



Short communication

Comparison of soil pollution concentrations determined using AAS and portable XRF techniques

Tanja Radu, Dermot Diamond*

CLARITY: Centre for Sensor Web Technologies, National Centre for Sensor Research, School of Chemical Sciences, Dublin City University, Dublin 9, Ireland

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ABSTRACT

Past mining activities in the area of Silvermines, Ireland, have resulted in heavily polluted soils. The possibility of spreading pollution to the surrounding areas through dust blow-offs poses a potential threat for the local communities. Conventional environmental soil and dust analysis techniques are very slow and laborious and consequently there is a need for fast and accurate analytical methods, which can provide real-time in situ pollution mapping.

Laboratory-based aqua regia acid digestion of the soil samples collected in the area followed by the atomic absorption spectrophotometry (AAS) analysis confirmed very high pollution, especially by Pb, As, Cu, and Zn. In parallel, samples were analyzed using portable X-ray fluorescence radioisotope and miniature tube powered (XRF) NITON instruments and their performance was compared. Overall, the portable XRF instrument gave excellent correlation with the laboratory-based reference AAS method.

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1. Introduction

Contamination of soil by heavy metals is an important environmental problem and in particular hotspots often occur around mining facilities in rural areas. The area of Silvermines in County Tipperary, Ireland, was for many years the centre for mining silver and barium. When mining operations ceased in 1993, the area was left with heavily polluted soils. The possibility of contamination of the surrounding areas through carriage by wind is of particular concern. Soil contamination of herbage was linked to several reported incidents of cattle deaths in the area [1]. Also, episodes of toxic dust blow during dry periods pose a constant treat for the local community. In 2000, the Environmental Protection Agency (EPA) of Ireland published a report on the problem of pollution in the Silvermines area [2], which highlighted local levels of lead, cadmium, arsenic, zinc, copper and mercury. The report concluded that the area is a safe place to live and to work, provided that certain precautions are taken and an active monitoring program exists in the area [2].

Heavy metals in soil can be detected by several conventional analytical techniques such as electrochemical methods, chromatographic separation and spectroscopic techniques. Analysis by atomic absorption spectrophotometry (AAS) is a well-known

method for the detection of metals in aqueous samples. However, extraction procedures for heavy metals from soil samples typically involve lengthy process that requires the use of harsh conditions. For example, the aqua regia method requires boiling of samples and the use of concentrated HCl and HNO₃ for pseudo total extraction of trace metals [3]. Clearly, the capability to perform direct, in situ analysis of solid soil samples, without the need for digestion as is potentially available through portable XRF instruments would be a major step forward. Rapid pollution monitoring is especially important in instances of toxic dust blow-offs, as timely on-site analysis and fast decision making are of the highest importance, in order to protect the health of local communities.

Handheld Thermo Scientific NITON energy-dispersive X-ray fluorescence (EDXRF) analyzers ("portable XRF analyzers") are able to perform fast and non-destructive analysis of environmental samples, including soils, dust collected on air monitoring filters or wipe samples, rocks, and metal samples. Providing simultaneous analysis of up to 25 elements, this technique significantly cuts the time required for sample characterization. The instrument can operate in several measurement modes, including bulk sample, thin sample and lead in paint testing.

Several official methods such as Environmental Protection Agency (EPA) Method 6200 [4] and National Institute for Occupational Safety and Health (NIOSH) Method 7702 [5] now involve the use of portable XRF technology. In addition it is being increasingly highlighted by numerous researchers for the determination of metals in soil [6–11] and air filters [12,13].

* Corresponding author. Tel.: +353 1 700 5404; fax: +353 1 700 8021.
 E-mail addresses: Tanja.Radu@dcu.ie (T. Radu), Dermot.Diamond@dcu.ie (D. Diamond).

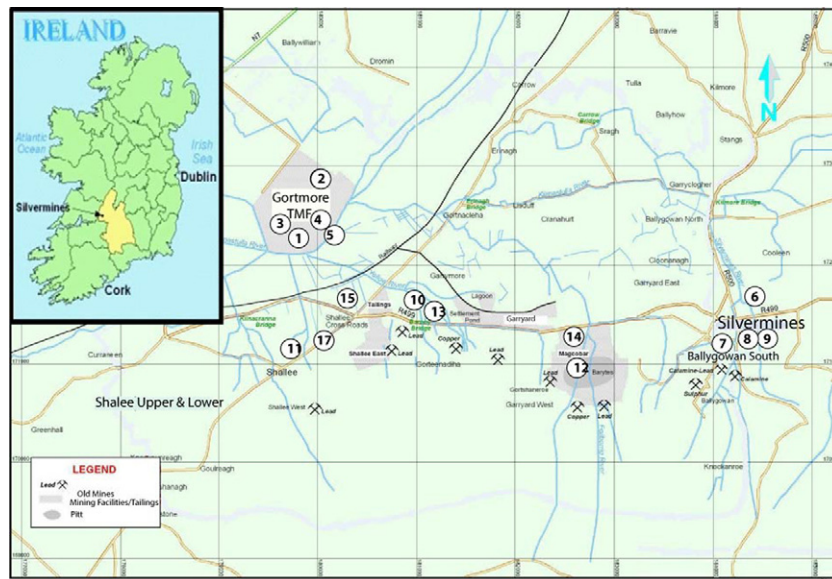


Fig. 1. Soil sampling locations centred on Silvermines, Co. Tipperary, Ireland.

2. Materials and methods

17 soil samples were collected in the area of North Tipperary, Ireland, including the village of Silvermines and abandoned mining sites. A detailed map of sampling locations is given in Fig. 1. Sampling locations included the Gortmore Tailing and Mining Facilities (TMF) (samples 1–5), Silvermines village (samples 6–9) and the surrounding area (samples 10–17). The areas of Gortmore TMF and Ballygowan (south of village Silvermines, see Fig. 1) were identified as pollution hotspots in the Final report of the Expert Group for Silvermines County, Tipperary [2]. The topsoil samples were collected, stored in a polyethylene bags and kept on ice until brought to the laboratory. In the laboratory, soil samples were spread on trays and air-dried at ambient conditions. After this, soil was ground by mortar and pestle, passed through a 1 mm mesh sieve and oven-dried at $\sim 50^{\circ}\text{C}$ for 48 h. The samples were then stored in polyethylene bags. Before being used, the samples were re-homogenized.

The soil samples were digested using the 11466 ISO standard method (the aqua regia digestion method) [3]. 3 g of soil was placed in a 100 mL round bottom flask with 21 mL of concentrated HCl (35%) and 7 mL concentrated HNO_3 (65%). The solution was kept at room temperature overnight before a water condenser was attached and the solution heated to boiling for 2 h. 25 mL of water was added down the condenser before filtration of the mixture through using a Whatman No. 42 filter. The filtered residue was rinsed twice with 5 mL of water and the solution was made up to 100 mL. All solutions were prepared with Milli-Q deionised water. The above procedure was also used to obtain a blank and control samples and all samples were blank-corrected.

Concentrations of Pb, As, Cu, and Zn in the digested samples were determined using AAS (Varian SpectraAA50). Calibration was carried out using standard solutions, and the instrument was adjusted to 283 nm, 193.7 nm, 324.7 nm, and 213.9 nm, for Pb, As, Cu, and Zn, respectively. For samples with very high levels of contamination, the digested soil solutions were diluted by a factor of 10 to bring them within the calibration range.

The portable XRF instruments used in this work were obtained from Thermo Scientific NITON UK. Two instruments were used: the XLP 703 Cd-109 source analyzer and the XLT 793 miniaturized X-ray tube for thin sample and bulk (soil) sample analysis. In both cases, operation involves a simple “point and shoot” technique. Prior to sample analysis, an internal instrument calibration was performed. All samples were analyzed using the bulk mode for soil sample. Each sample was analyzed for 45 s per sample. During the XRF trial, soil samples were analyzed through a freezer bag. An empty freezer bag was analyzed as a blank sample and all sample measurements were blank-corrected.

Statistical analysis of data was performed using Origin 6.0 and Microsoft Excel Analysis ToolPak. Linear regression was used to correlate AAS and XRF data, and each data set checked for potential outliers. Any measurement where the ratio of the calculated residual of the regression model and the standard error was larger than 2, was considered to be an outlier. Confidence bands were calculated using 95% limits.

3. Results and discussion

Initially, soil samples were digested by the aqua regia acid digestion method and the concentration of heavy metals was determined

Table 1

Summary of the results obtained from AAS and XRF analysis of Pb (tube and isotope instrument), As (tube), Cu (tube), and Zn (tube) for 17 samples collected from the Silvermines area. Concentrations are expressed in units of ppm. \pm Represents standard deviation.

	Pb (ppm)			As (ppm)		Cu (ppm)		Zn (ppm)	
	AAS	XRF tube	XRF isotope	AAS	XRF tube	AAS	XRF tube	AAS	XRF tube
Max	30,000 \pm 3,000	32,000 \pm 3,000	37,000 \pm 3,000	1230 \pm 90	1400 \pm 90	910 \pm 60	1250 \pm 90	9000 \pm 600	13,000 \pm 1,000
Min	80 \pm 6	24 \pm 2	40 \pm 3	^a	^a	10 \pm 1	^a	260 \pm 20	37 \pm 3
Average	800 \pm 600	7,100 \pm 500	7,900 \pm 600	350 \pm 30	440 \pm 30	230 \pm 20	220 \pm 20	2900 \pm 200	3,000 \pm 300
Mean	5,000 \pm 300	5,300 \pm 300	5,400 \pm 300	860 \pm 60	370 \pm 30	110 \pm 10	260 \pm 20	930 \pm 60	1,040 \pm 60

^a Concentration below limit of detection.

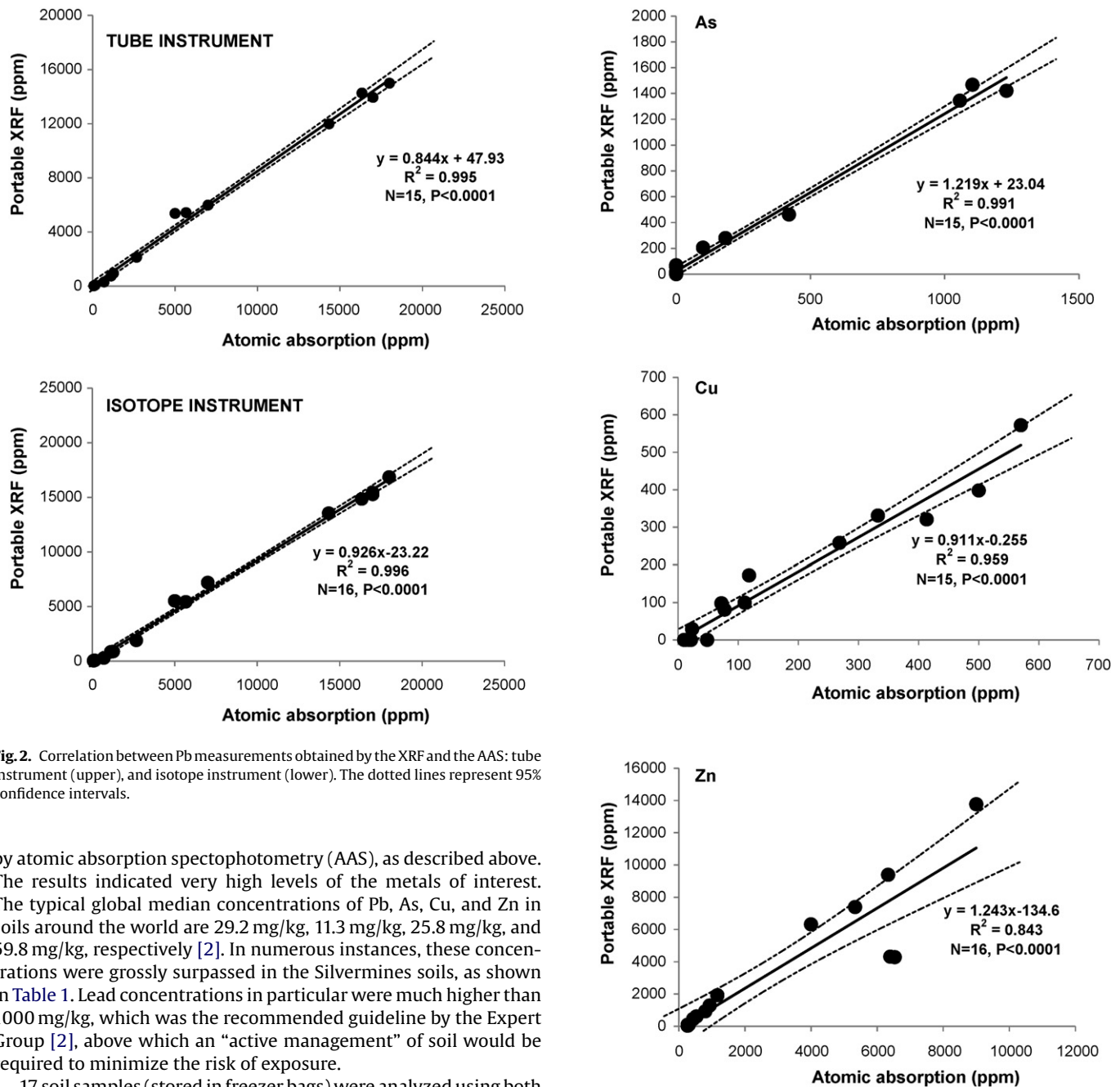


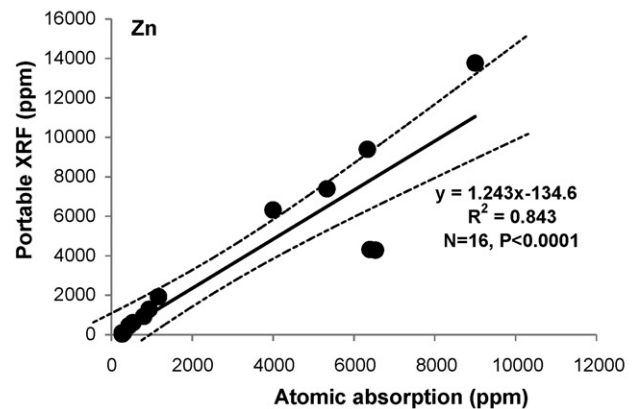
Fig. 2. Correlation between Pb measurements obtained by the XRF and the AAS: tube instrument (upper), and isotope instrument (lower). The dotted lines represent 95% confidence intervals.

by atomic absorption spectrophotometry (AAS), as described above. The results indicated very high levels of the metals of interest. The typical global median concentrations of Pb, As, Cu, and Zn in soils around the world are 29.2 mg/kg, 11.3 mg/kg, 25.8 mg/kg, and 59.8 mg/kg, respectively [2]. In numerous instances, these concentrations were grossly surpassed in the Silvermines soils, as shown in Table 1. Lead concentrations in particular were much higher than 1000 mg/kg, which was the recommended guideline by the Expert Group [2], above which an “active management” of soil would be required to minimize the risk of exposure.

17 soil samples (stored in freezer bags) were analyzed using both the isotope- and the miniature tube-powered portable XRF NITON instrument. For each sample, the instruments generate emission spectra with the major analytical peaks identified, transferred to a PC, and concentrations of elements estimated in ppm. Even though this methodology provides simultaneous analysis of 25 elements, focus was directed towards Pb, As, Cu, and Zn, as these metals were previously identified as the major contaminants in the area. The instrument's limit of detection for the above metals in soil samples is 13 ppm, 11 ppm, 35 ppm, and 25 ppm, respectively.

Fig. 2 shows the correlation between the XRF and AAS measurements of lead concentrations, using isotope- and miniature tube-powered instruments, operating in the bulk mode. For both instruments, an excellent agreement of the two techniques was achieved. R^2 values of 0.995 and 0.996 were obtained for the tube and isotope instrument, respectively. This confirmed an excellent performance over a range of concentrations. Similarly, a very good correlation between the flame AAS and the portable XRF techniques was reported by Clark et al. [8]. However, it should be appreciated

Fig. 3. Correlation between As (top), Cu (middle), and Zn (bottom) measurements obtained by the miniature X-ray tube powered XRF and the AAS. The dotted lines represent 95% confidence intervals.



that lower concentrations of metals in soils are more likely to occur in normal environmental samples, and some of the soils used in this research contain unusually high concentrations of pollutants. The soil detection mode used primarily for this work is a unique method of combination of fundamental parameters (FP) mode with Compton normalisation (for background matrix automatic correction). This method is excellent for analysis of metals in typical soil samples with concentrations <1% and certainly no greater than 3%. Other detection modes available on the instrument would be more suitable for those samples containing unusually high concentrations of analytes, for instance the mining mode (full FP capability up to high concentrations) or even empirical calibration options. The above data indicated that the both instruments appear to be

technically suitable for analysis of the targeted elements. Due to so close correlation of the two instruments, and because the tube instrument is the latest technology, further results will be shown only for the miniature tube-powered instrument.

Interestingly, both XRF instruments (tube and isotope) showed slightly negative bias versus reference laboratory method (AAS) on measurements of lead. Similar observations were made by Shefsky et al. [10] and Clark et al. [8] and attributed to the size of sample particles. However, the bias most likely originates due to the hereby used methodology for analysis of the samples with unusually wide distribution of concentrations, as explained in the previous paragraph.

Comparison of the data obtained from As, Cu, and Zn analysis is given in Fig. 3. In all three instances satisfactory correlations were achieved (R^2 values for As, Cu, and Zn were 0.991, 0.959, and 0.843, respectively). Where necessary, outliers were calculated and removed when performing linear regression. In most cases, the reported XRF values were slightly biased when compared to that of the AAS analysis, with the slope being lesser than one for Pb and Cu, and slightly more than one for As and Zn analysis. Fig. 3 shows some deviations of values for concentrations of examined metals especially in the region of high concentrations. We suspect that the soil detection mode contributes to the bias especially in the region of unusually high metal concentrations.

4. Conclusions

The long history of mining activities in the Silvermines area of Co. Tipperary, Ireland, has left behind highly polluted soil. This soil poses a constant threat to local communities, due to the possibility of pollution spreading to the surrounding areas. Results of the AAS analysis presented in this research confirm high soil pollution from heavy metals in the area. Even though the AAS technology is widely recognized used and very precise, it is very expensive, laborious and slow. Since Silvermines area is under a constant risk, there is a need for a fast and reliable analytical methodology that can be fast, low cost and performed in field conditions.

In addition, portable XRF instruments such as the NITON model tested in this research are highly correlated with AAS but do not require sample digestion. In principle, these instruments could be employed to provide rapid in situ detection of the presence of toxic metals such as Pb, As, Cu, and Zn in soil samples.

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