

Rapid, Nondestructive Total Elemental Analysis of Vertisol Soils using Portable X-ray Fluorescence

Timothy I. McLaren*
Christopher N. Guppy
Matthew K. Tighe

School of Environ. and Rural Science
 Univ. of New England
 Armidale, NSW 2351, Australia

Nicola Forster
Peter Grave

Dep. of Archaeology and
 Palaeoanthropology, Archaeomaterials
 Science Hub
 Univ. of New England
 NSW 2351, Australia

Leanne M. Lisle

School of Environ. and Rural Science
 Univ. of New England
 Armidale, NSW 2351, Australia

John W. Bennett

Australian Nuclear Science and
 Technology Organisation (ANSTO)
 Locked Bag 2001
 Kirrawee DC
 Lucas Heights
 NSW 2232, Australia

Portable X-ray fluorescence (PXRF) spectrometry can provide rapid and nondestructive analyses of agriculturally important elements in soil. To assess the applicability of PXRF for total element analysis of Vertisols, 20 soils were collected across northern New South Wales (NSW), Australia. Comparison of PXRF results were made with conventional standard microwave aqua regia (AR) digestion followed by inductively couple plasma optical emission spectroscopy (ICP-OES) analysis, laboratory X-ray fluorescence (LXRF), and neutron activation analysis (NAA). Strong linear correlations were found for As, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Pb, Si, Ti, and Zn. We demonstrate that nondestructive analyses for total soil element determination, particularly Ca, Fe, Mn, and P, should now allow rapid elucidation of important chemical processes in Vertisols that are commonly only available following rigorous sample preparation and digestion. The integrated and robust character of PXRF instrumentation, requiring minimal or no dedicated laboratory infrastructure, is readily adaptable to a wide range of analytical situations.

Abbreviations: AR, aqua regia; ICP-OES, inductively couple plasma optical emission spectroscopy; LXRF, laboratory X-ray fluorescence; NAA, neutron activation analysis; NIST, National Institute of Standards Technology; NSW, New South Wales; PXRF, portable X-ray fluorescence; USEPA, United States Environmental Protection Agency; XRF, X-ray fluorescence.

Total soil element concentrations are conventionally measured using acid digestion followed by various forms of spectroscopy (Rayment and Lyons, 2011). Standard digestion procedures are protracted and laboratory intensive (sample drying, sieving, and homogenization; followed by acid digestion). Laboratory based XRF, requires solid-state preparation through sample pelletisation with various binding agents (e.g., Lithium tetra- and metaborate) (Berrow and Ure, 1981; Rayment and Lyons, 2011; Tighe et al., 2004). Laboratories restricted to acid digestion for total element determination typically use AR and/or hydrofluoric (HF) acid digestion techniques before spectroscopy analysis (Chen and Ma, 2001; Falciani et al., 2000; Tighe et al., 2004). Soil digestion, which involves single or combinations of strong acids such as nitric (HNO₃), hydrochloric (HCl), or HF acid, is limited by the least acid-soluble compound (Chen and Ma, 1998; Tighe et al., 2004). Many elements associated with silicate matrices are either indigestible or mostly insoluble by most acids (Tighe et al., 2004). In comparison, X-rays generated by PXRF, interact with individual elements throughout the bulk matrix (Melquiades and Appoloni, 2004; Potts et al., 1995). Recent advances in PXRF technology, offer the potential for rapid, in situ and nondestructive analysis for total element determination (Kilbride et al., 2006; Potts et al., 2005). The purpose of this paper is to critically evaluate this type of PXRF application.

Soil Sci. Soc. Am. J. 76:1436–1445

doi:10.2136/sssaj2011.0354

Received 11 Oct. 2011.

*Corresponding author (tmclare3@une.edu.au).

© Soil Science Society of America, 5585 Guilford Rd., Madison WI 53711 USA

All rights reserved. No part of this periodical may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Permission for printing and for reprinting the material contained herein has been obtained by the publisher.

Portable XRF measures the energy levels of X-rays emitted from elements when irradiated with an excitation source (e.g., X-ray tube) (Kilbride et al., 2006). Each element has a unique and characteristic binding energy that is associated with the element's electron configuration. When irradiated with X-rays of greater energy than the absorption edge of the element, an inner shell electron is ejected and the space filled with an electron from an outer shell (Piorek, 1997). This energy, emitted in the form of X-rays, is a unique elemental characteristic for detection (Kalnicky and Singhvi, 2001; Piorek, 1997). Using this photoelectric effect in PXRF analyzers, researchers across many disciplines are able to perform simultaneous multi-element analyses on a variety of matrices and compounds (Forster et al., 2011; Potts et al., 2005).

Hou et al. (2004) reviewed the common applications of PXRF across several disciplines, including contaminated soils, solutions, air quality determination, archeology, paint, and geology. Routine PXRF elemental validation in agricultural soils has not yet been accomplished. Soil PXRF analysis publications are usually focused on heavy elements in contaminated sites (Argyaki et al., 1997; Kilbride et al., 2006; Radu and Diamond, 2009). There has also been a trend in soil PXRF analysis to use "fundamental parameters" to quantify soil elements (Argyaki et al., 1997; Hou et al., 2004; Omote et al., 1995; Radu and Diamond, 2009). Fundamental parameters typically use algorithms obtained from pre-established standard curves, using a mixture of single elements in a SiO₂ matrix (Cameron, 2010; Kalnicky and Singhvi, 2001). Further calibration of the standard curve involve using de-convolution matrix co-efficient, and normalization to the tube Compton scatter peak (Kalnicky and Singhvi, 2001; Kenna et al., 2011). Caution is required when using fundamental parameters for soil analysis, as over- or underestimation of actual total soil concentrations can readily occur due to spectral interferences in different matrices (Kenna et al., 2011; Kilbride et al., 2006).

There are several spectral interferences involved with PXRF analysis that can affect the elemental X-ray emissions (raw counts) (Kawahara and Shoji, 2006; Kilbride et al., 2006; USEPA, 2007). Sources of these spectral interferences or related factors include scanning time (count time), air attenuation, absorption energy overlaps between element electron shells (e.g., As and Pb) PXRF detector resolution, sample homogeneity, moisture content, and polyethylene film thickness (Johnson et al., 1995; Kalnicky and Singhvi, 2001; Kilbride et al., 2006; USEPA, 2007). The aim of this study was to evaluate the effectiveness of PXRF for total soil elemental determination in agricultural soils, particularly elements below Ca in atomic number. Factory settings for rapid "point and shoot" analysis, and optimized settings that incorporate features designed to reduce spectral interference, were also evaluated.

MATERIALS AND METHODS

Aqua Regia

An AR digest was performed at the University of New England (UNE), Armidale, Australia (Milestone, 2009). Each sample was subsequently analyzed via a Varian Vista MPX CCD ICP-OES equipped with a VISTA SPS-5 autosampler. Briefly, 0.50 g (± 0.05 g) of each sample was digested in 9 mL of HCl acid (36%) and 3 mL of HNO₃ acid (70%) using an ETHOS Plus microwave digestion system (Milestone, 2009; Tighe et al., 2004).

Analytical recoveries (method accuracy) were calculated using reported values of the National Institute of Standards and Technology (NIST) 2711 (Montana I) soil standard. Three replicates of the NIST 2711 standard, three internal replicates and four blanks were used to ensure quality control. Analytical precision of each "total" element technique was calculated using the internal replicates of the reference materials (AR and LXRF), or the three PXRF replicates of each unknown soil sample (Tighe et al., 2004; USEPA, 2007). Precision (RSD %) was calculated by dividing the standard deviation by the mean and converting to a percentage. Internal replicates of the AR digest gave precision values below 20% for all elements. All values were blank corrected before standard volume and weight conversions.

Laboratory X-ray Fluorescence

Fifteen samples were taken randomly from the original soil sample collection for LXRF and NAA. Laboratory XRF analyses were performed at the Geoscience Australia laboratories, Canberra, Australia. A Philips PW2404 4 kW sequential wavelength dispersive spectrometer fitted with a Rhodium X-ray tube was used to analyze fused beads made from X g soil/Y g 12:22 flux (35% Lithium tetraborate/65% Lithium metaborate). The Canadian Certified Reference Materials Project (CCRMP) soil standard (Till-1) was used to assess elemental recovery and precision. High (<20%) precision values were found for all tested elements using LXRF and accuracies reported as elemental recovery from the CCRMP soil standard. Nickel and Cu were not included in soil analyses by LXRF and NAA due to instrument limitations. For optimal regressions, only optimized light and heavy element PXRF raw peak area counts were used for PXRF/(LXRF and NAA) correlations.

Neutron Activation Analysis

Neutron activation analysis of the samples was performed using the 20 MW OPAL research reactor (Bennett, 2008). At the NAA irradiation positions used for this work the neutron flux was around 1.5×10^{13} cm⁻²/s. The flux at these locations is very well thermalized, with a thermal to epithermal flux ratio of >1000. To maximize the number of elements that could be quantified the k_0 -method of standardization (k_0 -NAA) was used and samples were irradiated in both the short and long residence time facilities. Certified reference material IRMM-530R, produced by the Institute for Reference Materials and Measurements (IRMM) and containing 0.1% gold, was used as the neutron flux monitor.

Two aliquots of 30 to 60 mg were taken from each sample for measurement. In the short residence time facility the samples were irradiated for 30 s and γ -ray spectra were acquired for 3 and 12 min after decay periods of around 5 and 18 min, respectively. Samples were irradiated in the long residence time facility for 12 h and were measured for 30 min and 2 h after decay periods of around 3.5 d and 2 wk. The γ -ray spectra were analyzed (HyperLab) to produce peak table files and the elemental concentrations were calculated (Kayzero for Windows). The NIST 2711a (Montana II) soil standard was used to assess elemental recovery and precision. Acceptable accuracy values were found for all tested elements.

Sample Preparation

At 20 sites across northern NSW, Vertisols (IUSS Working Group WRB, 2006) were collected using a 25-mm tubular soil corer using bore oil for internal tube lubrication for ease of soil removal. At each site, 10 cores encompassing two depths (0–100 and 100–300 mm) were randomly sampled within a circular area of 20-m diam., then homogenized, subsampled, and placed into plastic bags before drying. Each soil sample was then placed into aluminum trays and oven dried at 40°C for 2 wk. After drying, samples were ground using a “Retsch” rotor cross beater grinder and passed through a 2-mm sieve before further manual homogenization. A representative subsample of 40 g was taken from the bulk soil and further ground using an agate mortar and pestle to pass through a 0.25-mm sieve.

Before scanning ~2.0 g of Vertisol was weighed into separate 5-mL cylindrical polyethylene containers. The containers were then sealed with a 76 by 40 mm rectangular sheet of Mylar (Somar International) X-ray polyethylene film (thickness depending on treatment), and secured with a 20 mm rubber band. Each sample was scanned in triplicate and repositioned slightly to obtain the optimal representation of the bulk sample.

Portable X-ray Fluorescence

A Bruker Tracer III-V PXRF (Table 1) with associated software (Bruker X-rayOps, S1PXRF and Spectra 5.1) was used to analyze soil samples. Due to software upgrades Cr, Mg (only for LXRF and NAA correlations) and Pb were analyzed using Spectra 7.2.1.1. Portable XRF results for all tested elements were measured by the K-line emission, except for Pb which used the L-line emission (Bruker, 2010c). Collimation of the PXRF beam covered 7 by 5 mm².

The PXRF was used in “laboratory” mode where it is mounted on a simple frame where soil samples are positioned on top of the PXRF window. To assess the ability of PXRF to quantitatively determine light elements the “best possible” conditions (controlled and reduced variables) were chosen. Future studies will aim to apply these techniques under field conditions.

Factory settings were set as per manufacturer recommendations (Bruker, 2010a). By combining several factors (e.g., Mylar, scan time, and helium) that have been reported or recommended from studies (Bruker, 2010a; Kilbride et

Table 1. Bruker AXS Tracer III-V instrument details (Bruker, 2010c).

Instrument module	Setting/parameters
Detector	Si-Pin detector ca. 190 eV FWHM at the eMnK α peak at 5.9 keV (at 10,000 counts/s)
Excitation source	Rh target X-ray tube
Excitation energy range	Max 30 μ A at 40 keV and 55 μ A at 15 keV

al., 2006; USEPA, 2007) to improve PXRF sensitivity, an “optimized” setting was also used to compare against “factory” settings. In addition, a “light” analysis scan focused on elements with K-shell emissions ≤ 7.11 keV (Fe), and a “heavy” analysis scan focused on elements with K-shell emissions ≥ 7.11 keV (Fe) (Table 2) (Bruker, 2010a). All optimization factors are set prior and maintained for the duration of the complete analysis. Four elements (Ca, Fe, Mn and Ti) were scanned on both settings to assess the likelihood of their inclusion in a heavy analysis scan. Both light and heavy scans were undertaken under two sets of scan conditions as listed below (Table 3).

When heavy analysis scans were undertaken a filter was used to improve the efficiency of element excitation from atomic number 26 (Fe) to 42 (Mo) (Table 3) (Bruker, 2010a). The filter contained a triple layer consisting of 0.1524 mm Cu, 0.0254 mm Ti, and 0.3048 mm Cu “sandwich” (green filter) and was positioned between the excitation source and the sample. To further reduce spectral interference soil samples were placed in a desiccator for 7 d before optimized PXRF scans. Ultra high purity helium gas (~ 99.9999% He) was also used to reduce air attenuation by channelling gas through a glass pipette positioned alongside and between the PXRF window and sample.

Table 2. Summary of elemental K-edge absorption energies that were scanned under light (15 keV) and heavy (40 keV) analysis settings (Sourced from Bruker (2010b)).

PXRF scan setting†	Element	K-edge (keV)
Light	Na	1.07
Light	Mg	1.31
Light	Al	1.56
Light	Si	1.84
Light	P	2.15
Light	S	2.47
Light	K	3.61
Light/Heavy	Ca	4.04
Light/Heavy	Ti	4.97
Light/Heavy	Cr	5.99
Light/Heavy	Mn	6.54
Light/Heavy	Fe	7.11
Heavy	Co	7.71
Heavy	Ni	8.33
Heavy	Cu	8.98
Heavy	Zn	9.66
Heavy	As	11.87
Heavy	Pb	88.00 (L ₁ -edge = 15.86 keV)

† Based on manufacturer recommended portable X-ray fluorescence (PXRF) scan settings for light and heavy analyses (Bruker, 2010c).

Table 3. Bruker AXS Tracer III-V experimental instrument settings based on light and heavy elements under factory and optimized settings.

Parameters/Settings	Light analysis		Heavy analysis	
	Factory	Optimized	Factory	Optimized
Energy specifications	15 keV and 20 μ A	15 keV and 20 μ A	40 keV and 13 μ A	40 keV and 13 μ A
Scan time, s	180	300	180	300
Mylar thickness, μ m	20	1.5	20	1.5
Filter	No	No	Cu/Ti	Cu/Ti
Vacuum	Yes	Yes	No	No
Helium	No	Yes	No	No

Statistical Analysis

Using R 2.10.1 (Ihaka and Gentleman, 1996) the relationship between the raw PXRF data and the AR determined soil concentrations for each element and setting combination was tested using simple linear modeling. The variation accounted for by the model was determined using both the significance of fit of the intercept and the slope of the line (at $P = 0.05$), and the adjusted regression coefficient (r^2). To satisfy the assumptions of the linear model, the residual vs. fitted values were inspected for each linear regression analysis. Outliers were identified by the Cook's distance plot and removed. Data quality parameters (Table 4) were determined for each element based on criteria designated by the United States Environmental Protection Agency (USEPA) (USEPA, 2007). Priority was given to the r^2 value for classification, as in most instances no more than 5% of samples were above USEPA PXRF RSD % criteria (Table 4) (USEPA, 2007).

RESULTS AND DISCUSSION

Aqua Regia

Elemental recoveries of the NIST 2711 standard agree with published literature for AR digestion (Table 5) (Chen and Ma, 2001; Tighe et al., 2004). Acceptable ranges for elemental recovery of all standards were designated between 80 to 120% (Chen and Ma, 1998). Elements outside the acceptable range for AR include Al, Co, Cr, K, Na, Si, and Ti (Table 5). As acids used in the AR technique are limited by the least acid-soluble compound, it is not possible to extrapolate these elemental recoveries to a 100% recovery (Chen and Ma, 1998; Tighe et al., 2004). Elements with incomplete AR recovery must be interpreted with caution.

All blanks except for Mg and Zn were below the detection limit of the ICP-OES (Tighe et al., 2004), which had blank concentrations of 0.47 μ g/mL and 0.68 μ g/mL, respectively (Table 5). Aqua regia analytical precisions of the NIST 2711 standard were all high except for Co (RSD 21%) and Si (RSD 20%) (Table 5) (Tighe et al., 2004).

Table 4. Statistical criteria developed by the U.S. Environmental Protection Agency for establishing data quality levels for relationships between portable X-ray fluorescence (PXRF) and other total element determination techniques (Adapted from the USEPA [USEPA, 2007]).

Data quality level	Statistical requirement
Definitive level (DL)	$r^2 = 0.85 - 1$. The precision (RSD) must be $\leq 10\%$ and the inferential statistics indicate that the two data sets are statistically identical.
Quantitative screening (Quant)	$r^2 = 0.70 - 1$. The precision (RSD) must be $< 20\%$ and the inferential statistics indicate the data sets are statistically different.
Qualitative screening (Qual)	$r^2 < 0.70$. The precision (RSD) is $> 20\%$.
Below detection limit (BDL)	Element concentration is below the detection limit.

Laboratory X-ray Fluorescence and Neutron Activation Analysis

Elemental recovery for LXRF and NAA appeared closer to 100% for most tested elements than the AR digestion (Table 5). Only As, Cr, and Pb were outside the acceptable range for elemental recovery for LXRF (Chen and Ma, 2001). The As K-edge overlaps with the Pb L-edge, and it is possible that overestimation of As and Pb in LXRF is due to limitations in software segmentation (Kilbride et al., 2006; USEPA, 2007).

Portable X-ray Fluorescence/Aqua Regia Correlations

Portable X-ray Fluorescence Settings and Sensitivity

There were considerable differences between PXRF/AR regression slopes and y -intercepts for all quantitatively determined elements using different PXRF settings (Table 3) (Fig. 1). Using Ca as an example, the gradient slope increased between PXRF/AR regressions from factory heavy, factory optimized, factory light, and optimized light settings in ascending order (Fig. 1). Differences in incident X-ray energy and intensity will affect the number of atoms in the bulk sample that will be excited (Bruker, 2010a; Kalnicky and Singhvi, 2001). To improve element detection, instrument parameters can be manipulated to improve the detection of irradiated X-ray energy from excited atoms, thus increasing raw PXRF counts (Kalnicky and Singhvi, 2001; Kilbride et al., 2006). In addition, the linearity of Ca should extend below 2500 mg Ca/kg especially under optimized conditions as element sensitivity is improved compared to factory settings. There are no reported limitations to regression linearity above 18,000 mg Ca/kg.

The PXRF/AR regression slope of Ca more than doubled when optimized settings were used, relative to factory settings (Fig. 1). Portable XRF sensitivity to Ca most likely increased as a result of minimizing air attenuation with helium, longer count time, and reducing spectral interference with thinner polyethylene film (Migliori et al., 2011; USEPA, 2007). Hence PXRF X-rays increased the number of atoms undergoing the photoelectric effect, increasing raw count data and raising the regression slope. Element sensitivity using optimized settings demonstrate the potential for detecting elements with K-edge

Table 5. Quality assurance values obtained for blanks and standards using aqua regia (AR) digestion, laboratory X-ray fluorescence (LXRF) analysis, and neutron activation analysis (NAA).

Method/Standard quality assurance	Element†,‡																		
	Al	As	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Sb	Si	Ti	Zn
	%	mg/kg	%	— mg/kg —		— % —			mg/kg	%	— mg/kg —		%	mg/kg	%	mg/kg	%	— mg/kg —	
AR ICP–OES§																			
Blanks (µg/mL)																			
Mean	1.5	0.0	0.2	0.0	0.0	0.0	0.7	0.2	0.5	0.0	0.0	0.0	0.1	0.0	0.4	0.0	1.1	0.0	0.7
MDL¶	6.3	0.1	0.8	0.0	0.0	0.0	6.9	2.5	0.2	1.1	0.1	0.0	0.2	0.0	0.9	0.0	n/d	n/d	0.3
AR/NIST 2711#																			
Mean	3.5	107.4	2.5	3.8	31.0	130.7	2.9	0.8	0.9	530.6	0.0	21.4	0.1	1328.1	0.0	21.4	0.0	0.1	331.5
RSD %††	9.2	2.5	3.9	20.6	3.2	1.6	4.6	4.4	3.4	2.8	5.0	3.9	2.6	0.9	0.8	5.5	19.4	2.8	2.9
Rec %‡‡	53.1	102.3	85.3	37.5	65.9	114.7	100.3	31.1	87.1	83.2	4.1	104.0	90.0	114.3	90.4	110.1	0.0	41.1	94.6
LXRF/Till-1§§																			
Mean	6.8	24.7	1.8	16.8	49.3	n/d	4.6	1.7	1.2	1332.1	2.0	n/d	0.1	29.2	0.0	n/d	27.3	5490.0	83.7
RSD %††	1.6	5.5	1.7	1.7	6.7	n/d	1.6	1.6	1.9	1.6	1.4	n/d	1.7	6.8	7.4	n/d	1.6	1.9	3.5
Rec %‡‡	94.4	136.9	92.2	93.3	75.8	n/d	96.9	91.2	95.4	95.6	99.9	n/d	95.7	132.7	95.0	n/d	95.9	93.5	85.4
NAA/NIST 2711a¶¶																			
Mean	6.5	103.5	2.3	9.8	46.0	n/d	2.8	2.4	1.0	647.7	1.2	n/d	n/d	n/d	n/d	22.4	n/d	3025.0	419.0
Rec %‡‡	96.6	96.7	94.2	99.6	88.0	n/d	99.4	94.6	90.9	96.0	96.0	n/d	n/d	n/d	n/d	94.0	n/d	95.4	101.2

† n/d = There is insufficient data available to determine detection limit, or no values reported.

‡ Values are reported to two significant figures.

§ Number of replicates = 4.

¶ Method detection limit (MDL) for AR analyzed using an ICP–OES (Tighe et al., 2004).

Number of replicates = 3.

†† Precision (RSD %) is calculated by dividing the standard deviation by the mean and converting to a percentage.

‡‡ Elemental recovery (Rec %) is calculated by dividing the standard means by the reported values and converting to a percentage.

§§ Number of replicates = 2.

¶¶ Number of replicates = 1.

binding energies lower than K and lowering PXRF element detection limits in soils.

Regression slopes for PXRF/AR doubled between factory and optimized settings, though the effect was more pronounced for light element analyses than heavy element analyses (Fig. 1). In addition, PXRF/AR regression slopes for heavy element analyses were generally lower than light element analyses (Fig. 1). Elements that have K-shell absorption edge energies closer to the emitted X-ray energy of the PXRF also have a higher probability of the photoelectric effect occurring for each atom (Bruker,

2010a; Kalnicky and Singhvi, 2001; USEPA, 2007). Calcium's K-edge absorption energy of 4.04 keV is closer to the emitted X-ray energies of light element analysis (15 keV) compared with heavy element analysis (40 keV). The lower *y*-intercept values for heavy element analyses compared with light element analyses is most likely a function reduced spectral sensitivity (Piorek, 1997).

Light Element Analysis

Three main PXRF/AR correlation groups were observed in agricultural soils. The first group consisted of elements that were

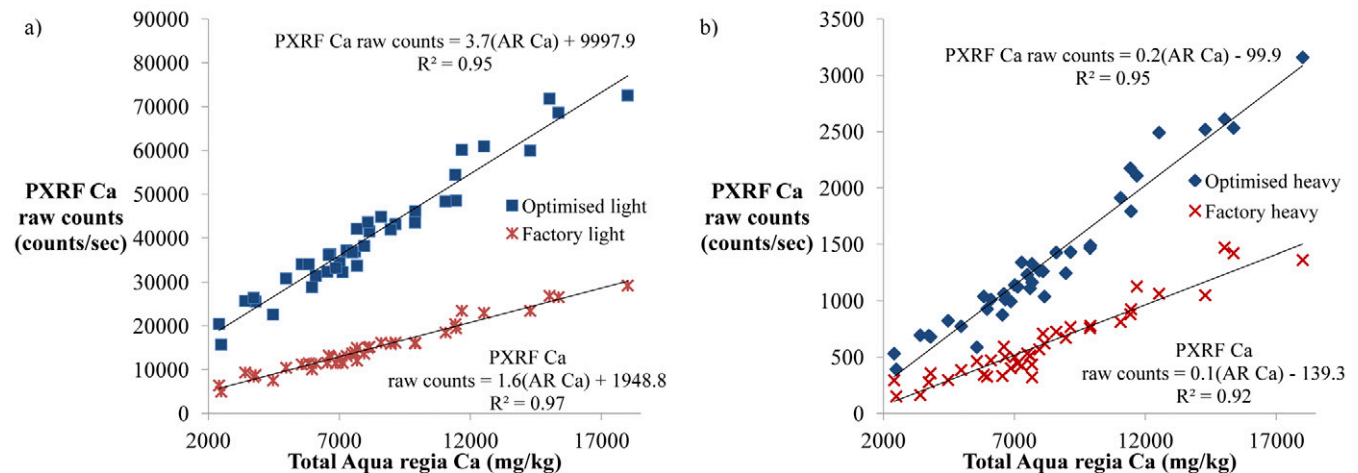


Fig. 1. Portable X-ray fluorescence (PXRF)/aqua regia (AR) regression differences between factory and optimized settings for Ca under (a) light and (b) heavy element analysis.

quantitatively determined through PXRF. The second group consisted of elements that were only qualitatively screened, and the third group included elements that were nondetectable by PXRF under current settings. These elemental groupings are consistent with results reported in previous publications for PXRF analysis in contaminated soils (Goldstein et al., 1996; Kenna et al., 2011; Kilbride et al., 2006).

Quantitative. There was a general improvement in data quality between factory and optimized settings, particularly for light elements (Table 6). When optimized settings were compared with factory settings, the PXRF/AR relationship improved for most elements either qualitatively (Al and Mg) or quantitatively (P), and the PXRF raw counts increased for all elements except Na. Calcium, Fe, Mn, and P were at least quantitatively determined using optimized PXRF settings compared with values from the AR digest (Table 6). While data quality for Ca, Fe, and Mn did not change from factory to optimized settings, PXRF raw counts doubled (Table 6). These elements are consistent with the literature reporting strong correlations in soils with concentrations higher than this current study (Kenna et al., 2011; Kilbride et al., 2006; Zhu and Weindorf, 2009).

Definitive P determination was only achievable through novel PXRF optimized techniques (Table 3). Light element sensitivity increased by using thinner polyethylene film, reduced air attenuation through the creation of a helium atmosphere, and improved spectral resolution by longer count times (300 s) (Kalnicky and Singhvi, 2001; Migliori et al., 2011; USEPA, 2007). In addition to total Ca, Fe, and

Mn PXRF analysis, P determination requires extra time and cost when using optimized settings (Table 3). However, the capability for nondestructive PXRF for P detection in soils may help improve our understanding of P mobilization in soils both spatially and temporally.

Qualitative. Low PXRF/AR correlations were reported for Cr, K, Mg, Na, S, Si, Ti, and Al (Tables 5 and 6) (Chen and Ma, 1998; Tighe et al., 2004). Sulfur analysis using PXRF in Vertisols is difficult due to low abundance and spectral interferences (Potts et al., 2005; USEPA, 2007). Low PXRF/AR correlations are due to interference from the Rhodium (Rh) L-edge energies that scatter the emitted S K-edge energy X-rays (Bruker, 2010a). However, S detection in soils may still be possible using a specific filter designed to block Rh L-edge X-rays (Bruker, 2010a).

Below Detection Limit. The PXRF was unable to detect Na in soil samples containing no more than 1% Na under either factory or optimized settings in soil (Table 6). The very low K-edge binding energy of Na can overlap with the K- or L-edge binding energies of other light elements (e.g., Al, Mg, and Si) (Simionovici and Chevallier, 2006). Similarly, PXRF analysis of other light elements (e.g., Al and Mg), can also be affected by X-ray energy interference from irradiated Si atoms (Kawahara and Shoji, 2006). It is likely that these light elements were affected by a combination of air attenuation, interference from Si, and low elemental recoveries in the AR digest (Migliori et al., 2011).

Elements Scanned on both Settings

Calcium and Fe were the only two elements that consistently reported definitive data quality on both light and heavy element analysis settings (Tables 6 and 7). Portable XRF/AR Mn correlations were higher under factory heavy element settings compared with light element settings (factory and optimized) (Tables 6 and 7). It is unclear why this occurred, as studies by Kenna et al. (2011) reported similar definitive PXRF/LXRF correlations for Mn comparing light and heavy settings on estuarine sediments. A more complete elemental recovery may provide an improved assessment of PXRF correlations for Mn.

There is the potential for additional elements capable of quantitative determination to be included in both light and heavy element analyses (Bruker, 2010a). However, element X-ray emissions

Table 6. Summary of portable X-ray fluorescence (PXRF) and aqua regia (AR) correlations for total element determination using a linear regression model under factory and optimized settings for light elements. Aqua regia determined values, and PXRF raw counts are also reported with their corresponding elemental recovery (Rec %) of the NIST 2711 standard.

Element	Total AR mg/kg	AR Rec ‡ %	Factory settings†			Optimized settings†		
			Data quality§	n	r ²	Data quality§	n	r ²
Ca	2,407–18,003	85	DL++	39	0.97¶	DL++	39	0.95¶
Fe	28,518–88,046	100	DL++	40	0.96¶	DL++	40	0.95¶
P	159–1,257	90	Qual§§	38	0.07¶	DL##	37	0.86¶
Mn	614–1,385	83	Quant++	40	0.77¶	Quant##	38	0.80¶
Cr	90–211	66	Qual§§	39	0.67¶	Qual§§	39	0.32¶
K	2,581–10,397	31	Qual##	36	0.61¶	Qual++	36	0.60¶
Mg	24–22,662	87	BDL§§	40	n/a	Qual##	40	0.07#
S	16–147	90	Qual++	39	0.09¶	Qual++	39	0.04#
Si	70–259	0	Qual++	40	0.00#	Qual++	40	0.00#
Ti	1,010–5,552	41	Qual++	39	0.67¶	Qual++	39	0.64¶
Al	19,878–92,530	53	BDL§§	40	n/a	Qual++	40	0.08¶
Na	2–6,882	4	BDL§§	40	n/a	BDL§§	40	n/d

† n/d = Elements not detected by PXRF as operated.

‡ Elemental recoveries for the NIST 2711 standard.

§ Data quality levels attributed by the USEPA (Table 4).

¶ There is a significant ($p \leq 0.05$) linear association.

There is not a significant ($p \geq 0.05$) linear association.

++ Precision (RSD %) is $\leq 10\%$.

The RSD % is $\leq 20\%$.

§§ The RSD % is $>20\%$ or element is not detected by PXRF as operated.

Table 7. Summary of portable X-ray fluorescence (PXRF) and aqua regia (AR) correlations for total element determination using a linear regression model under factory and optimized settings for heavy elements. Aqua regia determined values, and PXRF raw counts are also reported with their corresponding elemental recovery (Rec %) of the NIST 2711 standard.

Element	Total AR	AR Rec ‡	Factory settings†			Optimized settings†		
			Data quality§	n	r ²	Data quality§	n	r ²
	mg/kg	%						
Ca	2,407–18,003	85	DL††	37	0.92 ¶	DL††	39	0.95 ¶
Fe	28,518–88,046	100	DL††	40	0.96 ¶	DL††	39	0.95 ¶
Zn	32–117	95	Quant††	40	0.73 ¶	DL††	39	0.89 ¶
Cu	17–65	115	Qual##	38	0.36 ¶	Quant##	39	0.70 ¶
Mn	614–1,385	83	DL##	38	0.93 ¶	Quant##	39	0.81 ¶
Ni	21–196	104	Qual##	40	0.32 ¶	Quant##	39	0.78 ¶
Pb##	7–15	114	Qual§§	38	0.67 ¶	Quant##	35	0.83 ¶
Ti	1,010–5,552	41	Quant††	39	0.78 ¶	Quant††	40	0.74 ¶
As	3–14	102	Qual§§	40	0.64 ¶	Qual§§	37	0.63 ¶
Co	6–32	38	Qual††	37	0.18#	Qual††	38	0.26 ¶
Cr	89–212	66	Qual§§	40	0.34 ¶	Qual§§	40	0.41 ¶
Sb	1–9	110	Qual§§	40	0.00#	Qual§§	40	0.31 ¶

† n/d = Elements not detected by PXRF as operated.

‡ Elemental recoveries for the NIST 2711 standard.

§ Data quality levels attributed by the USEPA (Table 4).

¶ There is a significant ($p \leq 0.05$) linear association.

There is not a significant ($p \geq 0.05$) linear association.

†† Precision (RSD %) is $\leq 10\%$.

The RSD % is $\leq 20\%$.

§§ The RSD % is $>20\%$ or element is not detected by PXRF as operated.

Analyzed using Spectra7.2.1.1 due to software upgrade.

may be reduced and potentially affect data quality (Kalnicky and Singhvi, 2001; Kenna et al., 2011).

Heavy Element Analysis

Quantitative. Generally, elemental recovery of the AR digest did not limit any PXRF/AR correlation for heavy analyses except Co (Table 7). Overall data quality appeared to significantly improve between factory and optimized settings for Zn, Cu, Ni, and Pb (Table 7). The improved PXRF/AR correlations are as a result of longer count time, as heavy elements are less affected by air attenuation compared with light elements (Bruker, 2010a; Kalnicky and Singhvi, 2001).

Under optimized settings this study has markedly improved data quality for Ni compared to previous publications (Goldstein et al., 1996; Kilbride et al., 2006). Data quality for Zn and Pb were similar to results reported by Kilbride et al. (2006), though soil Zn and Pb concentrations in this current study were lower. Publications on soil PXRF analysis have been typically confined to heavy elements in contaminated soils (Jang, 2010; Kilbride et al., 2006). The ability to optimize PXRF has enabled the quantification of many heavy elements in agricultural soils.

Qualitative. Arsenic and Sb were only qualitatively screened under both factory and optimized settings (Table 7). Strong correlations between PXRF/acid digestion values have been reported for As in contaminated soils (Jang, 2010; Kilbride et al., 2006; Radu and Diamond, 2009). It is possible that changing scan conditions may improve As PXRF/AR correlations (Kalnicky and Singhvi, 2001).

Portable X-ray Fluorescence / (Laboratory X-ray Fluorescence and Neutron Activation Analysis) Correlations

Portable XRF/(LXRF and NAA) correlations for most elements generally improve when elemental recovery reached 100%. When PXRF/AR correlation data are included this trend is generally supported (with the exception of Mg, Mn, and As). In addition, As PXRF/(AR and NAA) regression coefficients are 0.63 and 0.82, respectively, with both analyses reporting 100% ($\pm 3\%$) elemental recovery. It is possible that AR digestion of the NIST 2711 standard is not providing an accurate representation of Vertisol element recovery (Chen and Ma, 1998). Validation of PXRF by LXRF and particularly NAA, has in most instances created more accurate calibration curves than traditional acid digestion techniques using, for examples AR.

Optimized Light Element Analysis

Quantitative. In general, PXRF/(LXRF and NAA) correlations for several elements tended to have a bias toward strong definitive relationships ($r^2 = 0.85 - 1$) compared to PXRF/AR correlations (Tables 6 and 8). Using optimized light settings, strong PXRF/(LXRF and NAA) correlations were found for Ca, Cr, Fe, K, Mg, Ti, P, Mn, and Si (Table 8). Many of these elements were either nondetectable under light element factory settings (Mg), or only qualitatively screened under light element optimized settings (Cr, K, Mg, Si, and Ti) using PXRF/AR correlations (Table 6). The ability of this current study to determine K, Si, and Ti using optimized settings can negate the use of hazardous chemicals such as HF acid (Chen and Ma,

Table 8. Summary of portable X-ray fluorescence (PXRF), laboratory X-ray fluorescence (LXRF) and neutron activation analysis (NAA) correlations for total element determination using a linear regression model under optimized settings for light elements. Elemental recovery (Rec %) of the Till-1 and NIST 2711a for LXRF and NAA respectively are also reported.

Element†	Optimized settings‡							
	LXRF Rec, %§	n	r ²	Data quality¶	NAA Rec, %#	n	r ²	Data quality¶
Ca	92.19	14	0.97##	DL	94.21	14	0.98##	DL
Cr††	75.77	14	0.88##	DL	87.97	14	0.94##	DL
Fe	96.93	13	0.99##	DL	99.43	13	0.97##	DL
K	91.24	14	0.95##	DL	94.62	15	0.95##	DL
Mg††	95.37	15	0.93##	DL	90.93	15	0.89##	DL
Ti	93.47	14	0.95##	DL	95.43	15	0.91##	DL
P	95.68	15	0.87##	DL	n/d	15	n/d	n/d
Mn	95.56	15	0.73##	Quant	95.96	14	0.75##	Quant
Si	95.89	14	0.77##	Quant	n/d	15	n/d	n/d
Al	94.39	14	0.27##	Qual	96.59	14	0.29##	Qual
S	95.00	15	0.18§§	Qual	n/d	15	n/d	n/d
Na	99.93	15	n/d	n/d	96.00	15	n/d	n/d

† The RSD % is the same reported values in Table 6 under optimized settings.

‡ n/d = Elements not detected by PXRF as operated or data not obtainable.

§ Elemental recoveries for the Till-1 standard.

¶ Data quality levels attributed by the USEPA (Table 4).

Elemental recoveries for the NIST 2711a standard.

†† Analyzed using Spectra7.2.1.1 due to software upgrade.

There is a significant ($p \leq 0.05$) linear association.

§§ There is not a significant ($p \geq 0.05$) linear association.

2001). The nondestructive nature of PXRF may also improve our understanding of Ca, K, P, and Si fertilizer movement and root mobilization processes in situ.

Relating total soil elements for plant response is problematic, as elements exist in soils at various stages of availability (Rayment and Lyons, 2011). There is a significant gap in the literature relating total soil elements to plant growth (Rayment and Lyons, 2011). However, recent studies by Rayment (2011) have

attempted to show the potential of including total element data with plant available extractions.

Sulfur and Mg were the only elements that had low PXRF/AR correlations while reporting near complete elemental recovery in the AR digest (Table 6). Limitations to S PXRF analyses have already been discussed (Qualitative section under Portable X-ray Fluorescence/Aqua Regia Correlations-Light Element Analysis). It is possible that elemental recoveries closer to 100% for LXRF and NAA

Table 9. Summary of portable X-ray fluorescence (PXRF), laboratory X-ray fluorescence (LXRF) and neutron activation analysis (NAA) correlations for total element determination using a linear regression model under optimized settings for heavy elements. Elemental recovery (Rec %) of the Till-1 and NIST 2711a for LXRF and NAA respectively are also reported.

Element†	Optimized settings‡							
	LXRF Rec, %§	n	r ²	Data quality¶	NAA Rec, %#	n	r ²	Data quality¶
Ca	92.19	13	0.95##	DL	94.21	13	0.96##	DL
Fe	96.93	14	0.98##	DL	99.43	14	0.97##	DL
Mn	95.56	13	0.86##	DL	95.96	12	0.87##	DL
Ti	93.47	13	0.98##	DL	95.43	13	0.98##	DL
Zn	85.36	12	0.86##	DL	101.21	12	0.93##	DL
As	136.94	14	0.64##	Qual	96.73	13	0.82##	Quant
Co	93.33	13	0.61##	Qual	99.58	14	0.58##	Qual
Cr††	75.77	14	0.29##	Qual	87.97	13	0.09§§	Qual
Pb††	132.73	12	0.28##	Qual	n/d	15	n/d	n/d
Sb	n/d	15	n/d	n/d	94.03	15	0.07§§	Qual

† The RSD % is the same reported values in Table 7 under optimized settings.

‡ n/d = Elements not detected by PXRF as operated or data not obtainable.

§ Elemental recoveries for the Till-1 standard.

¶ Data quality levels attributed by the USEPA (Table 4).

Elemental recoveries for the NIST 2711a standard.

†† Analyzed using Spectra7.2.1.1 due to software upgrade.

There is a significant ($p \leq 0.05$) linear association.

§§ There is not a significant ($p \geq 0.05$) linear association.

improved Vertisol Mg data quality improving Mg PXRF/(LXRF and NAA) correlations (Tables 6 and 8) (Chen and Ma, 2001). However, it is most likely that software upgrades from Spectra5.1 to Spectra7.2.1.1 for Mg segmentation significantly improved PXRF/(LXRF and NAA) correlations. A discussion of differences between PXRF software is beyond the scope of this study.

Qualitative. Portable XRF/(LXRF and NAA) correlations for Al remain unchanged when compared with PXRF/AR correlations (Tables 6 and 8). With Al elemental recoveries for LXRF and NAA close to 100%, and PXRF Al raw counts relatively high, it is likely that limitations exist in the Al software segmentation. It is also possible that the low emitted K-edge energies of Al are being reabsorbed by other soil constituents or interfering with emitted Si K-edge X-rays (Kalnicky and Singhvi, 2001; Kawahara and Shoji, 2006; USEPA, 2007).

Optimized Heavy Element Analysis

Laboratory XRF and NAA improved data quality for As and slightly increased the PXRF/NAA correlation for Zn compared with PXRF/AR correlations (Tables 7 and 9). Portable XRF correlations for these elements also appeared to improve slightly with NAA compared to LXRF (Table 8). Portable XRF has the potential to quantitatively determine additional elements that were not tested in this study.

Optimal Portable X-ray Fluorescence /(Aqua Regia, Laboratory X-ray Fluorescence, and Neutron Activation Analysis) Regressions

Optimized PXRF settings using LXRF and NAA data generally provided definitive elemental determination for light elements (Table 10). In only one occasion was factory PXRF settings used to provide the highest PXRF/AR correlation (Table 10). For heavy elements, AR data in most instances provided the highest PXRF/AR correlations under optimized settings (Table 10). Portable XRF has the potential for consistent and reliable soil analysis based on soil matrix specific calibrations (Kalnicky and Singhvi, 2001). This study has developed several calibration curves for Vertisols that can be used for routine total element analysis (Table 10) (Kilbride et al., 2006). These calibration curves could potentially be used in all Vertisol analysis. However, the same make and model PXRF gun, PXRF settings, optimized parameters, and similar Vertisol matrices would be needed, thus initial calibration work for confirmation is required (USEPA, 2007).

Regression slopes ranged from 0.06 (Mg) to 80.98 (Pb) using regressions from the highest correlating PXRF settings and total element data (Table 10). In general, the gradient slope tended to increase with increasing K-edge absorption value (Tables 2 and 10). This trend was generally observed across all elements, though is more defined within light or heavy element analysis groups. Previously (Portable X-ray Fluorescence Settings and Sensitivity section under Portable X-ray Fluorescence/Aqua Regia Correlations), this study demonstrated the effect

Table 10. A summary of optimal portable X-ray fluorescence (PXRF) correlations between three different total element techniques, aqua regia (AR), laboratory X-ray fluorescence (LXRF) and neutron activation analysis (NAA).

Element	r^2	PXRF regression†	PXRF analysis settings‡,§
As	0.82	$y = 40.85x + 169$	HON
Ca	0.98	$y = 3.35x + 11,300$	LON
Cr	0.94	$y = 9.04x + 515$	LON
Cu	0.70	$y = 3.92x + 496$	HOA
Fe	0.99	$y = 8.30x + 257,269$	LOX
K	0.95	$y = 1.94x + 2,534$	LON
Mg	0.93	$y = 0.09x + 290$	LOX
Mn	0.94	$y = 1.28x + 87$	HFA
Ni	0.78	$y = 3.39x + 735$	HOA
P	0.87	$y = 0.27x - 72$	LOX
Pb	0.83	$y = 80.98x - 430$	HOA
Si	0.77	$y = 0.64x - 35,802$	LOX
Ti	0.98	$y = 0.55x + 111$	HON
Zn	0.93	$y = 11.40x + 428$	HON

† y = PXRF raw counts, and x = AR, LXRF or NAA determined values.

‡ PXRF analysis settings reported in Table 3.

§ H = Heavy element analysis, L = Light element analysis, O = Optimized settings, F = Factory settings, A = Based on AR calibration, N = Based on NAA calibration, and X = Based on LXRF calibration.

of PXRF/AR regression slopes with different PXRF settings for Ca, ranging from 0.1 (heavy element factory settings) to 3.7 (light element optimized settings). It is possible that as each element's K-edge absorption energy becomes closer to the emitted X-ray energy of the PXRF, the probability of element excitation also increases (Bruker, 2010a; Kalnicky and Singhvi, 2001; USEPA, 2007).

Routine soil analysis using PXRF will require calibration curves similarly used in traditional chemical digestion followed by various spectroscopy instrumentation. It is important that sample matrices are similar to unknown samples for correct total element determination. As a consequence, when additional analyses are required of a similar matrix, the calibration curves like those developed in Table 10 can be used routinely with an internal standard for confirmation.

It is difficult to compare equipment and analysis costs, and analysis time between PXRF and traditional soil digestion. Due to economies of scale each laboratory will have different proficiencies in time and cost. Using PXRF we estimate that analysis time is reduced with approximately 100 samples or below, as the time spent with chemical incubation and spectroscopy analysis often exceeds 2 d. Portable XRF also provides nondestructive analysis at minimal cost as small amounts of polyethylene Mylar and helium gas is used. While the capability of PXRF compared to laboratory based instrumentation is still somewhat reduced, this paper demonstrates comparable results that are nondestructive.

CONCLUSIONS

Following a critical evaluation and comparison of PXRF and conventional destructive techniques this study has been able to demonstrate the viability of current generation PXRF technology for routine rapid quantitative and nondestructive

analysis of total element concentrations in Vertisols, a globally important agricultural soil type. This experiment was able to quantitatively determine 14 (As, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Pb, Si, Ti, and Zn) elements of agricultural importance (Table 10), illustrating the wider agricultural applicability of PXRF to commercially important soil types. The implications of this study are that application of PXRF to agricultural soils represents a significant reduction in the cost and time required for routine soil elemental analysis. The integrated and robust character of PXRF instrumentation, requiring similar sample preparation to traditional methods, is readily adaptable to a wide range of analytical situations and may prove a major new analytic and training facility in world agricultural science contexts.

ACKNOWLEDGMENTS

Financial support from the Cotton Catchment Communities Cooperative Research Centre (Cotton CRC, project 1.03.44) is greatly acknowledged. The authors would like to thank the Australian Institute of Nuclear Science and Engineering (AINSE Ltd., Award ALNGRA11108) for providing financial assistance for sample analysis. Thanks are also extended to Dr. Bruce Kaiser for technical assistance.

REFERENCES

Argyriaki, A., M.H. Ramsey, and P.J. Potts. 1997. Evaluation of portable X-ray fluorescence instrumentation for *in situ* measurements of lead on contaminated land. *Analyst* (London) 122:743–749. doi:10.1039/a700746i

Bennett, J.W. 2008. Commissioning of NAA at the new OPAL reactor in Australia. *J. Radioanal. Nucl. Chem.* 278:671–673. doi:10.1007/s10967-008-1502-0

Berrow, M.L., and A.M. Ure. 1981. The determination of metals and metalloids in soils. *Environ. Technol. Lett.* 2:485–502. doi:10.1080/0959338109384079

Bruker. 2010a. Filter, voltage and current selection for optimum XRF elemental group analysis. Bruker PXRF Tracer III–V manual. Bruker AXS, Madison, WI.

Bruker. 2010b. Periodic table and X-ray energies. Bruker PXRF Tracer III–V manual. Bruker AXS, Madison, WI.

Bruker. 2010c. Handbook for the Tracer III–V. Bruker PXRF Tracer III–V manual. Bruker AXS, Madison, WI.

Cameron, M. 2010. Light element analysis by portable XRF in mining applications. Proceedings Denver X-ray Conference, Denver, CO. 2–6 Aug. 2010. Joint Committee on Powder Diffraction Standards-International Centre for Diffraction Data, Denver, CO.

Chen, M., and L.Q. Ma. 1998. Comparison of four USEPA digestion methods for trace metal analysis using certified and Florida soils. *J. Environ. Qual.* 27:1294–1300. doi:10.2134/jeq1998.00472425002700060004x

Chen, M., and L.Q. Ma. 2001. Comparison of three Aqua Regia digestion methods for twenty Florida soils. *Soil Sci. Soc. Am. J.* 65:491–499. doi:10.2136/sssaj2001.652491x

Falciani, R., E. Novaro, M. Marchesini, and M. Gucciardi. 2000. Multi-element analysis of soil and sediment by ICP-MS after a microwave assisted digestion method. *J. Anal. At. Spectrom.* 15:561–565. doi:10.1039/b000742k

Forster, N., P. Grave, N. Vickery, and L. Kealhofer. 2011. Non-destructive analysis using PXRF: Methodology and application to archaeological ceramics. *XRAY SPECTROM.* 40:389–398. doi:10.1002/xrs.1360

Goldstein, S.J., A.K. Slemmons, and H.E. Canavan. 1996. Energy-dispersive X-ray fluorescence methods for environmental characterization of soils. *Environ. Sci. Technol.* 30:2318–2321. doi:10.1021/es950744q

Hou, X., Y. He, and B.T. Jones. 2004. Recent advances in portable X-ray fluorescence spectrometry. *Appl. Spectrosc. Rev.* 39:1–25. doi:10.1081/ASR-120028867

Ihaka, R., and R. Gentleman. 1996. R: A language for data analysis and graphics. *J. Comput. Graph. Statist.* 5:299–314. doi:10.2307/1390807

IUSS Working Group WRB. 2006. World reference base for soil resources 2006. World Soil Resources Rep. 103. FAO, Rome. ftp://ftp.fao.org/agl/agll/docs/wsr103e.pdf (accessed 29 Aug. 2011).

Jang, M. 2010. Application of portable x-ray fluorescence (pXRF) for heavy metal analysis of soils in crop fields near abandoned mine sites. *Environ. Geochem. Health* 32:207–216. doi:10.1007/s10653-009-9276-z

Johnson, B., J. Leethem, and K. Linton. 1995. Effective XRF field screening of lead in soil. DuPont Environmental Remediation Services, Houston, TX. http://info.ngwa.org/gwol/pdf/950161762.PDF (accessed 3 July 2011). p. 629–642.

Kalnicky, D.J., and R. Singhvi. 2001. Field portable XRF analysis of environmental samples. *J. Hazard. Mater.* 83:93–122. doi:10.1016/S0304-3894(00)00330-7

Kawahara, N., and T. Shoji. 2006. 4.4 Wavelength dispersive XRF and a comparison with EDS. In: B. Beckhoff et al., editors, *Handbook of practical X-ray fluorescence analysis*. Springer-Verlag, Berlin, Germany.

Kenna, T.C., F.O. Nitsche, M.M. Herron, B.J. Mailloux, D. Peteet, S. Sritrairat, E. Sands, and J. Baumgarten. 2011. Evaluation and calibration of a field portable X-ray fluorescence spectrometer for quantitative analysis of siliciclastic soils and sediments. *J. Anal. At. Spectrom.* 26:395–405. doi:10.1039/c0ja00133c

Kilbride, C., J. Poole, and T.R. Hutchings. 2006. A comparison of Cu, Pb, As, Cd, Zn, Fe, Ni, and Mn determined by acid extraction/ICP-OES and ex situ field portable X-ray fluorescence analyses. *Environ. Pollut.* 143:16–23. doi:10.1016/j.envpol.2005.11.013

Melquiades, F.L., and C.R. Appoloni. 2004. Application of XRF and field portable XRF for environmental analysis. *J. Radioanal. Nucl. Chem.* 262:533–541. doi:10.1023/B:JRNC.0000046792.52385.b2

Migliori, A., P. Bonanni, L. Carraresi, N. Grassi, and P.A. Mando. 2011. A novel portable XRF spectrometer with range of detection extended to low-Z elements. *XRAY SPECTROM.* 40:107–112. doi:10.1002/xrs.1316

Milestone. 2009. Soil partial digestion. Milestone, Sorisole, Italy. http://www.milestonesci.com/index.php/resources/resources/finish/164/969.html (accessed 2 Sept. 2011).

Omote, J., H. Kohno, and K. Toda. 1995. X-ray fluorescence analysis utilizing the fundamental parameter method for the determination of the elemental composition in plant samples. *Anal. Chim. Acta* 307:117–126. doi:10.1016/0003-2670(95)00033-V

Piorek, S. 1997. Field-portable x-ray fluorescence spectrometry: Past, present, and future. *Field Anal. Chem. Technol.* 1:317–329. doi:10.1002/(SICI)1520-6521(199712)1:6<317::AID-FACT2>3.0.CO;2-N

Potts, P.J., A.T. Ellis, P. Kregsamer, C. Strelci, C. Vanhoof, M. West, and P. Wobruschek. 2005. Atomic spectrometry update. X-ray fluorescence spectrometry. *J. Anal. At. Spectrom.* 20:1124–1154. doi:10.1039/b511542f

Potts, P.J., P.C. Webb, O. Williams-Thorpe, and R. Kilworth. 1995. Analysis of silicate rocks using field-portable X-ray fluorescence instrumentation incorporating a mercury (II) iodide detector: A preliminary assessment of analytical performance. *Analyst* (London) 120:1273–1278. doi:10.1039/an9952001273

Radu, T., and D. Diamond. 2009. Comparison of soil pollution concentrations determined using AAS and portable XRF techniques. *J. Hazard. Mater.* 171:1168–1171. doi:10.1016/j.jhazmat.2009.06.062

Rayment, G.E. 2011. Total K to exchangeable K ratios as a guide to sustainable soil K supply. In: Y.P. Kalra, editor, *Proceedings 12th International Symposium on Soil and Plant Analysis*, Chania, Greece. 6–10 June. PAQ Interactive, Monticello, IL.

Rayment, G.E., and D.J. Lyons. 2011. Phosphorus soil chemical methods-Australasia. CSIRO Publ., Collingwood, VIC.

Simionovici, A., and P. Chevallier. 2006. 7.2 Micro-XRF with synchrotron radiation. In: B. Beckhoff et al., editors, *Handbook of practical X-ray fluorescence analysis*. Springer-Verlag, Berlin, Germany. p. 474–497.

Tighe, M., P. Lockwood, S. Wilson, and L. Lisle. 2004. Comparison of digestion methods for ICP-OES analysis of a wide range of analytes in heavy metal contaminated soil samples with specific reference to arsenic and antimony. *Commun. Soil Sci. Plant Anal.* 35:1369–1385. doi:10.1081/CSS-120037552

USEPA. 2007. Field portable X-ray fluorescence spectrometry for the determination of elemental concentrations in soil and sediment. USEPA, Washington, DC.

Zhu, Y., and D.C. Weindorf. 2009. Determination of soil calcium using field portable x-ray fluorescence. *Soil Sci.* 174:151–155. doi:10.1097/SS.0b013e31819c6e1b