sieved	44	0.55	0.10	410.73	0.54	0.01	348.64	-2.47	21.18	28.59	0.02	(20, 37)	(-0.002, 0.035)	No Correlation
	Dried	52	0.58	0.01	379.46	0.59	0.00	310.35	-2.05	21.52	42.06	0.00	(34, 50)	(-0.023, 0.014)	No Correlation
	Vessel	59	0.59	0.00	437.81	0.62	0.00	355.23	-1.94	18.21	48.76	0.00	(40, 58)	(-0.019, 0.018)	No Correlation
	Ground	97	0.78	0.04	299.70	0.77	0.08	198.55	-0.66	13.86	132.28	0.08	(97, 167)	(-0.007, 0.159)	No Correlation
	Ignited	99	0.80	0.03	290.91	0.76	0.08	186.91	-0.57	14.83	149.13	0.07	(110, 189)	(-0.025, 0.166)	No Correlation
Ti	Raw	101	0.45	0.54	1475.12	0.67	-0.68	1368.15	-3.95	22.02	2836.97	-1.00	(2526, 3148)	(-1.195, -0.815)	No Correlation
	Sieved	98	0.44	0.53	1529.70	0.71	-0.68	1402.84	-4.17	11.43	3006.23	-1.05	(2672, 3341)	(-1.251, -0.842)	No Correlation
	Dried	102	0.37	0.59	1816.72	0.52	-0.61	1551.33	-6.56	11.75	3980.78	-1.43	(3589, 4373)	(-1.668, -1.19)	No Correlation
	Vessel	101	0.30	0.56	2218.51	0.44	-0.45	1754.94	-10.17	10.30	4885.29	-1.72	(4378, 5393)	(-2.033, -1.414)	No Correlation
	Ground	102	0.37	0.42	1791.06	0.53	-0.41	1181.68	-6.35	3.78	3916.31	-1.06	(3506, 4326)	(-1.31, -0.809)	No Correlation

	Ignited	102	0.35	0.43	1918.80	0.50	-0.38	1246.43	-7.44	3.44	4161.60	-1.15	(3717, 4606)	(-1.425, -0.882)	No Correlation
Zn	Raw	95	0.63	0.00	3866.63	1.06	0.00	3015.38	-1.56	22.09	134.28	0.00	(109, 160)	(-0.008, 0.005)	No Correlation
	Sieved	92	0.64	0.01	3750.18	1.08	0.00	2880.86	-1.46	15.32	141.12	0.00	(115, 167)	(-0.01, 0.003)	No Correlation
	Dried	94	0.63	0.00	3841.95	1.06	0.00	2976.65	-1.52	14.66	163.94	0.00	(137, 191)	(-0.009, 0.005)	No Correlation
	Vessel	93	0.64	0.01	3827.65	1.06	0.00	2953.09	-1.49	15.83	167.06	0.00	(139, 195)	(-0.01, 0.004)	No Correlation
	Ground	90	0.64	0.00	3853.04	1.05	0.00	2989.87	-1.51	10.06	77.31	0.00	(63, 92)	(-0.003, 0.005)	No Correlation
	Ignited	90	0.64	0.01	3845.79	1.05	0.00	2979.57	-1.49	10.49	83.10	0.00	(66, 100)	(-0.003, 0.006)	No Correlation
P	Raw	57	0.05	0.00	12653.65	0.09	0.00	12455.28	-439.42	19.55	15628.81	-0.04	(9316, 21942)	(-2.079, 1.992)	No Correlation
	Sieved	58	0.05	0.01	12043.25	0.09	0.00	11916.04	-439.46	18.62	15470.79	-0.21	(10203, 20739)	(-1.964, 1.549)	No Correlation
	Dried	65	0.03	0.02	17831.68	0.06	0.00	17697.17	-873.63	17.45	19155.57	0.52	(12767, 25544)	(-1.539, 2.581)	No Correlation
	Vessel	100	0.02	0.05	34502.26	0.03	0.00	33375.75	-3207.38	17.56	26479.46	3.30	(2609, 50350)	(-4.499, 11.098)	No Correlation
	Ground	100	0.01	0.07	54404.54	0.02	0.00	52900.50	-7693.93	12.90	39451.18	5.45	(4078, 74824)	(-6.013, 16.91)	No Correlation
	Ignited	100	0.01	0.12	57118.08	0.02	0.00	55726.43	-8792.02	11.72	37013.67	7.24	(3990, 70037)	(-3.551, 18.027)	No Correlation
K	Raw	75	1.12	0.40	3101.67	1.69	0.62	2094.43	0.20	21.83	1324.43	0.65	(-20, 2669)	(0.45, 0.849)	No Correlation
	Sieved	69	1.10	0.36	3177.33	1.59	0.60	2135.33	0.15	9.02	2028.60	0.63	(514, 3543)	(0.41, 0.848)	No Correlation
	Dried	74	0.84	0.39	4169.31	1.24	0.55	3179.41	-0.45	11.02	2102.08	0.89	(201, 4003)	(0.612, 1.176)	No Correlation
	Vessel	79	0.48	0.42	7187.06	0.76	0.39	5666.95	-3.32	9.09	2374.62	1.36	(-182, 4931)	(0.968, 1.747)	No Correlation
	Ground	52	0.46	0.23	7324.65	0.76	0.30	6136.14	-3.81	4.51	3632.63	1.03	(-603, 7869)	(0.47, 1.582)	No Correlation
	Ignited	61	0.45	0.30	7758.42	0.72	0.34	6132.34	-3.92	6.48	2042.89	1.27	(-1763, 5849)	(0.736, 1.799)	No Correlation
Mn	Raw	100	0.68	0.71	9692.21	0.84	0.24	8578.54	-1.21	17.47	405.32	0.34	(-278, 1089)	(0.297, 0.388)	Quantitative
	Sieved	97	0.70	0.71	9433.14	1.00	0.26	8336.62	-1.06	11.81	458.72	0.35	(-269, 1187)	(0.306, 0.402)	Quantitative
	Dried	100	0.78	0.71	8332.14	0.97	0.35	7277.00	-0.65	7.64	344.79	0.44	(-530, 1219)	(0.381, 0.497)	Quantitative
	Vessel	100	0.88	0.70	7409.55	1.09	0.44	6353.54	-0.31	8.14	209.45	0.52	(-853, 1271)	(0.447, 0.588)	Quantitative
	Ground	100	1.89	0.81	3466.43	2.36	0.85	2135.64	0.72	1.28	960.72	0.78	(-224, 2146)	(0.705, 0.861)	Quantitative
	Ignited	100	1.98	0.81	3301.39	2.47	0.86	1917.49	0.74	1.93	1287.60	0.78	(98, 2477)	(0.704, 0.861)	Quantitative
Ca	Raw	102	0.35	0.75	132687.87	0.49	0.36	106837.19	-7.34	20.05	-35599.57	2.36	(-65624, -5575)	(2.086, 2.636)	Quantitative
	Sieved	99	0.37	0.76	125474.64	0.55	0.39	99947.27	-6.39	9.26	-38359.54	2.32	(-67745, -8974)	(2.053, 2.597)	Quantitative
	Dried	102	0.25	0.68	182437.59	0.36	0.26	141342.44	-14.77	8.95	-43470.33	2.82	(-85923, -1018)	(2.427, 3.205)	Qualitative
	Vessel	102	0.14	0.72	325437.00	0.20	0.15	260328.75	-49.17	10.50	-78703.31	4.39	(-139664, -17743)	(3.828, 4.946)	Quantitative
	Ground	102	0.14	0.85	318958.24	0.20	0.15	275607.52	-47.19	1.01	-41431.88	4.17	(-80100, -2763)	(3.816, 4.526)	Quantitative
	Ignited	102	0.14	0.85	329506.66	0.20	0.14	286489.88	-50.43	2.10	-34098.08	4.21	(-72876, 4680)	(3.855, 4.567)	Quantitative
Fe	Raw	102	1.40	0.66	39750.62	2.15	0.74	30182.14	0.48	17.33	7913.17	0.74	(-6023, 21849)	(0.631, 0.849)	Qualitative
	Sieved	99	1.53	0.72	36853.44	2.38	0.78	27176.68	0.57	8.45	4688.81	0.77	(-7786, 17163)	(0.67, 0.865)	Quantitative
	Dried	102	1.97	0.80	28192.05	3.03	0.89	20204.24	0.74	8.98	5599.59	1.00	(-7374, 18573)	(0.898, 1.1)	Quantitative
	Vessel	102	1.94	0.82	28736.13	2.97	0.88	21603.57	0.73	8.99	7488.60	1.03	(-4914, 19891)	(0.935, 1.128)	Quantitative
	Ground	102	0.68	0.88	81495.87	1.05	0.60	71253.52	-1.17	1.36	-4578.30	1.61	(-19966, 10809)	(1.494, 1.734)	Quantitative
	Ignited	102	0.56	0.88	99007.85	0.86	0.52	87527.17	-2.20	1.76	-1506.48	1.73	(-17836, 14823)	(1.606, 1.861)	Quantitative

A.8 Regression plots of pXRF measurements before and after drying samples (n=102) collected from an iron slag heap in Teesside, UK pXRF. OLS regression (black solid line); ideal 1 to 1 relationship (black dashed line); slag matrix (circles); soil matrix (triangles); surface samples (red); subsurface samples (blue).



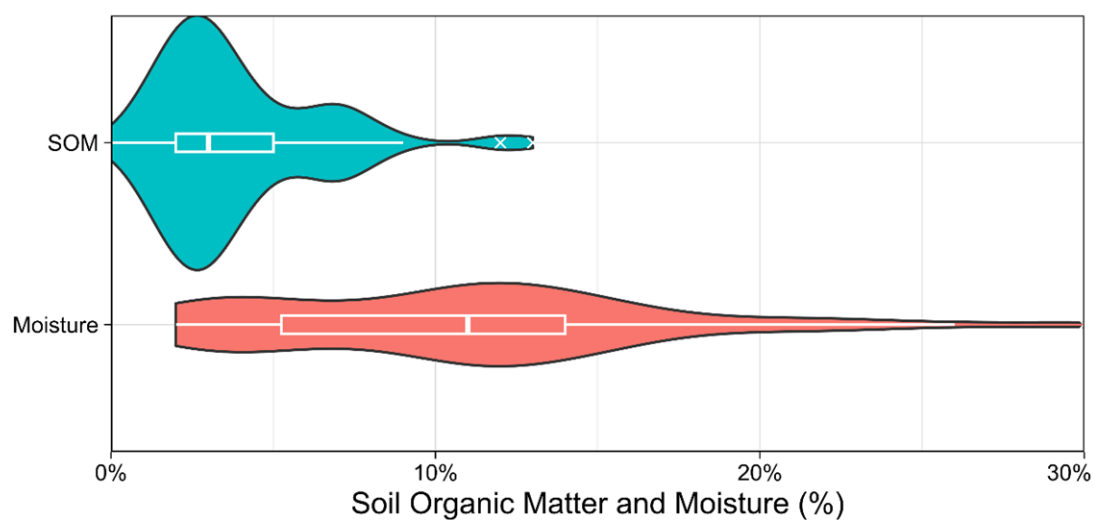
A.9 Regression plots of pXRF measurements before and after combusting samples (n=102) collected from an iron slag heap in Teesside, UK. pXRF. OLS regression (black solid line); ideal 1 to 1 relationship (black dashed line); slag matrix (circles); soil matrix (triangle); surface samples (red); subsurface samples (blue).



A.10 Additional summary statistics of ordinary least squared regression on pXRF measurements before and after drying / igniting of samples (n=102). n is the number of samples above pXRF LOD; residual prediction deviation (RPD); Person's correlation coefficient squared (r^2); ratio of performance to inter-quartile Distance (RPIQ); Lin's concordance correlation coefficient (r_c); mean absolute error (MAE); coefficient of determination (R^2); relative standard deviation (RSD).

Processing Step	element	n	RDD	r^2	RMSE	RPIQ	r_c	MAE	R^2	Intercept	Slope	Intercept 95% CI	Slope 95% CI
Drying	As	57	1.090	0.647	3.2	1.346	0.589	2.5	0.132	2.3	0.611	(0, 4)	(0.446, 0.776)
	Pb	94	2.174	0.859	51.4	1.611	0.867	24.3	0.786	5.5	0.698	(-4, 15)	(0.635, 0.760)
	Sr	105	1.974	0.903	29.4	1.759	0.873	24.2	0.741	-4.8	0.885	(-15, 5)	(0.826, 0.943)
	Cr	106	1.740	0.822	92.4	3.250	0.816	69.1	0.666	20.5	0.738	(-4, 45)	(0.667, 0.809)
	Ni	116	0.900	0.499	12.3	1.065	0.515	10.2	-0.259	5.7	0.663	(-3, 14)	(0.474, 0.851)
	Ti	106	2.266	0.968	544.7	4.284	0.888	435.9	0.803	-8.7	0.773	(-73, 55)	(0.745, 0.802)
	Zn	100	1.966	0.850	41.8	2.859	0.866	32.3	0.738	-2.1	0.844	(-16, 11)	(0.769, 0.919)
	P	110	0.457	0.001	6768.6	0.636	-0.007	5692.7	-3.884	15281.4	-0.016	(11450, 19113)	(-0.200, 0.168)
	K	81	2.113	0.975	2324.3	4.410	0.866	1823.6	0.773	249.9	0.727	(-7, 507)	(0.698, 0.755)
	Mn	106	2.223	0.907	1548.4	3.953	0.884	1171.4	0.796	388.1	0.772	(28, 748)	(0.721, 0.823)
	Ca	105	2.511	0.948	62726.1	5.237	0.906	44887.0	0.840	12114.8	0.765	(2064, 22165)	(0.729, 0.801)
Igniting	Fe	105	1.929	0.939	32102.8	3.473	0.853	26605.2	0.728	-1049.7	0.785	(-6444, 4344)	(0.745, 0.826)
	As	57	0.861	0.550	2.3	0.826	0.509	2.0	-0.420	2.0	0.711	(-2, 6)	(0.392, 1.030)
	Pb	94	6.723	0.995	14.1	7.031	0.988	9.3	0.978	1.0	0.897	(-1, 3)	(0.881, 0.913)
	Sr	105	4.053	0.981	17.5	2.542	0.967	13.7	0.939	9.7	0.891	(4, 15)	(0.867, 0.916)
	Cr	106	7.222	0.984	36.0	14.404	0.990	24.6	0.981	-18.9	1.007	(-36, -1)	(0.982, 1.033)
	Ni	116	2.086	0.794	47.4	2.055	0.871	22.8	0.768	20.8	0.785	(5, 37)	(0.705, 0.866)
	Ti	106	6.104	0.985	193.1	6.038	0.985	114.5	0.973	107.8	0.915	(48, 168)	(0.892, 0.937)
	Zn	100	3.567	0.965	13.2	4.021	0.955	9.0	0.921	5.3	0.849	(2, 9)	(0.815, 0.883)
	P	110	5.965	0.980	3691.0	11.170	0.986	2935.7	0.972	-1346.7	0.985	(-2740, 47)	(0.956, 1.013)
	K	81	5.849	0.982	1345.2	12.469	0.984	820.3	0.970	248.5	0.918	(-234, 731)	(0.883, 0.952)
	Mn	106	13.486	0.997	441.5	18.322	0.997	344.1	0.994	-264.1	0.996	(-405, -123)	(0.985, 1.007)
	Ca	105	13.422	0.997	15653.7	24.247	0.997	12611.0	0.994	-7300.4	0.990	(-11790, -2810)	(0.980, 1.000)
	Fe	105	5.401	0.997	18919.8	10.795	0.982	16897.2	0.965	-3113.3	0.931	(-5192, -1034)	(0.921, 0.940)

A.11 Range and distribution of all moisture and soil organic matter measured by oven drying 105 °C and incineration 450 °C in samples (n=102) collected from an iron slag heap in Teesside.



Appendix B

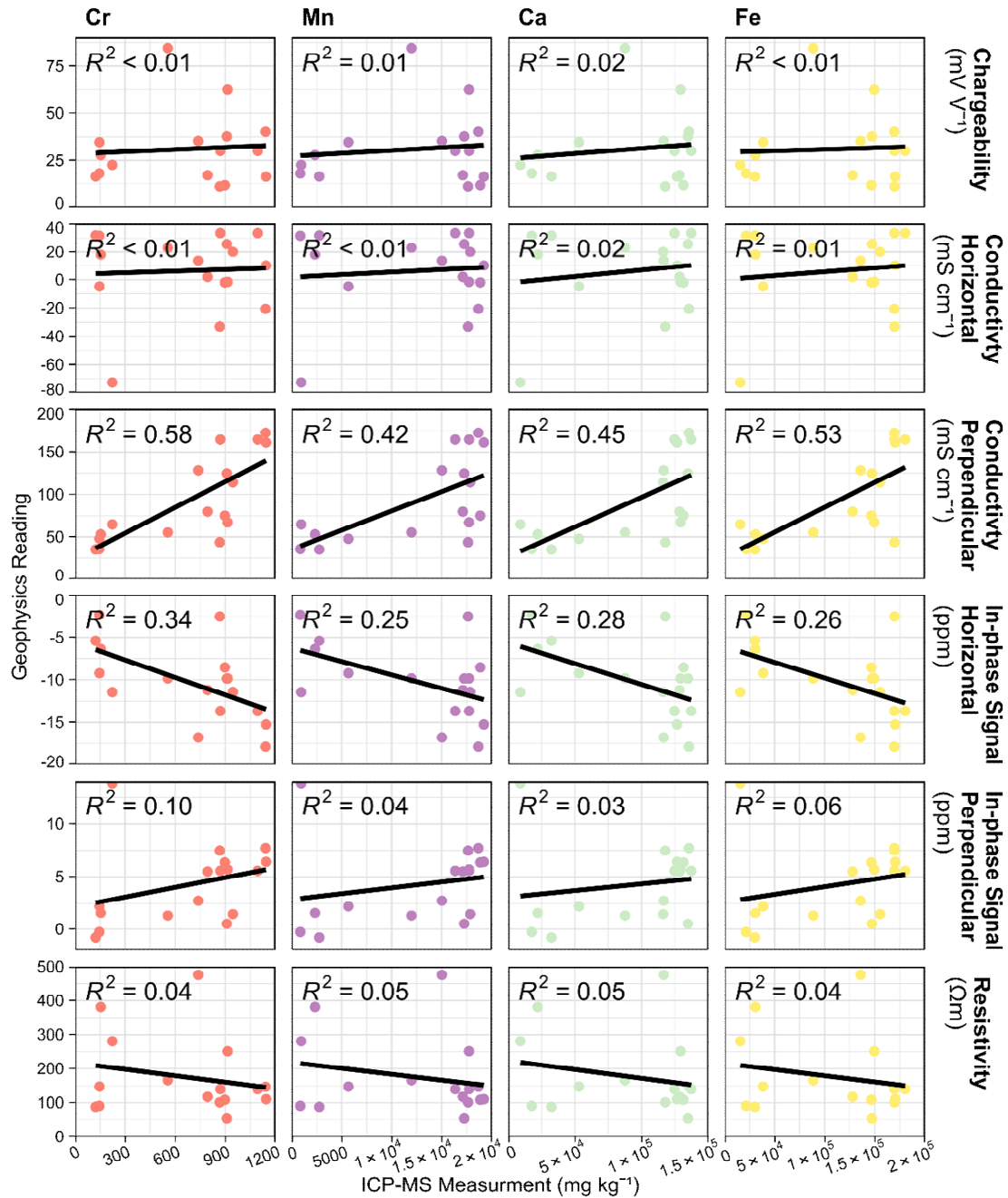
B.1 Limits of detection for ICP-MS and pXRF LODs were provided by instruments based on the factory calibration of pXRF

Element	pXRF (mg/kg)
P	477.00
S	87.00
Cl	43.00
K	194.00
Ca	32.00
Ti	30.00
Cr	2.30
Mn	3.70
Fe	11.00
Co	7.00
Ni	8.00
Cu	3.90
Zn	2.10
As	1.50
Se	1.00
Rb	1.20
Sr	0.80
Zr	1.60
Mo	2.30
Ag	11.00
Cd	13.00
Sn	20.00
Sb	22.00
Ba	4.20
Hg	3.10
Pb	2.40

B.2 Elemental concentrations measured by pXRF (mg kg⁻¹).

Element	Count	Min	Lower quantile	Median	Mean	Upper quantile	Max
Fe	102	16702	49640	94946	92584	128351	208438
Ca	102	4234.4	57312	242545	198879	299596	421808
Cr	99	37.8	123	271	238	325	454
Mn	100	267.2	2613	5928	4960	7025	9203

B.3 Regression of ICP-MS against geophysical measurements. Samples (n=102) collected from an iron slag heap in Teesside, UK, showing Fe Ca, Mn, and Cr concentrations measured by ICP-MS (x-axis) against geophysical measurements (y-axis) of electrical resistivity tomography (chargeability, resistivity) and electromagnetic induction (conductivity and in-phase signal in both horizontal coplanar and perpendicular modes). OLS regression (black solid line).



Appendix C

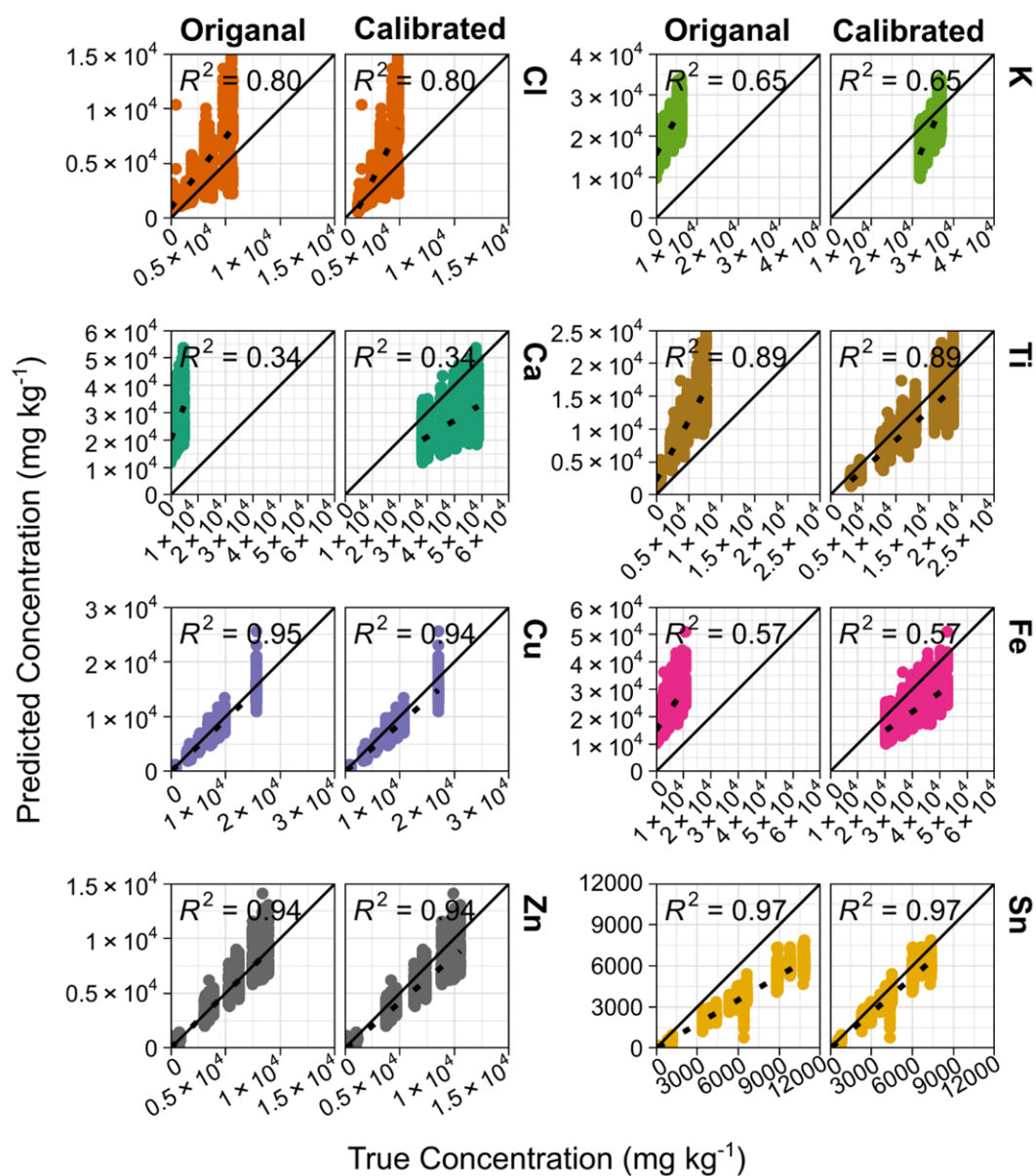
C.1 Limits of detection for ICP-MS and pXRF. LODs were provided by instruments based on the factory calibration of pXRF.

Element	Cl	K	Ca	Ti	Fe	Cu	Zn	Sn
pXRF (mg kg ⁻¹)	43.00	194.00	32.00	30.00	11.00	3.90	2.10	20.00

C.2 Masses of inorganic matrix, soil, and metal compounds added to each synthetic sample.

Percentages				Mass									
SOM (%)	Organic Soil Mass (%)	Total Element Mass (%)	Ignited Soil Mass (%)	Organic Soil Mass (g)	Ignited Soil (g)	Fe (g)	Cu (g)	Zn (g)	Ti (g)	KCL (g)	Sn (g)	Ca (g)	Total Mass (g)
0.0000	0%	0.00%	100%	0.000	150.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	150.000
3.1992	19%	0.00%	81%	27.900	122.100	0.000	0.000	0.000	0.000	0.000	0.000	0.000	150.000
6.3984	37%	0.00%	63%	55.800	94.200	0.000	0.000	0.000	0.000	0.000	0.000	0.000	150.000
9.5976	56%	0.00%	44%	83.700	66.300	0.000	0.000	0.000	0.000	0.000	0.000	0.000	150.000
12.7968	74%	0.00%	26%	111.600	38.400	0.000	0.000	0.000	0.000	0.000	0.000	0.000	150.000
15.9960	93%	0.00%	7%	139.500	10.500	0.000	0.000	0.000	0.000	0.000	0.000	0.000	150.000
0.0000	0%	0.07%	100%	0.000	149.895	0.015	0.015	0.015	0.015	0.015	0.015	0.015	150.000
3.1992	19%	0.07%	81%	27.900	121.995	0.015	0.015	0.015	0.015	0.015	0.015	0.015	150.000
6.3984	37%	0.07%	63%	55.800	94.095	0.015	0.015	0.015	0.015	0.015	0.015	0.015	150.000
9.5976	56%	0.07%	44%	83.700	66.195	0.015	0.015	0.015	0.015	0.015	0.015	0.015	150.000
12.7968	74%	0.07%	26%	111.600	38.295	0.015	0.015	0.015	0.015	0.015	0.015	0.015	150.000
15.9960	93%	0.07%	7%	139.500	10.395	0.015	0.015	0.015	0.015	0.015	0.015	0.015	150.000
0.0000	0%	0.70%	99%	0.000	148.950	0.150	0.150	0.150	0.150	0.150	0.150	0.150	150.000
3.1992	19%	0.70%	81%	27.900	121.050	0.150	0.150	0.150	0.150	0.150	0.150	0.150	150.000
6.3984	37%	0.70%	62%	55.800	93.150	0.150	0.150	0.150	0.150	0.150	0.150	0.150	150.000
9.5976	56%	0.70%	44%	83.700	65.250	0.150	0.150	0.150	0.150	0.150	0.150	0.150	150.000
12.7968	74%	0.70%	25%	111.600	37.350	0.150	0.150	0.150	0.150	0.150	0.150	0.150	150.000
15.9960	93%	0.70%	6%	139.500	9.450	0.150	0.150	0.150	0.150	0.150	0.150	0.150	150.000
0.0000	0%	2.80%	97%	0.000	145.800	0.600	0.600	0.600	0.600	0.600	0.600	0.600	150.000
3.1992	19%	2.80%	79%	27.900	117.900	0.600	0.600	0.600	0.600	0.600	0.600	0.600	150.000
6.3984	37%	2.80%	60%	55.800	90.000	0.600	0.600	0.600	0.600	0.600	0.600	0.600	150.000
9.5976	56%	2.80%	41%	83.700	62.100	0.600	0.600	0.600	0.600	0.600	0.600	0.600	150.000
12.7968	74%	2.80%	23%	111.600	34.200	0.600	0.600	0.600	0.600	0.600	0.600	0.600	150.000
15.9960	93%	2.80%	4%	139.500	6.300	0.600	0.600	0.600	0.600	0.600	0.600	0.600	150.000
0.0000	0%	4.90%	95%	0.000	142.650	1.050	1.050	1.050	1.050	1.050	1.050	1.050	150.000
3.1992	19%	4.90%	77%	27.900	114.750	1.050	1.050	1.050	1.050	1.050	1.050	1.050	150.000
6.3984	37%	4.90%	58%	55.800	86.850	1.050	1.050	1.050	1.050	1.050	1.050	1.050	150.000
9.5976	56%	4.90%	39%	83.700	58.950	1.050	1.050	1.050	1.050	1.050	1.050	1.050	150.000
12.7968	74%	4.90%	21%	111.600	31.050	1.050	1.050	1.050	1.050	1.050	1.050	1.050	150.000
15.9960	93%	4.90%	2%	139.500	3.150	1.050	1.050	1.050	1.050	1.050	1.050	1.050	150.000
0.0000	0%	7.00%	93%	0.000	139.500	1.500	1.500	1.500	1.500	1.500	1.500	1.500	150.000
3.1992	19%	7.00%	74%	27.900	111.600	1.500	1.500	1.500	1.500	1.500	1.500	1.500	150.000
6.3984	37%	7.00%	56%	55.800	83.700	1.500	1.500	1.500	1.500	1.500	1.500	1.500	150.000
9.5976	56%	7.00%	37%	83.700	55.800	1.500	1.500	1.500	1.500	1.500	1.500	1.500	150.000
12.7968	74%	7.00%	19%	111.600	27.900	1.500	1.500	1.500	1.500	1.500	1.500	1.500	150.000
15.9960	93%	7.00%	0%	139.500	0.000	1.500	1.500	1.500	1.500	1.500	1.500	1.500	150.000

C.3 Regression of pXRF measurements and True elemental concentrations before and after true values were calibrated with pXRF measurements to account for background concentrations in topsoil matrix.



C.4 Goodness of fit statistics for regression of pXRF measurements and true elemental concentrations before and after true values were calibrated with pXRF measurements to account for background concentrations in topsoil matrix.

Element	Method	r ²	r _c	RPIQ	RMSE	Intercept	Slope	Intercept 95% CI	Slope 95% CI
Cl	Uncalibrated	0.798	0.700	1.661	2043	935	1.287	(19829, 20457)	(2.368, 2.632)
Cl	Calibrated	0.798	0.606	1.086	2022	-1520	1.988	(1881, 4169)	(0.572, 0.635)
K	Uncalibrated	0.655	0.051	0.213	17589	15503	1.805	(866, 1005)	(1.262, 1.312)
K	Calibrated	0.655	0.320	0.573	5409	-31977	2.180	(-1629, -1412)	(1.95, 2.027)
Ca	Uncalibrated	0.338	0.026	0.128	23539	20143	2.500	(-102, -17)	(0.945, 0.961)
Ca	Calibrated	0.338	0.271	0.979	12785	3025	0.603	(-101, -17)	(0.867, 0.882)
Ti	Uncalibrated	0.887	0.481	0.787	4883	2179	1.834	(14832, 15239)	(1.404, 1.499)
Ti	Calibrated	0.887	0.900	3.508	2231	-674	0.900	(116, 1367)	(0.679, 0.725)
Cu	Uncalibrated	0.951	0.973	7.899	879	-59	0.953	(15348, 15657)	(1.755, 1.856)
Cu	Calibrated	0.951	0.961	6.754	1121	-59	0.874	(-33412, -30543)	(2.12, 2.241)
Fe	Uncalibrated	0.570	0.091	0.268	16884	15035	1.452	(-33, 16)	(0.583, 0.592)
Fe	Calibrated	0.570	0.456	1.117	8375	742	0.702	(-50, 0)	(0.86, 0.873)
Zn	Uncalibrated	0.937	0.968	7.227	821	27	0.990	(2095, 2262)	(1.809, 1.858)
Zn	Calibrated	0.937	0.943	5.788	1196	-87	0.849	(-788, -560)	(0.888, 0.912)
Sn	Uncalibrated	0.970	0.729	2.438	2351	-8	0.587	(-16, 71)	(0.98, 1)
Sn	Calibrated	0.970	0.960	6.027	645	-25	0.866	(-131, -43)	(0.841, 0.857)

C.5 Descriptive statistics of the calibrated true values of all parameters included in this study after calibration of elements using pXRF measurements where moisture and SOM were not present.

parameter	Unit	n	min	Q1	median	mean	Q3	max
Moisture	(%)	2699	0.00	6.36	13.24	13.48	20.75	29.57
SOM	(%)	2699	0.00	3.20	9.47	7.96	12.75	15.98
Ca	(mg kg ⁻¹)	2699	28369	28553	34875	35211	41066	48610
Cl	(mg kg ⁻¹)	2699	1235	1274	2444	2528	3471	4893
Cu	(mg kg ⁻¹)	2699	0	115	3313	3777	7685	17061
Fe	(mg kg ⁻¹)	2699	20363	20673	25975	26409	30029	42629
K	(mg kg ⁻¹)	2699	21775	21831	23482	23599	24930	26936
Sn	(mg kg ⁻¹)	2699	19	94	2322	2425	4062	7353
Ti	(mg kg ⁻¹)	2699	3169	3306	7698	7947	11132	18690
Zn	(mg kg ⁻¹)	2699	134	238	3762	3808	7158	10517

C.6 Descriptive Statistics of the true values of all parameters included in this study prior to calibration.

parameter	Unit	n	min	Q1	median	mean	Q3	max
Moisture	(%)	2699	0	6.36	13.24	13.48	20.75	29.57
SOM	(%)	2699	0	3.20	9.47	7.96	12.75	15.98
Ca	(mg kg ⁻¹)	2699	0	44	1570	1651	3064	4884
Cl	(mg kg ⁻¹)	2699	0	61	1868	1997	3455	5651
Cu	(mg kg ⁻¹)	2699	0	106	3039	3464	7048	15647
Fe	(mg kg ⁻¹)	2699	0	150	2713	2923	4674	10766
K	(mg kg ⁻¹)	2699	0	67	2061	2203	3810	6233
Sn	(mg kg ⁻¹)	2699	0	110	3395	3546	5960	10812
Ti	(mg kg ⁻¹)	2699	0	67	2223	2345	3909	7619
Zn	(mg kg ⁻¹)	2699	0	89	3111	3150	6023	8904

C.7 Regression metrics for SOM percentage recovery graph

Element	r ²	Intercept	Slope	Intercept 95% CI	Slope 95% CI
Cl	0.010	99	-0.461	(95, 103)	(-0.863, -0.059)
K	0.830	100	-1.433	(100, 101)	(-1.489, -1.378)
Ca	0.205	101	-0.647	(100, 102)	(-0.755, -0.539)
Ti	0.008	98	0.238	(96, 101)	(0.02, 0.456)
Fe	0.111	100	-0.520	(99, 101)	(-0.645, -0.395)
Cu	0.028	107	0.650	(103, 110)	(0.293, 1.007)
Zn	0.004	103	-0.201	(101, 106)	(-0.479, 0.077)
Sn	0.174	99	-1.258	(96, 102)	(-1.536, -0.979)

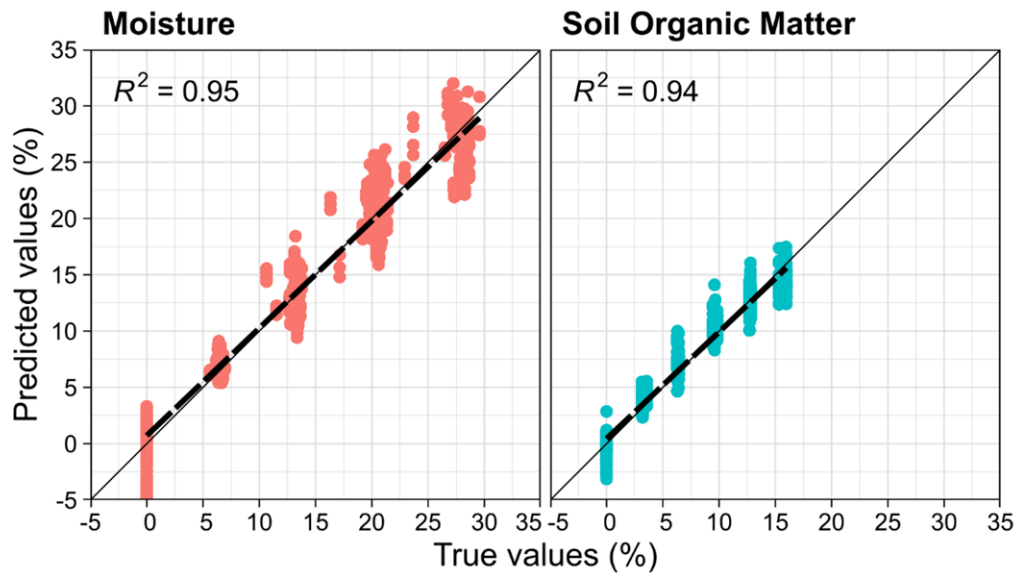
C.8 Infrared results

Step 6 (Figure 4.2) of the data fusion framework required the generation of a PLSR model using the full pre-processed Vis-NIR spectrum to predict moisture and SOM values. Initial models showed validation slopes of 0.995 for both moisture and SOM and high r^2 of 0.952 and 0.945 respectively (IR table and Figure). Due the high performance of the initial model and to avoid the risk of overfitting no further optimisation of the VIS-NIR models were undertaken.

IR Table goodness of fit statistics for the validation of Moisture and soil organic matter Vis-NIR model.

	r^2	r_c	RPIQ	RMSE	Intercept	Slope	Intercept 95% CI	Slope 95% CI
Moisture	0.952	0.976	6.711	2.145	1	0.957	(1, 1)	(0.951, 0.962)
SOM	0.945	0.972	7.506	1.270	0	0.950	(0, 0)	(0.944, 0.956)

IR Figure Regression of true values against the values predicted by Vis-NIR PLSR models for moisture and soil organic matter.



C.9 Pearson's correlation matrix

Step 3 (Figure 4.2) of the data fusion framework generated a Pearson's correlation matrix (Pearson's correlation matrix Figure) to analyse which factors were importance for model generation. Ln(pXRF) and pXRF showed the highest correlations with Ln(True) and True for Cl, Cu Sn Ti, and Zn with r of up to 0.94, 0.98, 1.00, 0.96 and 0.98 respectively. while Ca, Fe and K showed lower correlations of up to 0.59, 0.76, and 0.81 respectively. This corresponded with stronger correlations from moisture for Ca, Fe, and K which showed r values of up to -0.7 -0.57 and -0.34 respectively. Ca and K also showed the highest correlations with SOM with r values of up to -0.21 and -0.27 respectively. All elements showed negative or no correlations with SOM and moisture except for Cl which had r values ranging between 0.12 and 0.21 for the different transformations of moisture indicating moisture increased pXRF measurements of Cl which is corroborated by Figure 4.5. Based on the results in Pearson's correlation matrix Figure models were created to predict Ln(True), and True using combinations of pXRF and Ln(pXRF), Moisture, Ln(Moisture), Som, Ln(SOM), SOM², and SOM³.

Pearson's correlation matrix Figure: Pearson's correlation matrix of pXRF and Ln(pXRF) values for each element against calibrated true metal concentrations, moisture, and SOM values which have been naturally logged, squared, and cubed. Red indicates the size of Pearson's correlation coefficient; significant correlations are indicated by * for p<0.05, ** for p<0.01, * for p<0.001.**

	Ca_Ln_pxt	Ca_pxt	Cl_Ln_pxt	Cl_pxt	Cu_Ln_pxt	Cu_pxt	Fe_Ln_pxt	Fe_pxt	K_Ln_pxt	K_pxt	Sn_Ln_pxt	Sn_pxt	Ti_Ln_pxt	Ti_pxt	Zn_Ln_pxt	Zn_pxt
true_calibrated	0.59**	0.58**	0.92**	0.89**	0.84**	0.96**	0.76**	0.76**	0.79**	0.81**	0.88**	0.99**	0.94**	0.94**	0.9**	0.97**
true_ln	0.59**	0.58**	0.94**	0.88**	0.98**	0.73**	0.76**	0.75**	0.8**	0.81**	1**	0.88**	0.96**	0.92**	0.98**	0.87**
true_sqr	0.58**	0.58**	0.87**	0.88**	0.62**	0.91**	0.75**	0.75**	0.79**	0.81**	0.73**	0.95**	0.87**	0.92**	0.79**	0.94**
true_cub	0.58**	0.58**	0.81**	0.86**	0.46**	0.79**	0.73**	0.74**	0.79**	0.81**	0.63**	0.88**	0.8**	0.88**	0.71**	0.9**
h2o	-0.63**	-0.62**	0.13**	0.2**	-0.07**	-0.11**	-0.54**	-0.52**	-0.34**	-0.3**	-0.02	-0.05*	-0.18**	-0.19**	-0.08**	-0.14**
h2o_ln	-0.69**	-0.7**	0.13**	0.21**	-0.07**	-0.12**	-0.57**	-0.57**	-0.31**	-0.27**	-0.02	-0.04*	-0.2**	-0.22**	-0.09**	-0.15**
h2o_sqr	-0.52**	-0.5**	0.12**	0.19**	-0.06**	-0.09**	-0.47**	-0.44**	-0.31**	-0.27**	-0.02	-0.04*	-0.14**	-0.15**	-0.07**	-0.11**
h2o_cub	-0.45**	-0.43**	0.12**	0.17**	-0.05*	-0.08**	-0.41**	-0.39**	-0.27**	-0.24**	-0.02	-0.04	-0.11**	-0.12**	-0.06**	-0.1**
som	-0.21**	-0.2**	-0.06**	-0.05**	0.02	0.1**	-0.1**	-0.1**	-0.27**	-0.26**	-0.05*	-0.05*	0	0.04*	0.01	0.06**
som_ln	-0.19**	-0.19**	-0.04*	-0.03	0.02	0.07**	-0.07**	-0.07**	-0.23**	-0.23**	-0.04	-0.02	0	0.04	0.02	0.07**
som_sqr	-0.2**	-0.19**	-0.08**	-0.07**	0.01	0.11**	-0.11**	-0.1**	-0.27**	-0.26**	-0.06*	-0.07**	0	0.04*	0.01	0.06**
som_cub	-0.19**	-0.17**	-0.08**	-0.07**	0.01	0.12**	-0.1**	-0.1**	-0.26**	-0.26**	-0.06*	-0.07**	-0.01	0.04*	0	0.05*

C.10 Goodness of fit statistics and model functions for the best combination of variables for each element.

Element	Model Function	rsq	ccc	rpiq	rmse
Ca	True = f(Ln(pXRF))	0.345	0.513	2.178	5745
Ca	True = f(Ln(pXRF) × Ln(H2O))	0.668	0.801	3.059	4091
Ca	True = f(Ln(pXRF) × SOM)	0.354	0.523	2.193	5705
Ca	True = f(Ln(pXRF) × Ln(H2O) × SOM)	0.712	0.832	3.285	3809
Ca	Ln(True) = f(Ln(pXRF))	0.345	0.505	2.171	5764
Ca	Ln(True) = f(Ln(pXRF) × Ln(H2O))	0.672	0.801	3.073	4072
Ca	Ln(True) = f(Ln(pXRF) × SOM)	0.352	0.515	2.184	5729
Ca	Ln(True) = f(Ln(pXRF) × Ln(H2O) × SOM)	0.731	0.839	3.388	3694
Cl	True = f(Ln(pXRF))	0.839	0.913	4.359	504
Cl	True = f(Ln(pXRF) × Ln(H2O))	0.854	0.921	4.570	481
Cl	True = f(pXRF × SOM)	0.805	0.892	3.955	556
Cl	True = f(Ln(pXRF) × Ln(H2O) × Ln(SOM))	0.860	0.925	4.675	470
Cl	Ln(True) = f(Ln(pXRF))	0.843	0.916	4.397	500
Cl	Ln(True) = f(Ln(pXRF) × Ln(H2O))	0.880	0.935	5.028	437
Cl	Ln(True) = f(Ln(pXRF) × SOM)	0.851	0.921	4.517	486
Cl	Ln(True) = f(Ln(pXRF) × Ln(H2O) × SOM)	0.888	0.939	5.206	422
Cu	True = f(pXRF)	0.951	0.975	8.130	931
Cu	True = f(pXRF × Ln(H2O))	0.965	0.982	9.643	785
Cu	True = f(pXRF × SOM ²)	0.951	0.975	8.179	926
Cu	True = f(pXRF × Ln(H2O) × SOM²)	0.966	0.983	9.739	777
Cu	Ln(True) = f(Ln(pXRF))	0.849	0.721	1.523	4970
Cu	Ln(True) = f(Ln(pXRF) × H2O)	0.901	0.753	1.649	4591
Cu	Ln(True) = f(Ln(pXRF) × H2O × SOM)	0.910	0.765	1.713	4418
Cu	Ln(True) = f(Ln(pXRF) × SOM ³)	0.860	0.736	1.597	4741
Fe	True = f(Ln(pXRF))	0.578	0.732	2.223	4209
Fe	True = f(Ln(pXRF) × Ln(H2O))	0.866	0.928	3.952	2367
Fe	True = f(Ln(pXRF) × SOM)	0.579	0.734	2.227	4200
Fe	True = f(Ln(pXRF) × Ln(H2O) × SOM)	0.872	0.932	4.037	2317
Fe	Ln(True) = f(Ln(pXRF))	0.579	0.727	2.220	4214
Fe	Ln(True) = f(Ln(pXRF) × Ln(H2O))	0.883	0.936	4.211	2222
Fe	Ln(True) = f(Ln(pXRF) × Ln(H2O) × SOM)	0.888	0.939	4.310	2171
Fe	Ln(True) = f(Ln(pXRF) × Ln(SOM))	0.581	0.728	2.224	4207
K	True = f(pXRF)	0.659	0.794	2.989	1037
K	True = f(pXRF × H2O)	0.726	0.841	3.337	929
K	True = f(pXRF × SOM)	0.719	0.836	3.292	942
K	True = f(pXRF × H2O × SOM)	0.796	0.886	3.865	802
K	Ln(True) = f(pXRF)	0.660	0.794	2.996	1035
K	Ln(True) = f(pXRF × H2O)	0.722	0.839	3.312	936
K	Ln(True) = f(pXRF × SOM)	0.722	0.837	3.311	936
K	Ln(True) = f(pXRF × H2O × SOM)	0.792	0.885	3.828	810
Sn	True = f(pXRF)	0.971	0.985	9.448	411
Sn	True = f(pXRF × H2O)	0.974	0.987	9.933	391
Sn	True = f(pXRF × SOM)	0.974	0.987	10.062	386
Sn	True = f(pXRF × H2O × SOM)	0.977	0.988	10.658	365
Sn	Ln(True) = f(Ln(pXRF))	0.973	0.986	9.692	401
Sn	Ln(True) = f(Ln(pXRF) × H2O)	0.978	0.989	10.831	359
Sn	Ln(True) = f(Ln(pXRF) × SOM)	0.976	0.988	10.381	375
Sn	Ln(True) = f(Ln(pXRF) × H2O × SOM)	0.982	0.990	11.748	331
Ti	True = f(pXRF)	0.888	0.941	4.681	1672
Ti	True = f(pXRF × Ln(H2O))	0.936	0.967	6.210	1260
Ti	True = f(pXRF × SOM ³)	0.889	0.941	4.699	1665
Ti	True = f(pXRF × Ln(H2O) × SOM ³)	0.937	0.968	6.261	1250
Ti	Ln(True) = f(Ln(pXRF))	0.901	0.948	4.949	1581
Ti	Ln(True) = f(Ln(pXRF) × Ln(H2O))	0.965	0.982	8.314	941
Ti	Ln(True) = f(Ln(pXRF) × Ln(H2O) × Ln(SOM))	0.965	0.982	8.307	942
Ti	Ln(True) = f(Ln(pXRF) × SOM ³)	0.900	0.948	4.938	1585
Zn	True = f(pXRF)	0.937	0.968	7.417	933
Zn	True = f(pXRF × Ln(H2O))	0.961	0.980	9.438	733
Zn	True = f(pXRF × Ln(SOM))	0.938	0.968	7.453	928
Zn	True = f(pXRF × Ln(H2O) × Ln(SOM))	0.962	0.981	9.531	726
Zn	Ln(True) = f(Ln(pXRF))	0.943	0.971	7.636	906
Zn	Ln(True) = f(Ln(pXRF) × Ln(H2O))	0.987	0.993	16.123	429
Zn	Ln(True) = f(Ln(pXRF) × Ln(SOM))	0.937	0.968	7.247	955
Zn	Ln(True) = f(Ln(pXRF) × Ln(H2O) × Ln(SOM))	0.981	0.991	13.512	512

C.11 A comparison of this study's goodness of fit statistics against those of previous data fusion studies

While several studies have developed data fusion methods for pXRF and IR only three measured elements included in the present study. S.M. O'Rourke et al (2014) [21] who measured Ca, Cu, Fe, K, Sn, Ti, and Zn; G. Shrestha (2022) [26] who measured Cu and Zn and Chen et al (2021) [12] who measured Cu, Fe, Zn and inspired this studies data fusion framework. While CI has not had a data fusion method developed before. For a full table of all IR and pXRF data fusion models developed up August 2023 please see this studies CORD repository (DOI code hear)

A large number of preprocessing methods have been tested during data fusion testing including the internal Compton normalisation (ICN) used by instruments when they provide elemental predictions; Multiplicative scatter correction (MSC); 1st order Savitzky–Golay (SG1); absorbance transformation (AT) to convert reflectance to absorbance by $1/R$ where R is the reflectance; and finally, no preprocessing methods (NA). Models that were used before or after data fusion include: Partial least square regression (PLSR); Partial least square-support vector machine (PLS-SVG); Cubist; and the internal ordinary least square (IOLS) used to generate the elemental concentrations provided by the instrument. Fusion methods include Granger-Ramanathan averaging (GRA); Bayesian model averaging (BMA); Spectral concatenation (SC); the data fusion framework used in our study (Frwk) and no data fusion (NA) for the single instrument models.

The instruments used by different studies include Mid-infrared Spectroscopy (MIR); visible-near infrared spectroscopy (Vis-NIR); portable X-ray fluorescence spectroscopy (pXRF) and gravimetric (G) measurement of moisture and soil organic matter at 105 and 405 °C respectively.

Element	Instruments	Preprocessing	Model	Fusion	mean (mg kg ⁻¹)	r ²	r _c	RPIQ	Author
A)									
Ca	MIR	AT	Cubist	NA	1	0.960		0.42	S.M. O'Rourke et al (2014)
Ca	MIR + pXRF	AT (NA)	Cubist	GRA	1	0.970		0.76	S.M. O'Rourke et al (2014)
Ca	pXRF	NA	Cubist	NA	1	0.930		0.42	S.M. O'Rourke et al (2014)
Ca	pXRF	ICN	IOLS	NA	1	0.180		0.23	S.M. O'Rourke et al (2014)
Ca	Vis-NIR	AT	Cubist	NA	1	-0.01		0.06	S.M. O'Rourke et al (2014)
Ca	pXRF	ICN	IOLS	NA	35211	0.338	0.271	0.95	This Study
Ca	pXRF + G	ICN (NA)	IOLS	Frwk	35211	0.714	0.831	3.22	This Study
Ca	Vis-NIR + pXRF	MCN, SG1 (ICN)	PLSR (IOLS)	Frwk	35211	0.646	0.791	3.07	This Study
B)									
Cl	pXRF	ICN	IOLS	NA	2528	0.792	0.608	1.10	This Study
Cl	pXRF + G	ICN (NA)	IOLS	Frwk	2528	0.877	0.933	4.95	This Study
Cl	Vis-NIR + pXRF	MCN, SG1 (ICN)	PLSR (IOLS)	Frwk	2528	0.876	0.933	4.61	This Study
C)									
Cu	MIR	SG1	PLSR	NA	14	0.340	0.560	1.59	G. Shrestha (2022)
Cu	MIR	SG1	PLS-SVM	NA	14	0.440	0.640	1.76	G. Shrestha (2022)
Cu	MIR + pXRF	SG1 (NA)	PLSR	SC	14	0.750	0.860	2.45	G. Shrestha (2022)
Cu	MIR + pXRF	SG1 (NA)	PLSR	GRA	14	0.800	0.890	3.03	G. Shrestha (2022)
Cu	MIR + pXRF	SG1 (NA)	PLSR	BMA	14	0.800	0.890	3.03	G. Shrestha (2022)
Cu	MIR + pXRF	SG1 (NA)	PLS-SVM	SC	14	0.970	0.980	6.38	G. Shrestha (2022)
Cu	MIR + pXRF	SG1 (NA)	PLS-SVM	GRA	14	0.930	0.960	4.93	G. Shrestha (2022)
Cu	MIR + pXRF	SG1 (NA)	PLS-SVM	BMA	14	0.930	0.960	4.92	G. Shrestha (2022)

Cu	pXRF	NA	PLSR	NA	14	0.800	0.890	2.89	G. Shrestha (2022)
Cu	pXRF	NA	PLS-SVM	NA	14	0.930	0.970	5.29	G. Shrestha (2022)
Cu	Vis-NIR	AT, SG1	PLSR	NA	14	0.620	0.770	2.17	G. Shrestha (2022)
Cu	Vis-NIR	AT, SG1	PLS-SVM	NA	14	0.690	0.820	2.39	G. Shrestha (2022)
Cu	Vis-NIR + MIR	AT, SG1 (SG1)	PLSR	SC	14	0.510	0.710	1.68	G. Shrestha (2022)
Cu	Vis-NIR + MIR	AT, SG1 (SG1)	PLSR	GRA	14	0.630	0.780	2.23	G. Shrestha (2022)
Cu	Vis-NIR + MIR	AT, SG1 (SG1)	PLSR	BMA	14	0.630	0.770	2.22	G. Shrestha (2022)
Cu	Vis-NIR + MIR	AT, SG1 (SG1)	PLS-SVM	SC	14	0.760	0.870	2.71	G. Shrestha (2022)
Cu	Vis-NIR + MIR	AT, SG1 (SG1)	PLS-SVM	GRA	14	0.700	0.830	2.47	G. Shrestha (2022)
Cu	Vis-NIR + MIR	AT, SG1 (SG1)	PLS-SVM	BMA	14	0.700	0.820	2.45	G. Shrestha (2022)
Cu	Vis-NIR + MIR + pXRF	AT, SG1 (SG1) (NA)	PLSR	SC	14	0.750	0.860	2.38	G. Shrestha (2022)
Cu	Vis-NIR + MIR + pXRF	AT, SG1 (SG1) (NA)	PLSR	GRA	14	0.830	0.910	3.28	G. Shrestha (2022)
Cu	Vis-NIR + MIR + pXRF	AT, SG1 (SG1) (NA)	PLSR	BMA	14	0.830	0.910	3.28	G. Shrestha (2022)
Cu	Vis-NIR + MIR + pXRF	AT, SG1 (SG1) (NA)	PLS-SVM	SC	14	0.750	0.870	2.64	G. Shrestha (2022)
Cu	Vis-NIR + MIR + pXRF	AT, SG1 (SG1) (NA)	PLS-SVM	GRA	14	0.930	0.960	5.03	G. Shrestha (2022)
Cu	Vis-NIR + MIR + pXRF	AT, SG1 (SG1) (NA)	PLS-SVM	BMA	14	0.930	0.960	4.97	G. Shrestha (2022)
Cu	Vis-NIR + pXRF	AT, SG1 (NA)	PLSR	SC	14	0.820	0.910	3.15	G. Shrestha (2022)
Cu	Vis-NIR + pXRF	AT, SG1 (NA)	PLSR	GRA	14	0.830	0.910	3.28	G. Shrestha (2022)
Cu	Vis-NIR + pXRF	AT, SG1 (NA)	PLSR	BMA	14	0.830	0.910	3.28	G. Shrestha (2022)
Cu	Vis-NIR + pXRF	AT, SG1 (NA)	PLS-SVM	SC	14	0.960	0.980	6.81	G. Shrestha (2022)
Cu	Vis-NIR + pXRF	AT, SG1 (NA)	PLS-SVM	GRA	14	0.930	0.960	5.03	G. Shrestha (2022)
Cu	Vis-NIR + pXRF	AT, SG1 (NA)	PLS-SVM	BMA	14	0.930	0.960	4.97	G. Shrestha (2022)
Cu	pXRF	ICN	IOLS	NA	14	0.68	0.46	0.84	G. Shrestha (2022)

Cu	MIR	AT	Cubist	NA	22	0.070		0.41	S.M. O'Rourke et al (2014)
Cu	MIR + pXRF	AT (NA)	Cubist	GRA	22	0.830		2.47	S.M. O'Rourke et al (2014)
Cu	pXRF	NA	Cubist	NA	22	0.820		1.05	S.M. O'Rourke et al (2014)
Cu	pXRF	ICN	IOLS	NA	22	0.470		1.11	S.M. O'Rourke et al (2014)
Cu	Vis-NIR	AT	Cubist	NA	22	0.000		0.43	S.M. O'Rourke et al (2014)
Cu	pXRF	ICN	IOLS	NA	30	0.046			Chen et al (2021)
Cu	pXRF + G	ICN (NA)	IOLS (NA)	Frwk	30	0.368			Chen et al (2021)
Cu	pXRF	ICN	IOLS	NA	3777	0.952	0.962	6.74	This Study
Cu	pXRF + G	ICN (NA)	IOLS	Frwk	3777	0.968	0.984	9.97	This Study
Cu	Vis-NIR + pXRF	MCN, SG1 (ICN)	PLSR (IOLS)	Frwk	3777	0.967	0.983	10.17	This Study
D)									
Fe	MIR	AT	Cubist	NA	2	0.650		0.73	S.M. O'Rourke et al (2014)
Fe	MIR + pXRF	AT (NA)	Cubist	GRA	2	0.750		0.86	S.M. O'Rourke et al (2014)
Fe	pXRF	NA	Cubist	NA	2	0.630		0.63	S.M. O'Rourke et al (2014)
Fe	pXRF	ICN	IOLS	NA	2	0.830		2.93	S.M. O'Rourke et al (2014)
Fe	Vis-NIR	AT	Cubist	NA	2	0.590		0.67	S.M. O'Rourke et al (2014)
Fe	pXRF	ICN	IOLS	NA	26409	0.566	0.454	1.11	This Study
Fe	pXRF + G	ICN (NA)	IOLS	Frwk	26409	0.882	0.936	4.19	This Study
Fe	Vis-NIR + pXRF	MCN, SG1 (ICN)	PLSR (IOLS)	Frwk	26409	0.862	0.925	3.95	This Study
Fe	pXRF	ICN	IOLS	NA	40	0.572			Chen et al (2021)
Fe	pXRF + G	ICN (NA)	IOLS (NA)	Frwk	40	0.615			Chen et al (2021)

E)									
K	MIR	AT	Cubist	NA	1	0.810		1.52	S.M. O'Rourke et al (2014)
K	MIR + pXRF	AT (NA)	Cubist	GRA	1	0.800		1.27	S.M. O'Rourke et al (2014)
K	pXRF	NA	Cubist	NA	1	0.500		0.75	S.M. O'Rourke et al (2014)
K	pXRF	ICN	IOLS	NA	1	0.520		0.56	S.M. O'Rourke et al (2014)
K	Vis-NIR	AT	Cubist	NA	1	0.390		0.70	S.M. O'Rourke et al (2014)
K	pXRF	ICN	IOLS	NA	23599	0.645	0.314	0.57	This Study
K	pXRF + G	ICN (NA)	IOLS	Frwk	23599	0.791	0.883	3.82	This Study
K	Vis-NIR + pXRF	MCN, SG1 (ICN)	PLSR (IOLS)	Frwk	23599	0.783	0.877	3.50	This Study
F)									
Sn	MIR	AT	Cubist	NA	2	0.030		0.20	S.M. O'Rourke et al (2014)
Sn	MIR + pXRF	AT (NA)	Cubist	GRA	2	0.110		0.25	S.M. O'Rourke et al (2014)
Sn	pXRF	NA	Cubist	NA	2	0.100		0.22	S.M. O'Rourke et al (2014)
Sn	Vis-NIR	AT	Cubist	NA	2	0.160		0.25	S.M. O'Rourke et al (2014)
Sn	pXRF	ICN	IOLS	NA	2425	0.969	0.960	6.00	This Study
Sn	pXRF + G	ICN (NA)	IOLS	Frwk	2425	0.969	0.984	9.12	This Study
Sn	Vis-NIR + pXRF	MCN, SG1 (ICN)	PLSR (IOLS)	Frwk	2425	0.969	0.984	9.12	This Study
G)									
Ti	MIR	AT	Cubist	NA	2340	0.580		0.86	S.M. O'Rourke et al (2014)
Ti	MIR + pXRF	AT (NA)	Cubist	GRA	2340	0.730		1.11	S.M. O'Rourke et al (2014)

Ti	pXRF	NA	Cubist	NA	2340	0.720		1.08	S.M. O'Rourke et al (2014)
Ti	pXRF	ICN	IOLS	NA	2340	0.630		1.59	S.M. O'Rourke et al (2014)
Ti	Vis-NIR	AT	Cubist	NA	2340	0.430		0.75	S.M. O'Rourke et al (2014)
Ti	pXRF	ICN	IOLS	NA	7947	0.885	0.899	3.45	This Study
Ti	pXRF + G	ICN (NA)	IOLS	Frwk	7947	0.967	0.983	8.48	This Study
Ti	Vis-NIR + pXRF	MCN, SG1 (ICN)	PLSR (IOLS)	Frwk	7947	0.965	0.982	8.19	This Study
H)									
Zn	MIR	SG1	PLSR	NA	49	0.220	0.460	1.16	G. Shrestha (2022)
Zn	MIR	SG1	PLS-SVM	NA	49	0.380	0.600	1.47	G. Shrestha (2022)
Zn	MIR + pXRF	SG1 (NA)	PLSR	SC	49	0.870	0.930	3.20	G. Shrestha (2022)
Zn	MIR + pXRF	SG1 (NA)	PLSR	GRA	49	0.900	0.950	3.74	G. Shrestha (2022)
Zn	MIR + pXRF	SG1 (NA)	PLSR	BMA	49	0.900	0.950	3.74	G. Shrestha (2022)
Zn	MIR + pXRF	SG1 (NA)	PLS-SVM	SC	49	0.950	0.980	5.59	G. Shrestha (2022)
Zn	MIR + pXRF	SG1 (NA)	PLS-SVM	GRA	49	0.950	0.970	5.37	G. Shrestha (2022)
Zn	MIR + pXRF	SG1 (NA)	PLS-SVM	BMA	49	0.950	0.970	5.35	G. Shrestha (2022)
Zn	pXRF	NA	PLSR	NA	49	0.900	0.940	3.52	G. Shrestha (2022)
Zn	pXRF	NA	PLS-SVM	NA	49	0.960	0.980	5.72	G. Shrestha (2022)
Zn	Vis-NIR	AT, SG1	PLSR	NA	49	0.420	0.590	1.51	G. Shrestha (2022)
Zn	Vis-NIR	AT, SG1	PLS-SVM	NA	49	0.560	0.720	1.77	G. Shrestha (2022)
Zn	Vis-NIR + MIR	AT, SG1 (SG1)	PLSR	SC	49	0.380	0.610	1.36	G. Shrestha (2022)
Zn	Vis-NIR + MIR	AT, SG1 (SG1)	PLSR	GRA	49	0.450	0.620	1.63	G. Shrestha (2022)
Zn	Vis-NIR + MIR	AT, SG1 (SG1)	PLSR	BMA	49	0.450	0.610	1.62	G. Shrestha (2022)
Zn	Vis-NIR + MIR	AT, SG1 (SG1)	PLS-SVM	SC	49	0.640	0.790	1.94	G. Shrestha (2022)
Zn	Vis-NIR + MIR	AT, SG1 (SG1)	PLS-SVM	GRA	49	0.580	0.740	1.87	G. Shrestha (2022)
Zn	Vis-NIR + MIR	AT, SG1 (SG1)	PLS-SVM	BMA	49	0.580	0.730	1.86	G. Shrestha (2022)

Zn	Vis-NIR + MIR + pXRF	AT, SG1 (SG1) (NA)	PLSR	SC	49	0.860	0.920	3.13	G. Shrestha (2022)
Zn	Vis-NIR + MIR + pXRF	AT, SG1 (SG1) (NA)	PLSR	GRA	49	0.920	0.960	4.35	G. Shrestha (2022)
Zn	Vis-NIR + MIR + pXRF	AT, SG1 (SG1) (NA)	PLSR	BMA	49	0.920	0.960	4.32	G. Shrestha (2022)
Zn	Vis-NIR + MIR + pXRF	AT, SG1 (SG1) (NA)	PLS-SVM	SC	49	0.670	0.810	2.06	G. Shrestha (2022)
Zn	Vis-NIR + MIR + pXRF	AT, SG1 (SG1) (NA)	PLS-SVM	GRA	49	0.960	0.980	5.85	G. Shrestha (2022)
Zn	Vis-NIR + MIR + pXRF	AT, SG1 (SG1) (NA)	PLS-SVM	BMA	49	0.960	0.980	5.82	G. Shrestha (2022)
Zn	Vis-NIR + pXRF	AT, SG1 (NA)	PLSR	SC	49	0.910	0.950	3.88	G. Shrestha (2022)
Zn	Vis-NIR + pXRF	AT, SG1 (NA)	PLSR	GRA	49	0.920	0.960	4.31	G. Shrestha (2022)
Zn	Vis-NIR + pXRF	AT, SG1 (NA)	PLSR	BMA	49	0.920	0.960	4.31	G. Shrestha (2022)
Zn	Vis-NIR + pXRF	AT, SG1 (NA)	PLS-SVM	SC	49	0.960	0.980	6.15	G. Shrestha (2022)
Zn	Vis-NIR + pXRF	AT, SG1 (NA)	PLS-SVM	GRA	49	0.960	0.980	5.81	G. Shrestha (2022)
Zn	Vis-NIR + pXRF	AT, SG1 (NA)	PLS-SVM	BMA	49	0.960	0.980	5.81	G. Shrestha (2022)
Zn	pXRF	ICN	IOLS	NA	49	0.810	0.580	0.99	G. Shrestha (2022)
Zn	MIR	AT	Cubist	NA	76	0.080		0.37	S.M. O'Rourke et al (2014)
Zn	MIR + pXRF	AT (NA)	Cubist	GRA	76	0.330		0.60	S.M. O'Rourke et al (2014)
Zn	pXRF	NA	Cubist	NA	76	0.030		0.16	S.M. O'Rourke et al (2014)
Zn	pXRF	ICN	IOLS	NA	76	0.760		2.30	S.M. O'Rourke et al (2014)
Zn	Vis-NIR	AT	Cubist	NA	76	0.300		0.58	S.M. O'Rourke et al (2014)
Zn	pXRF	ICN	IOLS	NA	194	0.876			Chen et al (2021)
Zn	pXRF + G	ICN (NA)	IOLS (NA)	Frwk	194	0.972			Chen et al (2021)

Zn	pXRF	ICN	IOLS	NA	3808	0.936	0.943	5.76	This Study
Zn	pXRF + G	ICN (NA)	IOLS	Frwk	3808	0.989	0.994	17.33	This Study
Zn	Vis-NIR + pXRF	MCN, SG1 (ICN)	PLSR (IOLS)	Frwk	3808	0.989	0.994	17.15	This Study

Appendix D

D.1 Predicted vs actual plots for the lower range ($\text{Fe} < 5000 \text{ mg kg}^{-1}$) of a synthetic sample set ($n=47$) containing sand, Fe_2O_3 and FeSO_4 . true values were regressed against a) elemental Fe prediction by pXRF; b) ratio Fe_2O_3 and FeSO_4 predicted by Vis-NIR; c) Fe_2O_3 and FeSO_4 predictions by just Vis-NIR, partial fusion of Vis-NIR ratio and true elemental Fe, and full fusion of Vis-NIR ratio and pXRF elemental Fe.

