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ORIGINAL ARTICLE

Comparison between inductively coupled plasma and X-ray fluorescence performance for Pb analysis in environmental soil samples

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Abstract Comparison of two conventional analytical techniques such as X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) for measuring Pb concentrations in soil samples was achieved using field and laboratory work. Seventy-three samples were collected from urban areas surrounding the large lead smelter at South Australia, as an indicator of the environment impact of smelter activity. Soil Pb concentrations were determined using hand-held XRF analyser under laboratory conditions. ICP-MS analysis on digested soils (using a microwave-assisted nitric acid digestion-extraction) was applied to validate p-XRF data. The analysis showed that Pb concentrations determined by XRF correlated with high linearity with Pb concentrations determined by ICP-MS measurements ($R^2 = 0.89$). Statistical test (t test) was applied to the data of both methods applied without any significant difference between the two techniques. These results indicated that ICP-MS corroborated XRF for Pb soil measurements and suggests that XRF was a reliable and quick alternative to traditional analytical methods in studies of environmental health risk assessment, allowing for much larger sampling regimes in relatively shorter times and could be applied in the field.

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Introduction

Lead (Pb) is a toxic heavy metal and common environmental contaminant which can represent significant threats to public health at high concentration levels (Kachenko and Singh 2006; WHO 2010). Due to frequent hand-to-mouth childish behaviour, elevated blood lead levels (BPb) in children can result from elevated Pb concentration in dust and soil. (Zia et al. 2011). The accumulation of Pb in the kidney, liver, teeth and bones can be associated with negative health effects including inhibited brain development and haematological effects, such as anaemia (Bray et al. 2009; WHO 2010). Since 1889 the emission of dust particles from South Australia's smelter led to identify three different area, according to levels of risk: high, medium and low, based on the mean BPb, an accurate bioindicator of environmental lead exposure detected on children under five years (Maynard et al. 2005). From a previous survey in south Australia, which included 1239 children, representing 50% of the elementary school population near the lead smelter, 7% of them showed a lead capillary blood level equal to or greater than 30 µg/dL, which is considered by Australian National Health and Medical Research Council (ANHMRC) as "level of concern" (Wilson et al. 1986). A comparison between energy-dispersive X-ray fluorescence (EDXRF) and ICP-OES after microwave digestion of some major and minor elements (K, Ca, Mn, Fe, Cu, Sr, Pb and Zn) in four higher plants growing on the waste landfills surrounding and abandoned Pb–Zn ore concentration factory was performed using (EDXRF) instrument, where no statistically significant differences at the 98% confiner

level were found between EDXRF and Dig A results concerning some elements like Ca, Pb, while significant differences were found for others elements like K, Mn due to the presence of a silica residue (Margui et al. 2005). A summary of the lead issues and factors influencing perception of risk related to environmental lead exposure in Port Pirie (early 1980s) and Esperance (2007/2008) areas was presented by University of Wollongong (Australia) (Heyworth et al. 2009). A comparison study of ICP-OES and XRF for Pb and As performed for soil samples in Chihuahua City (Chihuahua, Mexico) showed no significant differences between the instrumental techniques for As concentrations, while in Pb case there were significant differences between these instruments (Delgado et al. 2011). XRF could provide less expensive, on-site measurements of soil Pb with the advantage of allowing chemical assessment of contamination in close to real time (Rouillon and Taylor 2016).

Nyrstar smelter

The Nyrstar Port Pirie smelter is one of the largest smelters in the world, producing approximately five per cent of the global Pb production (Tiller 1976; Kutlaca 1998; Van Alphen 1999; Taylor 2012). The children in this area have high BPb levels which were often associated with Pb deposition from smelter emissions or exposure to historic lead dust and soil contamination (Simon et al. 2013). The Nyrstar Port Pirie smelter is situated at the northern end of the town as shown in Fig. 1. The study area extended to a buffer zone of 5 km radius from the Nyrstar smelter, which was large enough to encompass all residential areas as well as covering a risk area that contained soil and dust with highest levels of lead contamination.

The town of Port Pirie is located on the eastern shore of the Spencer Gulf, 230 kms north of Adelaide, in South Australia. The small provincial city population of approximately 13,206 (Australian Bureau of Statistics 2006) covers an area of 18 km^2 and lies on a flat coastal plain between 10 and 30 km wide (Kutlaca 1998). Port Pirie is low-lying land, placed in a region with a warm semi-arid climate, fairly dry, dusty and mostly sparsely vegetated (Kutlaca 1998).

The dental clinic monitoring site (located near the smelter from 2008 to 2011) reported that the winds direction varies on a daily basis and the principal direction extends from NNW to SSE but varies with the seasons, emanating from the NW in the winter and from the SE in the summer. The average annual precipitation is around 345 mm year^{-1}, and the mean evaporation/precipitation ratio is approaching 6.5/1 (Kutlaca 1998). Port Pirie has been affected by Pb smelting emission for more than 120 years. The study area Fig. 2 included urban and rural populations which were exposed from old deposits of Pb and the current Pb emission from smelting and refining, which results in considerable contamination of the surrounding soil and is considered the major source of elevated blood Pb in children (Taylor et al. 2011). The highest Pb concentration in the surface soil was detected within 2 km of the smelter (kutlaca 1998), with average Pb soil concentration varying from 50 to 500 ppm (Tiller 1976).

Experimental methods, materials and apparatus

Soil sampling

Sampling sites were initially selected using aerial photographs (10 cm resolution, in the map grid of Australia (MGA) zone 54 as projection) of Port Pirie provided by Aerometrex Pty Ltd; taken on 25 February 2011 (http://aerometrex.com.au) and displayed using ArcMap 10.2.

Soil samples were collected at the four corners of a 1×1 km grid with one additional sample taken in the centre (Fig. 2a). Preliminary sampling locations included occupied houses, vacant lots, abandoned houses, communal areas (i.e. playgrounds), kindergartens, schools or other non-residences such as vacant land across the river, 500 m east of the smelter. Sites within privately owned properties were not sampled. Sampling locations were chosen to avoid obvious obstructions such as roads and buildings and as such were the nearest site of free soil that would enable sample collection. A final map of the study area based on SA Census Bureau boundaries (2011) shows all sampling locations and the smelter site (Fig. 2b). A total of 73 samples were collected in 2012 in three separate field trips over a period of three months (May, July and December) from within a 5 km radius of the Nyrstar smelter hereafter referred to as the buffer zone (a 5 km buffer was chosen containing all the town, regions and localities to be covered in the study). In addition, two background samples were collected outside the buffer zone. The geographical coordinates of each soil site sampled are 219392, 6320620 and 223392, 6320620. At each sampling location, a total of 3 discrete bare surface soil samples (0–5 cm) were collected. Sampling was operated at the surface (2–5 cm deep) because the upper soil layer is representative of lead contamination due to accumulation in urban soils (Wu et al. 2010).

Analytical methods and apparatus

XRF measurements

Portable X-ray fluorescence (XRF) instruments potentially offer a rapid (within seconds) and relatively inexpensive screening technique for measuring metal contamination in
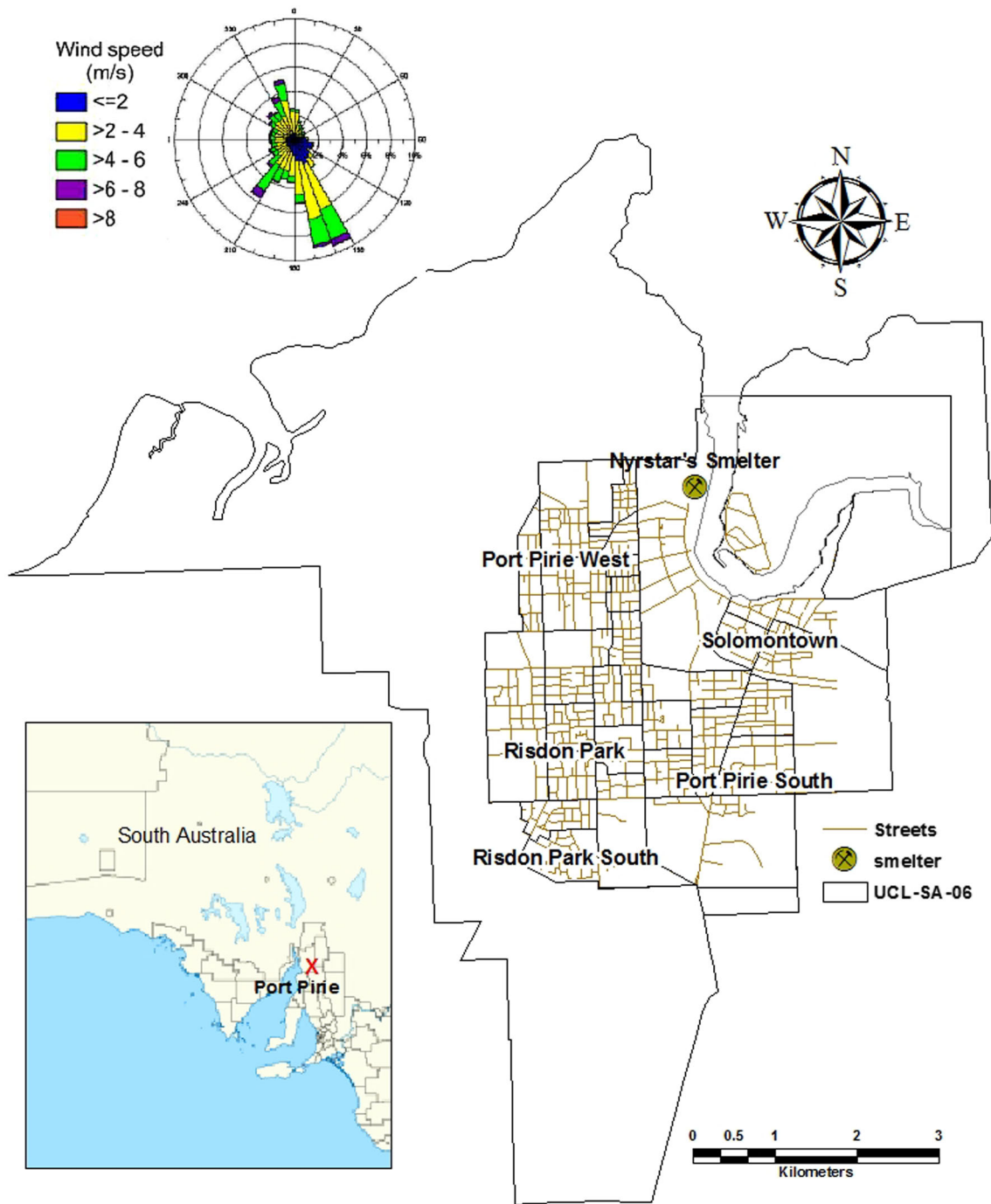
Fig. 1 Map of study location based on SA Census Bureau boundaries (2011) and the annual average wind rose sourced from Public Environmental Report (Thomas et al. 2013), the prevailing winds emanate principally from the SE in summer and from the NW in winter

soils. XRF is an alternative analytical technique widely used for quantitative determination of the chemical composition of several types of geological or industrial samples: rocks, soils, sediments, cement (Delgado et al. 2011; Congiu et al. 2013). XRF spectrometer with dispersion of energy (EDXRF), such as portable spectrometer, has achieved remarkable success for their capability of performing simultaneous multi-element analysis within seconds. Its applications include laboratory use, as well as in situ analysis of metals in soils and sediments, thin films, paints and coatings, oils and liquids, and hazardous waste. XRF is a non-destructive analytical technique allowing both qualitative and quantitative analyses of sample composition (Kalnicky and Singhvi 2001).

In contrast to all of these positive properties, there are some disadvantages. The critical penetration depth for
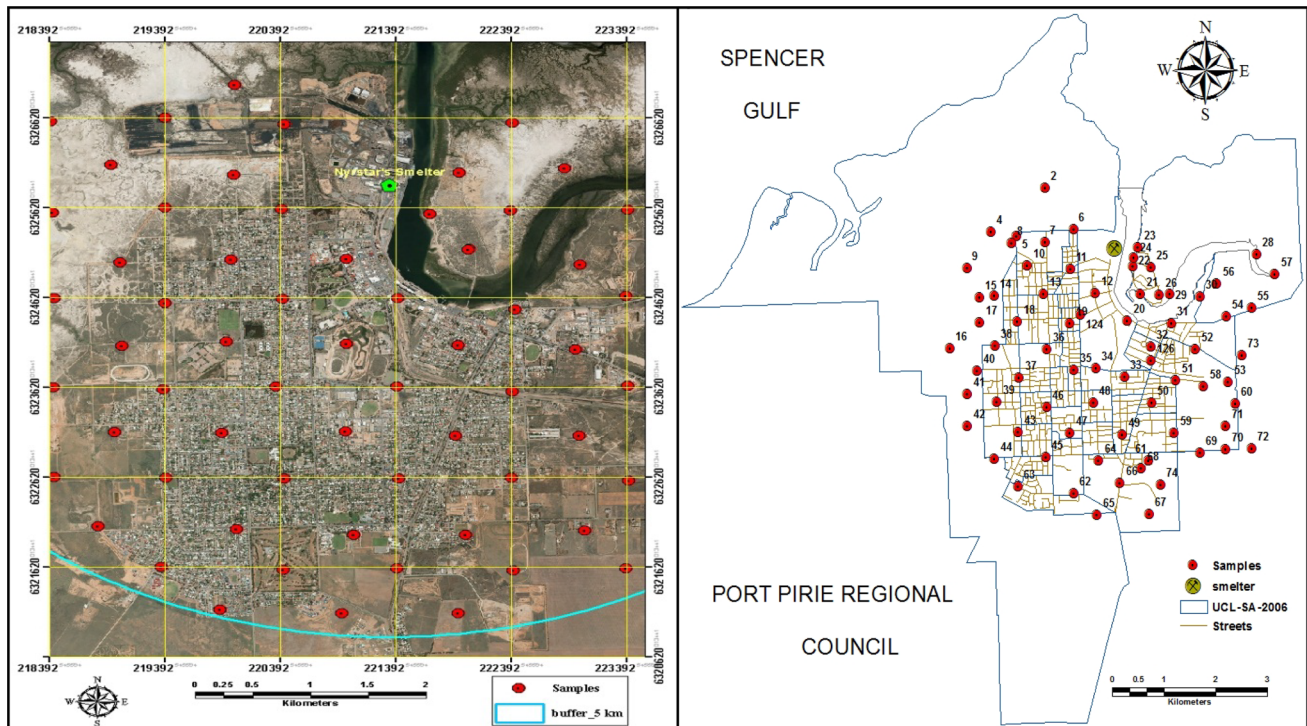
Fig. 2 Maps of study location showing **a** distribution of sampling points at the corners of (1 × 1) km MGA-zone 54 grid, and one sample in the centre within 5 km buffer from the Nyrstar smelter, **b** all sample numbers ($n = 73$) and locations (Al Maliki 2015)

fluorescence emission for lead in soil (considering mass absorption coefficient, density and the characteristic of instrumentation) is limited to the top layer (Kalnicky and Singhvi 2001). This requires a perfectly homogeneous sample which often occurs naturally but must sometimes be produced by acid dissolution into liquids or by grinding and the preparation of pressed pellets (Gauglitz and Vo-Dinh 2003). In addition, instrumentation is fairly expensive not widely available and detection limits are higher than ICP technique. XRF as a rapid, inexpensive and easy-to-use method is one possible alternative for estimating soil Pb in certain situations. For example, for a routine estimation of total Pb in a large number of soil samples taken at a given site, to monitor changes in soil Pb content at a given site or to estimate variability in total Pb in soil at a particular site.

XRF was used in the laboratory under supervision of the radiation certified operator to assess the potential of the technology to predict Pb concentration. Total contents of Pb and other metals were determined using a Thermo Scientific portable NITON XL3 XRF analyser; measurement conditions included a counting time of 30 s with three replicates per sample. The samples was measured with two modes, soil and mining. The XRF analyser was calibrated with National Institute of Standards and Technology (NIST) reference standards, specifically NIST 2780 (for the mining mode standard which is generally used for higher

concentration samples) and Resource Conservation and Recovery Act RCRA (for the soil mode standard) and Montana soil 2711 Standard Reference Materials (SRM). The analyser was initially calibrated with standards at the factory and subsequently the calibration adjusted particularly with Pb measurement by Portable Analytical Solutions Pty Ltd on 03-September-2012. More details about calibration and sample preparation are mentioned on (Mejía-Piña et al. 2016). Homogenized dried soil sample (80 g) was placed in plastic Petri-dish (90 × 15 mm) and the soil directly analysed with the hand-held XRF analyser. The analyser reported concentrations in milligrams of metal per kilogram of soil or parts per million (ppm). Standards for sealed material analysed in polyethylene XRF sample cups were new. The XRF value determined for standards agreed well with the actual value. For example, the value determined here for RCRA of 456 ± 36 ppm was in a good agreement with slandered reference of 500 ppm for it, and also the concentration value of 1052 ± 31 for SRM of Montana soil 2711 was near to reference value of 1164 for it.

Soil chemical analysis and digestion

In order to verify the soil Pb concentrations obtained via XRF, Pb concentrations were also determined via ICP-MS, following microwave-assisted digestion with *aqua regia* using
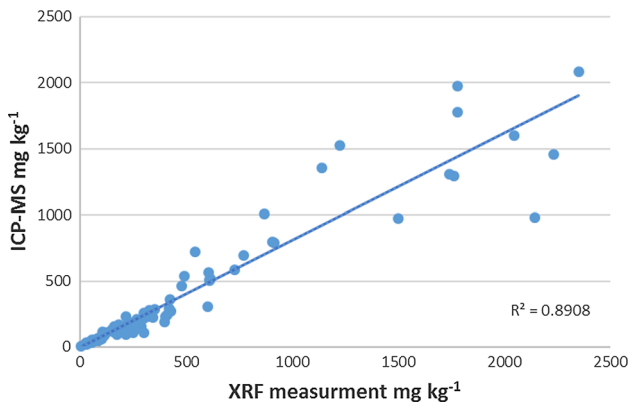
Fig. 3 Comparison between Pb concentrations measured in Port Pirie soil using two different analysis methods (XRF and ICP-MS)

the recommended USEPA method 3051 (USEPA 1998). Dried soil (0.250 g, <2 mm) was weighed into a Teflon microwave digestion vessel and cold digested for 10 min with freshly prepared *aqua regia* (10 mL). The microwave digestion vessel was subsequently sealed and heated with a suitable laboratory microwave-accelerated reaction system (MARS), using the recommended USEPA Method 3051 A *aqua regia* dissolution procedure (USEPA 1998). Each batch (20 samples) of microwave vessels included "5%" or "1/20" sample blanks (acid with no soil), 5% Standard Reference Materials (SRM)—Montana 2711 (available from the National Institute of Standards and Testing NIST) and 5% duplicate soil samples. Digested solutions were subsequently cooled for at least 15 min, before being opened carefully and the vessel contents (sample digests) washed down with 0.1% Mallinckrodt HNO_3 into 50-mL volumetric flasks and allowed to stand overnight prior to filtering through 0.45-μm filters directly into ICP sample tubes. Prior to analysis, samples were diluted up to 40 times with 0.1% (v/v) HNO_3. Major and trace element contents in the dilute soil digests and extracts were determined directly by inductively coupled plasma—mass spectrometry (ICP-MS) (using Octopole reaction system,

Agilent model 7500ce). The performance of the spectrometer was evaluated every 5–10 measurements during a run by including a continuous check of variation (CCV), (i.e. samples of a known 50 μg/L concentrate in an aqueous 2% (v/v) HNO3 solution). Likewise, periodic assessment of blank samples indicated no general contamination.

Statistical analysis

Microsoft excel 1997–2003 was used for all statistical procedures, and analysis of variance (ANOVA) was applied to evaluate the significance of relationships between heavy metal concentrations and other environmental parameters. The Student's t test was applied to assess the significance of variances found in heavy metal concentrations, especially Pb concentrations between different procedures.

Results and discussion

While ICP-MS has been commonly used as a reliable method for accurately determining metal concentrations at low levels (Griffith et al. 2009), it has the disadvantage of

Table 1 Statistical analysis for Pb concentration in six soil samples using two different methods

Sample ID	XRF ($n = 73 \times 20$)			ICP-MS ($n = 73 \times 2$)		
	Av	SD	Error (%)	Av	SD	Error (%)
5	638	48	7.5	729	74	10
14	543	52	9.6	611	167	27
124	2271	178	7.8	2350	297	13
32	1625	297	18.3	1779	62	3
42	162	11	7	266	7	3
44	30	4	13	39	11	29
Average	878	98	11	962	103	14

Fig. 4 Comparison between two analysis methods indicated the reliability of XRF in designating soil Pb. Numbers on columns refer to the concentration recorded, *error bars* are one standard deviation of the mean. XRF (*blue*), ICP-MS (*red*)
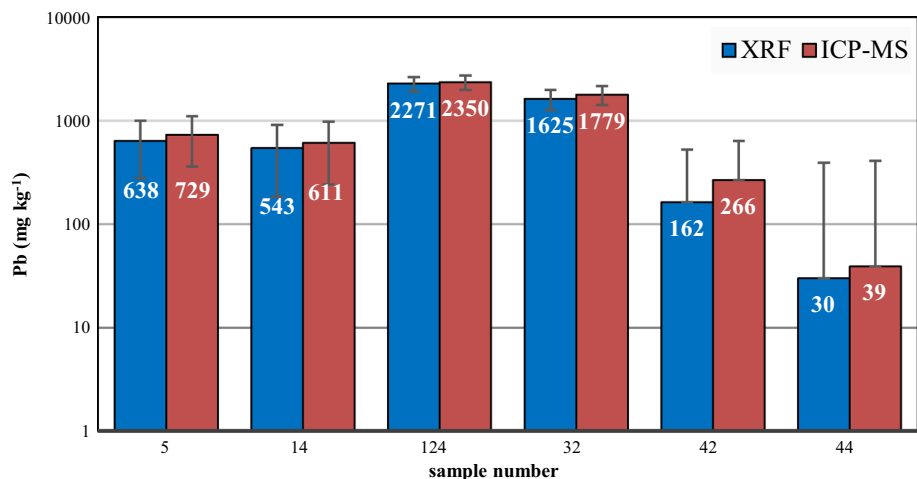
Table 2 Comparison between the two analytical methods used to determine soil Pb

Pb soil data	XRF ($n = 73 \times 20$)			ICP-MS ($n = 73 \times 2$)		
Parameter	Skewness	Kurtosis	SD	Skewness	Kurtosis	SD
Raw data	2.50	10.90	670	3.01	14.9	790
Log-transform	−0.10	2.74	1.26	−0.41	3.91	1.23

requiring significant sample preparation, which XRF does not. Previous studies indicates that field-portable XRF analysis is capable of detecting soil lead levels comparable to those detected by digestion in samples sieved to less than 2 mm in a laboratory (Markey et al. 2008). Soil Pb concentrations determined by XRF correlated with high linearity with Pb concentrations determined by ICP-MS measurements ($R^2 = 0.89$; Fig. 3). A t test showed that there was no statistical significant difference between ICP-MS- and XRF-determined soil Pb concentrations at the 5% probability level ($P = 0.0011$). These results indicated that ICP-MS corroborated XRF for Pb soil measurements and showed that XRF was a reliable and quick alternative for Pb determination in soils. Moreover, the average XRF measurement ($n = 20$) for six validation samples with different levels of Pb (high, medium, low) was compared with the average Pb content analysed using ICP-MS ($n = 2$) to determine whether the detection limits of XRF were satisfactory across a range of concentrations (Fig. 4). Statistical analysis (Table 1) showed that the mean and standard deviation (SD) of predicted metal content from both methods were very similar with ideal p values ($P = 0.001$) and correlation coefficients $= 0.99$ across all concentration ranges. A comparison between percentage error in Pb contents determined by XRF and that determined by ICP-MS, reported in Table 1, shows that a similar level of precision can be reached by both techniques, although XRF requires a significantly higher number of replicates with respect to ICP-MS to this aim.

The XRF technique was also an appropriate technique for the analysis and distribution of soil Pb concentrations being less expensive than traditional acidic digestion, allowing for much larger sampling regimes in relatively shorter times. The results of the statistical analysis performed for both XRF and ICP-MS data sets ($n = 73$) are reported in Table 2, showing not significant difference between the two methods.

Conclusion

The elevated levels of surface soil Pb observed in this study were in agreement with previous studies in the same region and also supported the risk–area divisions used historically to describe areas within Port Pirie. XRF spectroscopy has the advantage of being less expensive

and faster than traditional analysis. It was highly correlated with ICP-MS determinations of Pb concentration obtained from traditionally wet chemical acidic digestion of soils. Thus, the XRF technique was appropriate for analysis and ensuing studies of the spatial distribution of soil Pb concentrations, allowing for much larger sampling regimes in relatively shorter times and could be applied in the field.

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