Field Portable X-ray Fluorescence (FPXRF): A rapid and low cost alternative for measuring metals and metalloids in soils

1 INTRODUCTION

The Field Portable X-Ray Fluorescence (FPXRF) analyser is a portable analytical instrument for determining metal and metalloid concentrations in soils and other media (e.g. paint, alloys); producing a display of the 'total' metal and metalloid concentrations (Fig. 1). It has real potential for:

- Quickly and effectively determining soil metal and metalloid concentrations in the laboratory or field;
- Producing a contaminant profile for a site;
- Delineating contaminant hot spots;
- Evaluating the effects of remediation (Fig. 2).

The cost of sample analysis often compromises the extent of field sampling, which may increase the uncertainty regarding the estimation of contaminant extent and variability across a site. All sites do not need the same intensity and quality of data. This is determined by the cost of getting it wrong, which is low at a site in a low risk setting but potentially high at a site in a high risk setting.

Assessment of the 'total' metal and metalloid content of a soil is traditionally performed using an *aqua regia* or hydrofluoric acid (HF) digestion followed by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) or Atomic Absorption Spectrometer (AAS) analysis, which are relatively time-consuming and expensive methods of analysis. X-ray fluorescence (XRF) is more cost-effective as it is carried out on a dried and ground sample and does not involve digestion of the soil material. However, this method still requires the removal of the sample to a laboratory.

The Environment Agency has acknowledged that when used in combination with MCERTS laboratory analysis, on site testing using the FPXRF may improve the quality and reduce the costs of site investigation and remediation by providing faster and more detailed information on the spatial distribution of metal and metalloid contamination. These data can be used:

1. As an initial screening tool to design a targeted sampling strategy;
2. To supplement laboratory analysis to improve the Conceptual Site Model (CSM) and/or evaluate the success of remediation.

This bulletin provides guidance on the use of the FPXRF for the determination of metal and metalloid concentration in soils. This is based upon a laboratory experiment conducted to evaluate:

(i) The relationship between *aqua regia* extraction/ICP-OES and FPXRF analysed metal levels;
(ii) the detection limits of FPXRF to test whether they are sufficient in the context of current UK guidance.

The work used two FPXRF instruments; the dual isotope and the X-ray tube (Niton instruments, Niton UK Ltd, Hampshire). A more complete account of this work can be found in Kilbride *et al.* (2006).

2 PRINCIPLES AND CONSIDERATIONS

2.1 How Does Field Portable X-ray Fluorescence Work?

The FPXRF analyser measures the characteristic energy levels of X-rays emitted from elements when irradiated with a high-energy photon source (X-ray tube or radioactive source). The energy of each X-ray detected identifies a particular element present in the sample, and the rate at which X-rays of a given energy are counted, provides a determination of the quantity of that element present in the sample.

The FPXRF can be used either by placing the sampling window in direct contact with the field soil surface or with a soil sample in the laboratory. In the laboratory the instrument can be placed in a holding platform and the samples analysed in sample cups that fit within a drawer beneath the measurement window (Fig. 3). If being used in the field the instrument can be used both on the soil surface and, if analysis is required at depth, down a soil profile by first excavating deeper soil with a soil auger. Vegetation should first be removed from the soil surface and the soil compacted slightly to provide a smooth flat surface. The FPXRF can also be connected to a PC to allow data transfer (Fig. 3); data are easily converted into Excel files. The instruments tested are operated through a touch screen display, which includes internal calibration and selection of the sample analysis mode. Sample analysis is achieved by either depressing the trigger for the desired period of time or via a PC if the instrument is within the holding platform.
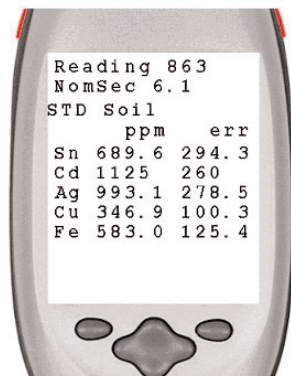

Fig. 1: Display of the FPXRF showing metal concentrations and associated errors

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Reading 863
NomSec 6.1
STD Soil
          ppm      err
Sn   689.6   294.3
Cd  1125     260
Ag   993.1   278.5
Cu   346.9   100.3
Fe   583.0   125.4
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Fig. 2: Field use of the FPXRF
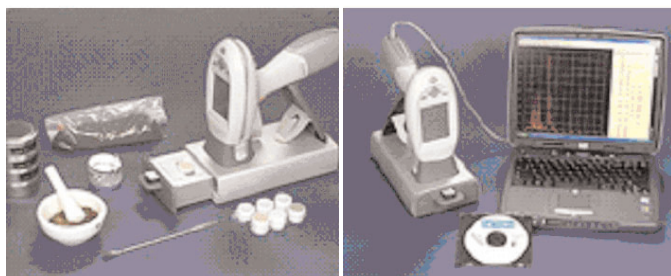
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Fig. 3: Laboratory use of the FPXRF

2.2 Health and Safety

The FPXRF contains a radiation source and appropriate measures should therefore be taken to minimise the risk of exposure to users. For example, the instrument should never be pointed at another individual and all people should stay behind the instrument when in operation. A risk assessment covering the use of the instrument both in the laboratory and field should be written. The instrument should only be used by trained operators (training is available from instrument providers). The FPXRF is supplied in a robust case which should be secured with a padlock and kept in a locked cupboard when not in use, the case and the instrument should be labelled with appropriate radiation labels. Radiation dosimeters should be worn at all times when working with the FPXRF (these can be obtained from the Health Protection Agency and replaced according to their recommendations). When carrying out analysis in the laboratory it may be appropriate to use the FPXRF in conjunction with a portable radiation dose rate monitor. The reading on the dose monitor must not exceed 0.5 microSv/hr (Ionising Radiation Regulations, 1999; IRR99).

3 EVALUATION

3.1 Sample Collection and Preparation

The FPXRF was tested on 81 soil samples collected from seven sites of former industrial land use in the UK. Samples were taken at four depth increments (0-10, 10-20, 20-40 and 40-80 cm), air-dried, ground to obtain the < 2 mm fraction and homogenised. One gram of each soil was subjected to *aqua regia* extraction (hydrochloric acid: nitric acid 3:1 and hydrogen peroxide, followed by boiling under reflux for 2 hours, cooling and filtering). The solutions were then analysed for As, Cd, Cu, Mn, Ni, Pb and Zn with an ICP-OES.

A broad concentration range exists for As, Cu, Cd, Mn, Ni, Pb and Zn, these have been presented in Table 1 along with the Soil Guideline Value (SGV), where available.

Table 1. Concentration of metals (mg/kg) determined by *aqua regia* followed by ICP-OES (n = 81)

Element	SGV[1]	SGV[2]	Mean	Minimum	25th percentile	50th percentile*	75th percentile	Maximum
As	20	500	467	2	19	58	389	5646
Cd	30	1400	13	0	1	3	4	447
Cu			261	3	62	141	237	5140
Mn			1544	6	166	609	988	38267
Ni	75	5000	22	1	11	22	30	84
Pb	450	750	696	5	62	101	173	40398
Zn			889	3	143	278	471	25389

*median; [1]Residential land without plant uptake, [2]Commercial/industrial (Defra and EA, 2002)

Ten millilitre FPXRF sample cups (Niton UK, Hampshire) were ¾ filled with the soil. Polyester filling (Niton UK, Hampshire) was used to fill the rest of the cup and the sample cups were sealed using sealing film (Niton UK, Hampshire).

Each sample was analysed by both dual isotope and X-ray tube FPXRF to obtain a comparative data set.

3.2 Dual Source FPXRF

Samples were analysed using a method from the United States Environmental Protection Agency (USEPA) to determine elemental concentrations in soils and sediments (Sackett and Martin, 1998). The Niton XLi environmental analyser was set for 300 seconds for each of the 81 samples. Each sample was analysed using the Cd^{109} isotope to determine the concentration of As, Cu, Mn, Ni, Pb and Zn. The instrument was then internally recalibrated with the Am^{241} isotope and the concentration of Cd in each sample was determined.

3.3 X-ray Tube FPXRF

The Niton XLt 700 series environmental analyser utilises a miniature X-ray tube, and has given field portable XRF instruments increased sensitivity and analytical range (Piorek, 2004). X-ray tube based sources offer a faster analytical time because the X-ray flux can be higher than most isotope based sources. They can also be used over a wider range of excitation energies, eliminating the need for multiple isotopic sources to produce X-rays over the entire excitation spectrum (USEPA, 2003). The instrument was set for 300 seconds analysing time for each of the 81 samples. Again each sample was analysed for As, Cd, Cu, Mn, Ni, Pb and Zn.

3.4 Effects of Analysis Time

The time the trigger is depressed (i.e. the analysis time) is displayed in nominal seconds on the FPXRF screen (Fig. 1). The magnitude of the error of results, which is displayed alongside the concentration of each metal (Fig. 1), generally reduces with increased analytical time. In order to ensure that 300 seconds was an appropriate time, the effect of analytical time on instrument accuracy was assessed. A set of twenty samples were analysed for 60, 120, 240, 300 and 600 nominal seconds using the X-ray tube FPXRF. Linear regression analysis on the log transformed data at each count time compared with the results from *aqua regia* extraction/ICP-OES analysis was used to evaluate the effect of count time.

Count time affected the quality of data produced for Cu, Mn and Pb, although the largest change occurred between 60 and 120 nominal seconds, with a much smaller degree of change above 120 nominal seconds. Count time had no significant effect on the concentrations reported for Cd, Ni or Zn. The analysis time, and therefore cost benefits of the FPXRF, obviously affects sample throughput. It is therefore important to achieve a balance between these considerations and the resulting accuracy of the data. The ideal situation would be to adjust the count times to the specific metal of interest. However, in practice, a compromise must be made in order to achieve the optimum results across a suite of metals. This pilot study indicated that a count time of 120 seconds would be appropriate for Cd, Cu, Mn, Ni, Pb and Zn.

3.5 Effect of Particle Size Distribution

It has been reported that FPXRF performance can be affected by soil moisture, organic matter content and particle size distribution (PSD) (Argyraki *et al.*, 1997). Therefore a subset of 30 samples was selected to determine the effect of PSD on the relationship between FPXRF and *aqua regia* extraction/ICP-OES for three particle fractions (< 2 µm, 2-63 µm and > 63 µm) by statistical analysis using linear regression on log transformed data.

PSD had no significant effect for As, Cu, Pb and Zn using either the dual isotope or the X-ray tube FPXRF. Data were insufficient for analysis of Cd, Mg and Ni. The results suggest that particle size does not have a significant influence on the performance of either the dual source or the X-ray tube FPXRF analyser, probably because of the use of the air-dried < 2 mm soil fraction. This has been shown previously to minimise the effect of PSD (Ridings *et al.*, 1999).

3.6 Statistical Analyses

A linear regression model was used to investigate the relationship between metal concentrations measured using conventional *aqua regia* extraction/ICP-OES and both the dual source and X-ray tube FPXRF instruments. The analysis produces a linear model (y=mx+c), which minimises the square of the differences between the dependent variable and the regression line. Data were log transformed prior to analysis to satisfy the assumptions of the linear regression (GenStat, 2003).

The estimate of the y-intercept, compared to c = 0, was tested for significance. Where it was found to be not significantly different from zero, the model was re-fitted without the y-intercept parameter (y = mx). The estimate for the slope, compared to m = 1, was then tested for significance. Where this estimate was not significantly different from 1, the model y = x was accepted as the linear model explaining the relationship between the FPXRF and *aqua regia* extraction/ICP-OES metal concentrations. The proportion of variation (r^2) accounted for by the model was used as a measure of 'goodness of fit'. The squared regression coefficient lies between 0 and 1; r^2 close to 1 implies that the regression line explains the linear relationship between the FPXRF data and the *aqua regia* data very well; r^2 close to 0 implies that the data do not show a clear linear relationship, as defined by the model. The Relative Standard Deviation (RSD), the size of the residual error relative to the mean, for each model was also calculated.

3.7 Data Quality

Data generated by the FPXRF were assigned to one of three quality levels depending on set criteria (USEPA, 1998). Definitive data are the highest quality level (Table 2).

Table 2. Criteria for characterising data quality (adapted from USEPA, 1998)

Data Quality Level	Statistical Requirement
Definitive	r^2 = 0.85 to 1. Relative Standard Deviation (RSD) $\leq$ 10 percent. Inferential statistics (test for slope = 1 & y-intercept = 0) must indicate the two data sets are statistically similar, i.e. relationship y = x accepted.
Quantitative Screening	r^2 = 0.70 to 1. Relative Standard Deviation (RSD) < 20 percent. Inferential statistics indicate the two data sets are statistically different, i.e. relationship y = mx or y = mx + c accepted.
Qualitative Screening	r^2 = less than 0.70. Relative Standard Deviation (RSD) > 20 percent. Inferential statistics indicate two data sets are statistically different.

The relationship between FPXRF and *aqua regia* extraction/ICP-OES was evaluated for each metal concentration. The RSD, r^2 and inferential statistics were then used to allocate a data quality level to each relationship.

4 ANALYTICAL ASSESSMENT

4.1 Cadmium and Nickel

Dual source and X-ray FPXRF achieved qualitative results across the entire range of samples for Cd and Ni (Tables 3 and 4). Both instruments tended to overestimate the concentration of Cd and Ni compared with the *aqua regia* extraction/ICP-OES (Fig. 4). However, when the range of Cd concentrations was restricted to > 20 mg/kg, a definitive level of data was achieved for the dual source FPXRF (Table 5). This suggests that at low Cd concentrations (< 20 mg/kg as determined by *aqua regia* extraction/ICP-OES), both FPXRF instruments were unable to reliably detect the level of Cd present. It is therefore advised that Cd is determined via traditional laboratory analysis where its concentration is less than 20 mg/kg. There was no benefit in restricting the range of Ni concentrations as the entire data set was overestimated by the FPXRF.

4.2 Arsenic

Dual source and X-ray FPXRF achieved quantitative results across the entire range of samples for As (Tables 3 and 4). Both instruments tended to underestimate the concentration compared with the *aqua regia* extraction/ICP-OES analysis by a factor of 0.54 for the dual source and 0.87 for X-ray tube (Fig. 4). Schneider *et al*. (1999) and Swift (1995) reported that the accuracy of FPXRF for As can be compromised if Pb is present in high concentrations, due to spectral overlapping between the As and Pb peaks; indeed As concentrations cannot be effectively determined in samples with a Pb:As ratio of 10:1 or greater (USEPA, 1995). Based upon the *aqua regia* extraction/ICP-OES data, 13 % and 14 % of the detected samples determined by the dual source and X-ray tube FPXRF respectively contained Pb:As ratios of 10:1 or greater. Therefore the linear

regression analysis was repeated for As, excluding the samples exceeding this criterion. The data showed an increased r^2; 0.97 for both instruments, and smaller RSD; 8.7 and 7.4 for the dual source and X-ray tube FPXRF respectively (Table 5). It is therefore advised that As is determined via traditional analysis where the Pb:As ratio is greater than 10:1.

4.3 Manganese and Zinc

Dual source and X-ray FPXRF achieved quantitative results across the entire range of samples for Mn and Zn (Tables 3 and 4). Both instruments tended to overestimate the concentration of Mn and Zn compared with the *aqua regia* extraction/ICP-OES (Fig. 4). However, when the range of Mn and Zn concentrations was restricted a definitive level of data was achieved for the dual source FPXRF (Table 5). Again this suggests that at low concentrations (< 330 mg/kg for Mn and < 51 mg/kg for Zn as determined by *aqua regia* extraction/ICP-OES), both FPXRF instruments were unable to reliably detect the level of Mn or Zn present. These values are below the mean soil concentrations reported in rural soils in the UK Soil and Herbage Report of 612 mg/kg for Mn and 81.3 mg/kg for Zn (EA, 2007) so this should not limit the use of the FPXRF on potentially contaminated sites.

4.4 Copper

Dual source and X-ray FPXRF achieved definitive and quantitative results respectively across the entire range of samples for Cu (Tables 3 and 4); the X-ray FPXRF tending to underestimate Cu concentrations (Fig. 4). Potts *et al*. (1995) evaluated the performance of FPXRF by analysing reference materials and reported strong linear trends for As, Cd, Mn, Ni, Pb and Zn. However, they reported a poor linearity for Cu which they suggested was due to the Cu concentration in the reference materials being at or below the detection limit of the FPXRF (80 mg/kg). The sample set used in the current study encompassed a wide range of Cu concentrations (3 – 5150 mg/kg) and therefore it is feasible that this has resulted in the definitive and quantitative levels presented here.

4.5 Lead

Dual source and X-ray FPXRF achieved definitive results respectively across the entire range of samples for Pb (Tables 3 and 4; Fig. 4).

Table 3. Data quality level for the samples measured with dual source FPXRF

Element	*Aqua regia* mg/kg	FPXRF mg/kg	n^a	r^2	RSD	Data quality level	MDL^b (mg/kg)
As	2 - 5646	10 - 3160	47	0.92	8.2	Quantitative	2
Cd	0 - 447	21 - 287	11	0.61	12.7	Qualitative	
Cu	3 - 5140	55 - 10400	66	0.88	6.4	Definitive	3
Mn	6 - 38267	422 - 83354	19	0.88	5.3	Quantitative	
Ni	1 - 84	67 - 258	16	0.10	6.7	Qualitative	1
Pb	5 - 40398	10 - 61286	79	0.97	4.0	Definitive	5
Zn	3 - 25389	21 - 47180	80	0.94	5.7	Quantitative	

^{a}n < 81 signifies where metal concentration was below the limit of detection of the FPXRF instrument; ^{b}MDL=Method Detection Limit

Table 4. Data quality level for the samples measured with X-ray tube FPXRF

Element	*Aqua regia* mg/kg	FPXRF mg/kg	n^a	r^2	RSD	Data quality level	MDL^b (mg/kg)
As	2 - 5646	2 - 3920	80	0.93	11.2	Quantitative	2
Cd	0 - 447	12 - 613	51	0.26	31.5	Qualitative	
Cu	3 - 5140	3 - 12436	71	0.85	12.3	Quantitative	3
Mn	6 - 38267	0 - 95478	79	0.71	16.2	Quantitative	
Ni	1 - 84	29 - 617	81	0.42	11.9	Qualitative	1
Pb	5 - 40398	2 - 74356	79	0.89	8.8	Definitive	5
Zn	3 - 25389	35 - 60820	80	0.87	7.5	Quantitative	

^{a}n < 81 signifies where metal concentration was below the limit of detection of the FPXRF instrument; ^{b}MDL=Method Detection Limit
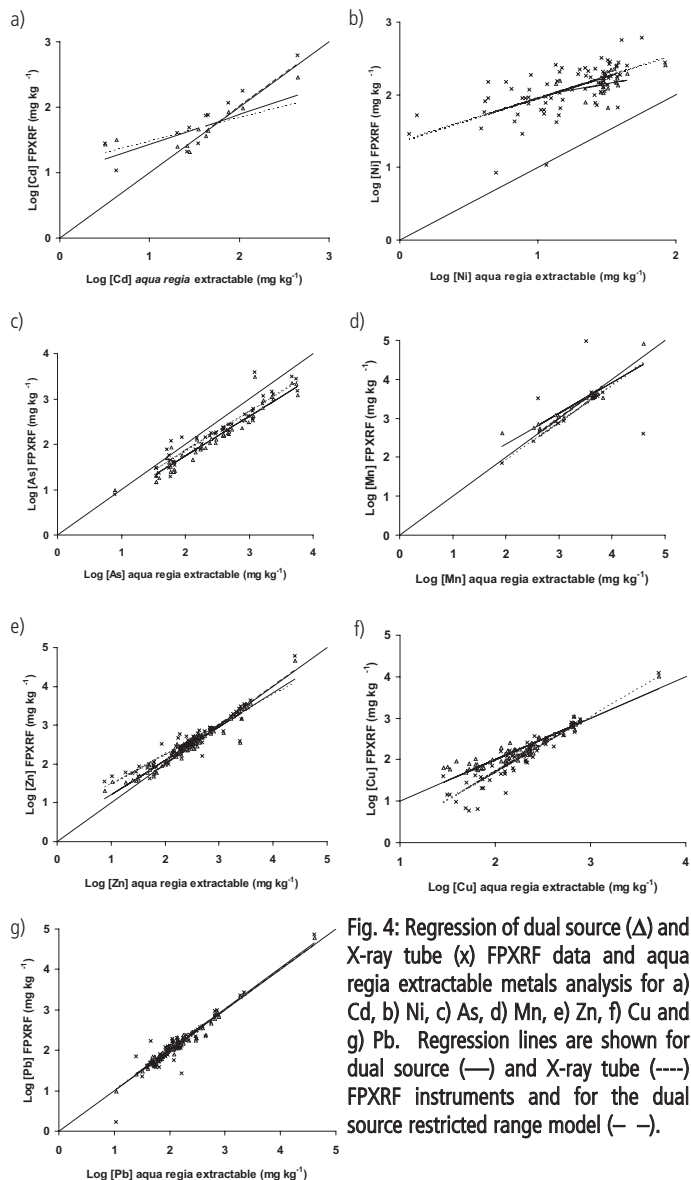
a) through g) regression plots

Fig. 4: Regression of dual source (Δ) and X-ray tube (x) FPXRF data and aqua regia extractable metals analysis for a) Cd, b) Ni, c) As, d) Mn, e) Zn, f) Cu and g) Pb. Regression lines are shown for dual source (—) and X-ray tube (----) FPXRF instruments and for the dual source restricted range model (– –).

Table 6: Advantages and limitations of using FPXRF over *aqua regia* extraction/ICP-OES

Advantages	Limitations
Can be used as a screening tool to design a targeted sampling strategy	Does not negate the need for laboratory analyses as these are a regulatory requirement
Can be used to supplement laboratory analysis	Detection limits and method limits of detection require careful consideration
Portable field equipment	More reliable for some metals than others
Quick (approximately 3 minutes *in situ* and, with mobile laboratory with drying and grinding facilities, 10 minutes *ex situ* including sample pot preparation)	Heterogeneity of the sample may affect the results
Multi-element characterisation	
No extraction necessary	
On site decision making at both the site investigation and remediation stages	
Allows prioritisation of sample analysis	

ACKNOWLEDGEMENTS

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Table 5. Dual source FPXRF data set showing the metal concentration at which the definitive quality criteria were met

Analyte	*Aqua regia* extractable analyte concentration (mg/kg)	r[2]	RSD	Data quality level	Percentage of data within definitive range	MDL[a] (mg/kg)
Cd	>20	0.92	5.6	Definitive	80	50
Mn	>330	0.91	4.3	Definitive	95	330
Zn	>51	0.89	5.4	Definitive	79	51

[a]MDL=Method Detection Limit

5   CONCLUSIONS

The dual source FPXRF instrument was able to produce definitive quality data for As, Cd, Cu, Mn, Pb and Zn and the X-ray tube FPXRF instrument was able to produce definitive quality data for Pb, but achieved a low accuracy in the measurement of Ni and Cd. Although the level of data produced by FPXRF for some metals was quantitative or qualitative, the results from traditional analysis gathered as part of the site investigation process could be used to calibrate the FPXRF data to provide site specific models for some metals (e.g. Cd, Ni). This would allow the user to predict the *aqua regia* extraction/ICP-OES concentrations, allowing a much larger number of samples to be analysed using the more cost-effective FPXRF. The FPXRF is a powerful tool useful in screening sites for major metal and metalloid contaminants, and a summary of its main advantages and limitations is presented in Table 6.