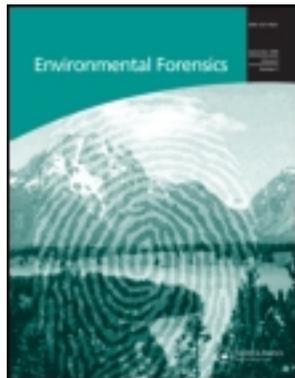


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How Reliable is X-Ray Fluorescence (XRF) Measurement for Different Metals in Soil Contamination?

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Although portable x-ray fluorescence (XRF) technology is widely accepted for environmental use in field screening test regarding the analytical approach, it needs to be evaluated with sufficient data and meet its performance characteristics to be employable for decision making purposes. Usually, for an XRF sample, the most interesting query is: How reliable is the XRF technique in detecting different targeted metals in soil? This study presents pairwise comparisons between the XRF and inductively coupled plasma atomic emission spectrometer (ICP-AES) results for individual elements of Ni, Cu, Zn, Pb, Cd, Cr, Hg, and As. The portable XRF analyzer was used to estimate the concentration levels of eight heavy metal elements, and then pairwise comparisons were made between the XRF and ICP-AES results. Results presented in this paper suggest that the use of XRF testing is highly reliable as a screening technique for the first sample group of metal element (Pb, Zn, Ni, and Cu) concentrations well in excess of the pollution threshold limits (PTLs). The order of reliability of the XRF measurements is Pb > Zn > Ni > Cu, and their relative proximity (RP) ranges from 85%–35%. In contrast, the results of another group of metal elements that include Hg, Cd, Cr, and As show poor correlation. Their RP ranges from 25%–2.3%.

Keywords: x-ray fluorescence (XRF), heavy metal, inductively coupled plasma atomic emission spectrometer (ICP-AES), soil pollution, relative proximity

During the year of 1970, industry was booming and great quantities of industrial wastes were dumped along the Erren River in Taiwan. Electronic waste recyclers and metal smelters accounted for approximately 80% of all illegal dumping activity along the Erren River. Since 2001, restoration of the Erren River has been ongoing and the Environmental Protection Agency (EPA) of Taiwan has spent NT\$ 50–60 million (Taiwan dollars) to clean up sites along the river even though funding for the clean-up effort has been difficult to secure. In 2007, a huge amount of hazardous contaminants of electronic wastes, which included stripped electronic circuit boards, plastic-coated metals, and unknown composites were found embedded in the subsurface soil on both sides of the riverbanks during a river-bank construction project along a 3-kilometer stretch down-

stream. This incident created some concern to nearby residents and gained high attention among environmental groups. The EPA then began to wonder how many other locations had the same situation as this incident case, which led to a comprehensive investigation for toxic contaminants within the river basin.

Currently, several laboratory experiments can detect contaminants in the form of heavy metals in soil. The two major methods used are the inductively coupled plasma atomic emission spectrometer (ICP-AES) and the atomic absorption spectrometer (AAS). Both of these methods require soil samples to be imported into the instrument as a solution in order to perform sample digestion or extraction of contaminants (Shefsky, 1997; Radu and Diamond, 2009). In this hazardous pollution incident, speedy pollution monitoring is needed, especially when urgency of detection is required in protecting the health of local communities. In these urgent cases, timely on-site analyses of hazardous contaminants for fast decision making are highly important (Radu and Diamond, 2009). Therefore, sufficiently accurate and well-documented field methods with speedy analytical results can offer significant

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advantages over laboratory methods for quick decision making necessary in these urgent situations. Field analysis requires less involvement of sample handling and transporting as well as chain-of-custody documentation compared to that of laboratory analysis, and, therefore, is often less expensive per sample allowing for a denser, more complete sampling (Shefsky, 1997; Shrivastava et al., 2005; Radu and Diamond, 2009).

One exemplary field method fitting the above criteria is the field portable x-ray fluorescence (XRF) technique, which has been extensively used in research and has several remarkable characteristics. Providing simultaneous analysis of up to 25 elements (Radu and Diamond, 2009), the portable device offers extremely rapid, cost-effective screening of heavy metals in soil by in-situ measurements (Shefsky, 1997). In addition, portable XRF analyzers have been successfully utilized for lead-based pollutant screening (Clark et al., 1999; Morley et al., 1999; Drake et al., 2003; Markey et al., 2008; Binstock et al., 2009) and can quickly and reliably provide lead concentration information for safety purposes (Drake et al., 2003). Further, this technique significantly cuts the time required for sample characterization (Morley et al., 1999; Bernick and Campagna, 1995; Song et al., 2001; Shrivastava et al., 2005; Markey et al., 2008; Radu and Diamond, 2009). Since XRF is completely non-destructive, any sample collected and measured in the field can be retained for verification in a laboratory (Shefsky, 1997; Somogyi et al., 1997; Kalnicky and Singhvi, 2001; Shrivastava et al., 2005; Radu and Diamond, 2009; Arenas et al., 2011). Ideally, this portable instrument has the capability to perform direct, in-situ analysis of concentrated soil samples without the need for laboratory digestion, which would be a major breakthrough in contaminant analysis (Radu and Diamond, 2009).

Several official methods such as the EPA Method 6200 (Environmental Protection Agency, 2007) and the National Institute for Occupational Safety and Health (NIOSH): Method 7702 (Drake et al., 2003; NIOSH, 1998) now involve the use of the portable XRF technology (Radu and Diamond, 2009). In addition, it is being increasingly highlighted by numerous researchers for the determination of metals in soil (Shefsky, 1997; Clark et al., 1999; Bernick et al., 1995; Carr et al., 2008; Mäkinen et al., 2005; Markey et al., 2008; Radu and Diamond, 2009; Arenas et al., 2011). Since XRF instruments have been extensively used for site measurements, the operator may be interested in its analysis results for various metals in comparison with the laboratory analysis (Markey et al., 2008; Drake et al., 2003; Song et al., 2001; Kalnicky and Singhvi, 2001; Carr et al., 2008; Arenas et al., 2011).

Since contaminant detection by the alternative XRF technique can replace the time consuming and costly conventional laboratory experiments with a rapid, cost-effective solution for conducting in-situ field sampling, one concern for the XRF operator is: How reliable is the XRF technique in detecting different targeted metals in soil? Therefore, this study presents how reliable and accurate the XRF tests are by comparing the results of an XRF analysis on 60 in-situ samples regarding eight heavy metal elements with the results of the ICP-AES experiments.

Table 1. Specifications of NITON XL-722

Source	Half-life (year)	Detector	Detection Element
Cd-109	1.3	SI PIN-diode	Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Zr, Mo, Pb, Hg, Rb
Am-241	470		Cd, Ba, Ag, Sn, Sb

The field XRF tests were conducted in the area of the Erren River Basin of Taiwan, and sixty samples were carried out by ICP-AES experiments simultaneously.

Materials and Methods

The portable field XRF model used in this work is the NITON XL-722, which is equipped with a Cd-109 radioisotope source and Am-241 radioisotope source. The specifications are shown in Table 1. The Cd-109 source with a measurement time of 800 s is used for detecting elements of chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), strontium (Sr), zirconium (Zr), molybdenum (Mo), mercury (Hg), lead (Pb), and rubidium (Rb). The Am-241 source with a measurement time of 200 s is used for elements of cadmium (Cd), silver (Ag), tin (Sn), antimony (Sb), and barium (Ba). With the confirmatory analysis using an ICP-AES, the laboratory-based aqua regia acid digestion (Radu and Diamond, 2009) was performed on the soil samples collected in the study area. The soil samples were digested using the method of standard ISO11466.2 (International Organization for Standardization, 1995) (known in Taiwan by EPA as NIEA S321.63B).

To comprehensively evaluate the raw data of XRF versus ICP-AES for these various elements, relative proximity (RP) was used. RP considers only the samples with values over the controlled threshold limit (i.e., over the pollution threshold limit (PTL), thus requiring monitoring). Therefore, the number of detected field samples of the ICP-AES results over the PTL divided by the number of detected XRF results over the PTL determines the RP, as shown in Equation (1):

$$RP = \frac{NO_{ICP-AES}}{NO_{XRF}} \quad (1)$$

Sampling Site

With approximately a 339-square kilometer drainage area, the Erren River is approximately 62.5 km long. It flows through Tainan County and Kaohsiung County, passes Tainan City, and runs into the Taiwan Strait. Six tributaries branching off of the Erren River from upstream to downstream are Ngau-Liao Creek, Ngau-Chou-Po Creek, Song-Zi-Jiao Creek, Shen-Keng-Zi Creek, Kang-Wei-Kuo Creek, and San-Yeh Creek (Figure 1).

The sampling site covering 339 km² was divided into 1,322 square grids. Each grid is with an area of 0.5 km by 0.5 km (Figure 2). An effective framework of site selection is for identifying and locating potential pollution sites within the Erren River

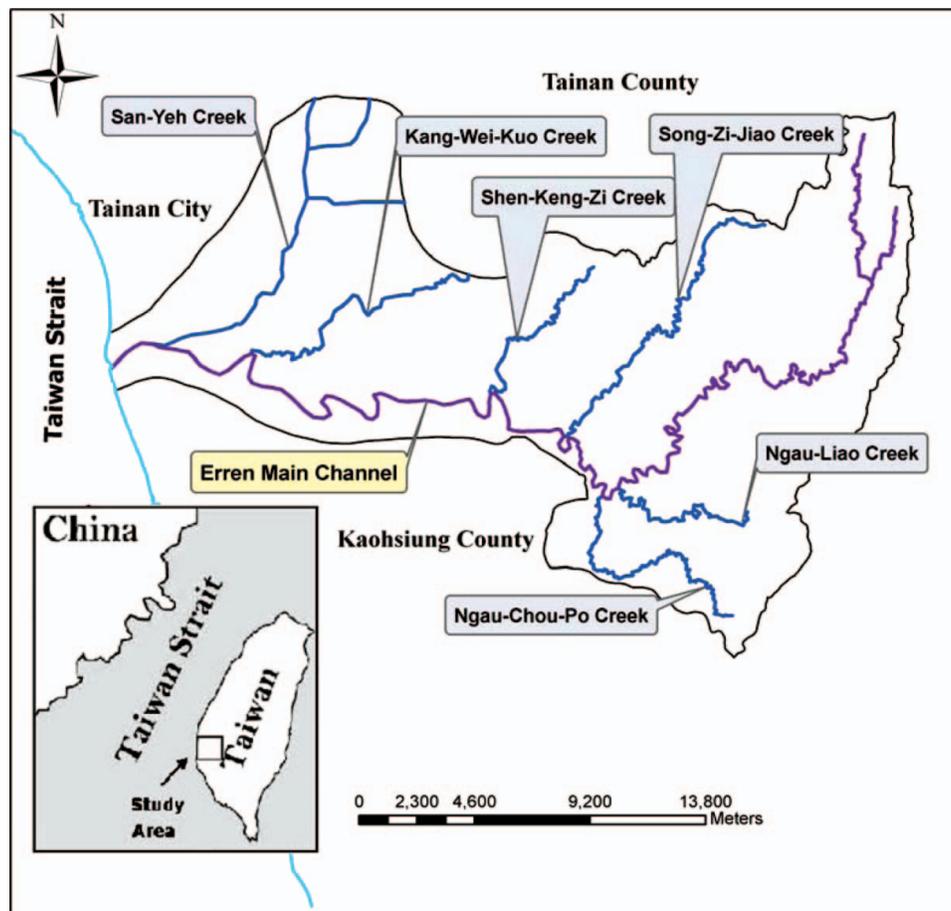


Figure 1. Map of the Erren River Basin (Taiwan). (color figure available online.)

Basin (Wu et al., 2010; Lee et al., 2012). Collected soil samples were tested for possible contamination. Soil samples were analyzed for possible metal ion concentrations or major pollutants based on the industrial activity in the surrounding area.

Experimental Details

Sampling sites were selected by following a procedure of site selection framework and field screening tests were carried out on forty-one selected sites in the area of the Erren River Basin of Taiwan (Wu et al., 2010; Lee et al., 2012). Using the XRF in the field screening tests, 117 soil samples were collected. From the collected on-site environmental samples, 60 top ranking samples within 41 sites were delivered to the laboratory for further ICP-AES testing. The XRF and ICP-AES experiments were based on Taiwan EPA standards (EPA Taiwan, 2000; 2006)

as shown in Table 2. The collected soil samples were found to be denser with contaminants between Kang-Wei-Kuo Creek and the estuary. Sampling locations are mapped in Figure 3.

All XRF data were collected with a NITON XL-722 equipped with a Cd-109 radioisotope source and Am-241 radioisotope source. Discrete sampling, where physical removal of a sample from soil, was carried out for analyzing the soil samples by the XRF technique, limiting the number of measurements normally performed in a site activity. The benefit is that analytical accuracy and precision are generally improved for prepared samples compared to in situ measurements (Kalnicky and Singhvi, 2001). Soil samples undergoing the XRF technique were analyzed through zip-locked plastic bags. The measurements of the soil samples in these plastic bags were measured according to an empty plastic bag analyzed as a blank sample and all sample measurements were blank-corrected (Radu and Diamond,

Table 2. Standards of field sampling and laboratory experiments for soil

Object	Environmental Protection Agency (EPA) Taiwan*	Related Standards	Description
Soil	NIEA S102.61B (2005) 1. NIEA S103.61C (2009) 2. NIEA M103.01C (2000)	ISO11466.2 U.S. EPA SW-846 ASTM D7691-11	Soil sampling method 1. General regulations and test methods for soil samples 2. Laboratory experiment methods for heavy metals (ICP-AES)

*Data from the Environmental Analysis Laboratory, EPA Taiwan. Available at: http://www.niea.gov.tw/analysis/method/m_t.asp, last update March 29, 2012 (in Chinese).

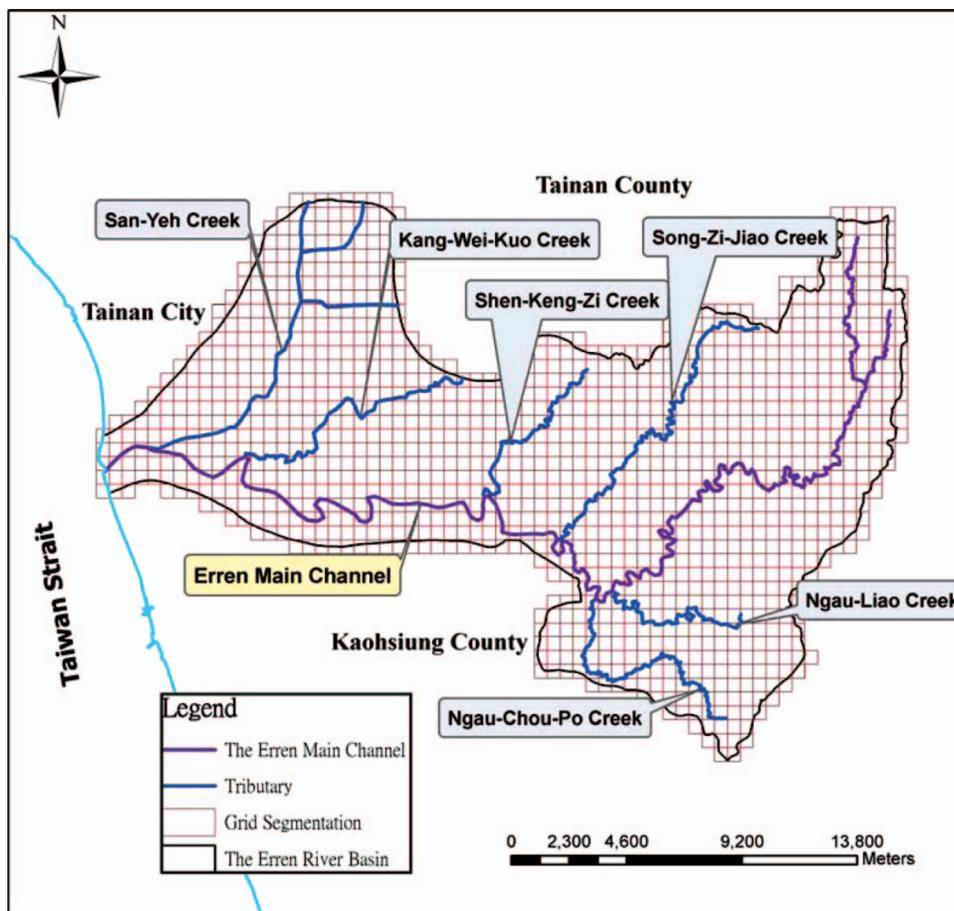


Figure 2. Map of the grid segmentation of sampling site. (color figure available online.)

2009). Prior to the sample measurement, an internal instrument calibration was performed (Radu and Diamond, 2009).

For a total element, the laboratory confirmatory method is required in order for it to be compatible with the XRF total element method and should as nearly as possible match the field method. The soil samples, collected in the area, having gone through the aqua regia acid digestion in the laboratory, were analyzed by an ICP-AES. The ICP-AES experiments require the soil sample to be imported as a solution into the instrument, but, beforehand, the laboratory must perform a sample extraction or digestion (Shefsky, 1997). A statistical analysis of data was performed using the Matlab statistical toolbox. Statistics include the mean, standard deviation, maximum, minimum, R-square (R^2), and RP concentrations for the eight elements of soil samples. Linear regression was used to correlate the XRF and ICP-AES data, and each data set was checked for potential outliers (Radu and Diamond, 2009; Kalnicky and Singhvi, 2001).

Results and Discussion

Individual Elements Interpretation

Pairwise comparisons between the XRF and ICP-AES results were made for elements Ni, Cu, Zn, Pb, Cd, Cr, Hg, and As; these eight heavy metal elements are presented in Figure 4 to

Figure 19. In Figure 4, Figure 6, Figure 8, Figure 10, Figure 12, Figure 14, Figure 16, and Figure 18, the green dash-dotted line represents the PTL (i.e., the permissible exposure level for pollutants) in Table 3. In contrast, Figure 5, Figure 7, Figure 9, Figure 11, Figure 13, Figure 15, Figure 17, and Figure 19 represent the XRF value versus ICP-AES value with their regression lines for these eight elements. The regression lines (black solid line) describe the minimized distance from the line to the data points of the individual methods. The blue dash line is the 1:1 line. The purpose for presenting the 1:1 line is to show how well the slope of regression line compares to the 1:1 line. Ideally, the scatter points lying on the 1:1 line means that the XRF measurements and ICP-AES experiments are exactly the same, and the regression line should fall on the 1:1 line. Pairwise comparisons between the XRF and ICP-AES results for each element are analyzed in following text.

Element nickel (Ni)

In Figure 4, the overall trend measured by the XRF technique is higher than the ICP-AES results for the element Ni. The values higher than the PTL (the green dash-dotted line in Figure 4 and the value in Table 3) were detected by the XRF method. However, the lower values of XRF below the PTL show a downward parallel gap with the ICP-AES values. As shown in Table 4 the

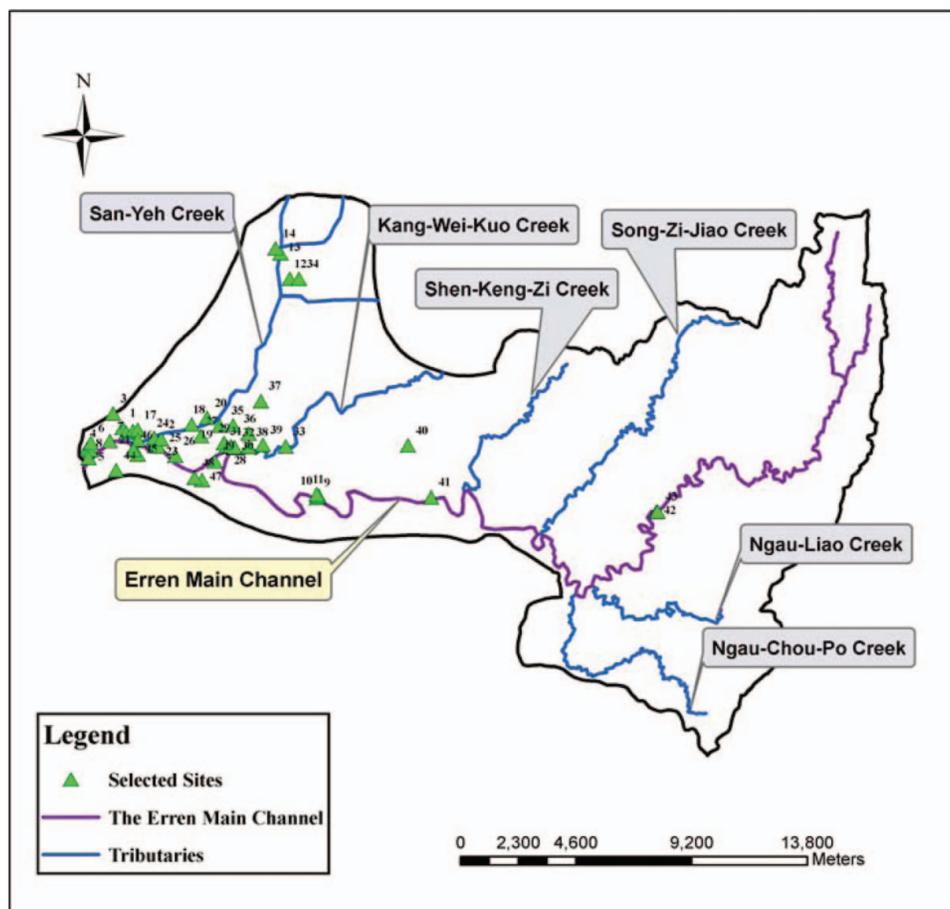


Figure 3. Map of the soil sampling locations within Erren River Basin. (color figure available online.)

RP is 50.00%. If controlling only the values over the PTL, the RP could be interpreted as only half of the soil pollution was captured by the XRF site screening. These soil samples have a linear regression slope of 1.144 and the correlation coefficient (R^2 value) of 0.7281 as shown in Figure 5. As can be seen (Tables 4 and 5), although the R^2 value of Ni is higher than all other elements, the regression line has shifted away from the 1:1 line.

Element copper (Cu)

Similar to Ni, the overall trend of Cu measured by the XRF technique is higher than the ICP-AES results (Figure 6). The

extremely high values above the PTL were detected by both the XRF method and ICP-AES. However, the values below the PTL show a large range between the XRF values and those of the ICP-AES. Contrast to Ni, the RP (in Tables 4 and 5) is 35.42%; only slightly over one-third of the soil pollution was captured by the XRF site screening. These soil samples have a linear regression slope of 1.184 and R^2 of 0.4095 as shown in Figure 7, which veers away from the 1:1 line.

Element zinc (Zn)

The result of the element Zn shows that sensitivity and accuracy of the XRF measurements compared with those of

Table 3. Soil contamination standard for heavy metals (data from EPA Taiwan, 2000; 2006)

Elements Concentration	Ni mg/kg	Cu mg/kg	Zn mg/kg	Pb mg/kg	Cd mg/kg	Cr mg/kg	Hg mg/kg	As mg/kg
Minimum detection limit [‡] (MDL)	1.35	0.72	6.62	1	0.1	1.37	0.037	0.499
Pollution threshold limit to be controlled [‡] (PTL)	200	400 (200 [§])	2000 (600)	2000 (500)	20 (5)	250	20 (5)	60
Monitored threshold limit [‡] (MTL)	130	220 (120)	1000 (260)	1000 (300)	10 (2.5)	175	10 (2)	30

[‡]Taiwan EPA Standard (EPA Taiwan, 2000; 2006)

[§]Limit for farmland

Table 4. Summary of the results from x-ray fluorescence (XRF) and inductively coupled plasma atomic emission spectrometer (ICP-AES) for 60 samples from the Erren River watershed

Element Method	Pb		Zn		Ni		Cu	
	ICP-AES	XRF	ICP-AES	XRF	ICP-AES	XRF	ICP-AES	XRF
max	36200	23200	326000	623000	10400	45100	174000	131000
min	4.33	11.4	30.6	4.5	10.3	100	3.86	70
mean	2306.92	1371.60	12184.91	24187.79	444.05	1590.92	3988.10	4055.38
std	7706.96	4407.41	51294.83	105543.53	1720.64	6911.18	22515.66	16953.84
R ² †	0.6689	0.6551	0.7281	0.4095				
Relative Proximity (RP)‡	85.17%		80.00%		50.00%		35.42%	

Element Method	As		Cr		Cd		Hg	
	ICP-AES	XRF	ICP-AES	XRF	ICP-AES	XRF	ICP-AES	XRF
max	70.059	570	1070	3020	23.74	120	12.9	144
min	2.786	16	7.315	160	0.1	14	0.037	3.9
mean	9.11	66.13	78.38	495.13	1.24	31.43	0.70	44.10
std	11.36	112.45	158.73	578.71	4.53	19.00	1.68	33.93
R ² †	0.3449		0.1504		0.07823		0.01143	
Relative Proximity (RP)‡	25.00%		16.67%		5.77%		2.30%	

†Value of R² for regression lines in Figure 5, Figure 7, Figure 9, Figure 11, Figure 13, Figure 15, Figure 17, and Figure 19.

‡Number of detected field samples of the ICP-AES results over the PTL divided by the number of detected field samples of the XRF results over the PTL

the ICP-AES are acceptable and that any interference by other factors is unlikely (Figure 8). The regression line (Figure 9) and the 1:1 line are approximately parallel to each other. These soil samples have a linear regression slope of 0.9468, and the

R² value is 0.6551. If controlling only the values over the PTL, then 80.00% of the data exist in close proximity to each other (Tables 4 and 5). The screening test of high values can be used as a reference for selecting sampling points.

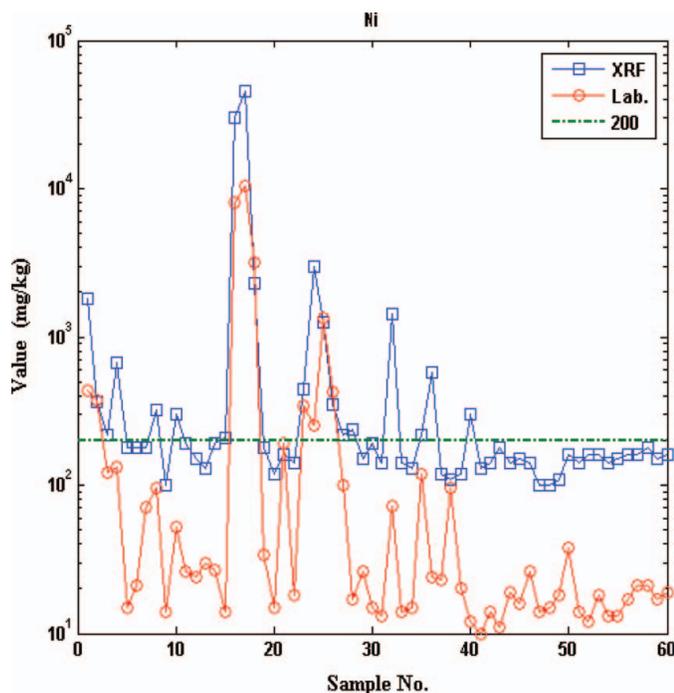


Figure 4. Graph of x-ray fluorescence (XRF) versus inductively coupled plasma atomic emission spectrometer (ICP-AES) (Ni: PTL is 200 mg/kg). (color figure available online.)

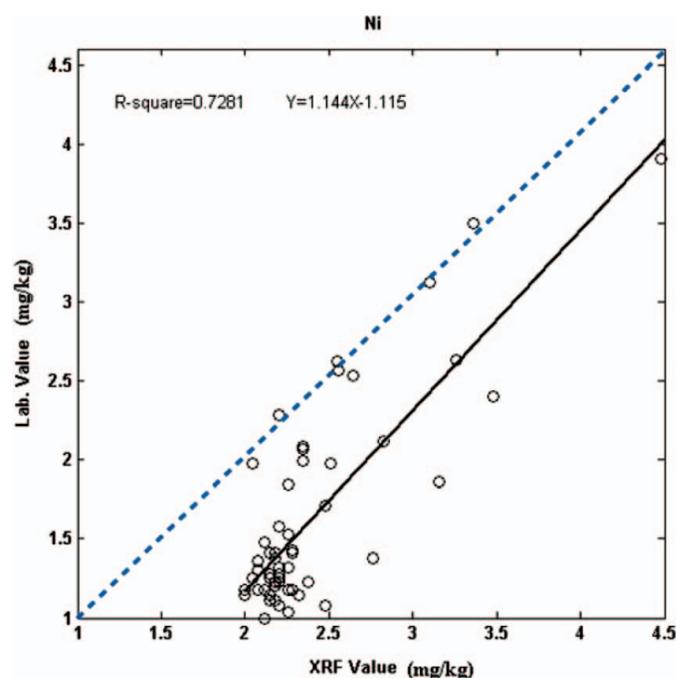


Figure 5. Graph of x-ray fluorescence (XRF) versus inductively coupled plasma atomic emission spectrometer (ICP-AES) (Ni). (color figure available online.)

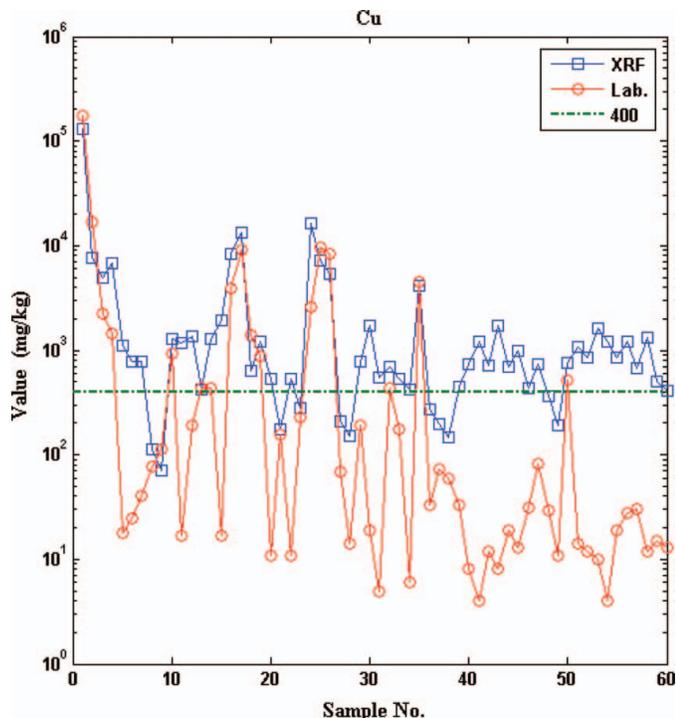


Figure 6. Graph of x-ray fluorescence (XRF) versus inductively coupled plasma atomic emission spectrometer (ICP-AES) (Cu: PTL is 400 mg/kg). (color figure available online.)

Element lead (Pb)

The overall trend of the XRF measurements agrees with the ICP-AES experiments for the element Pb (Figure 10). The regression line with a slope of 0.9781 (Figure 11) matches fairly

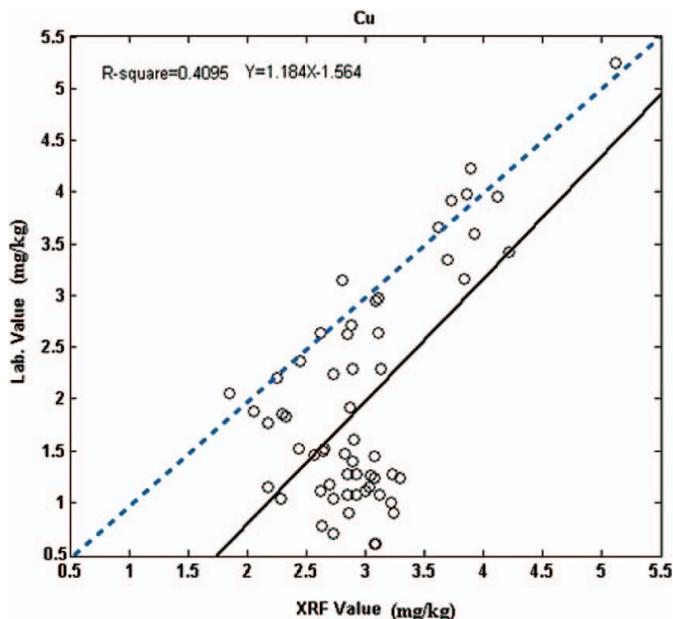


Figure 7. Graph of x-ray fluorescence (XRF) versus inductively coupled plasma atomic emission spectrometer (ICP-AES) (Cu). (color figure available online.)

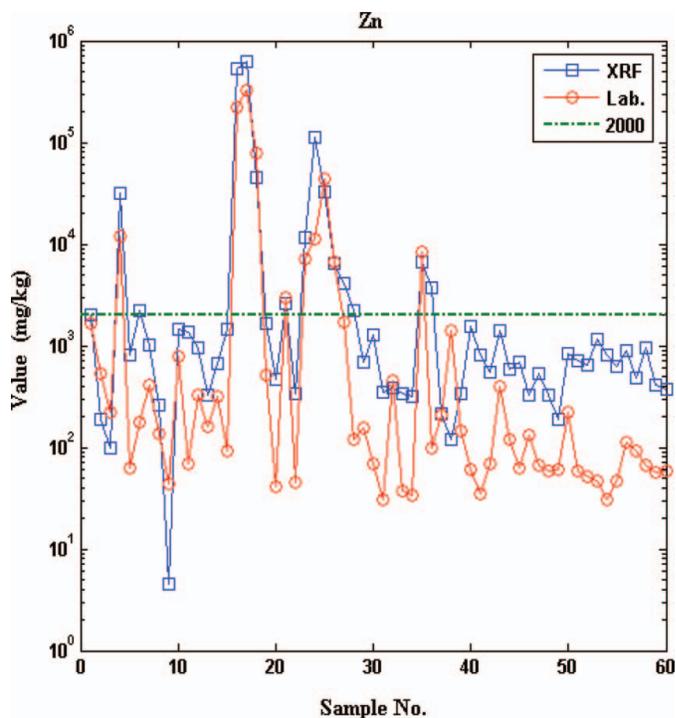


Figure 8. Graph of x-ray fluorescence (XRF) versus inductively coupled plasma atomic emission spectrometer (ICP-AES) (Zn: PTL is 2000 mg/kg). (color figure available online.)

well with the 1:1 line, and the R^2 value is 0.6689. If controlling only the values over the PTL, then 85.17% of the data are positioned in close proximity to each other (Tables 4 and 5). This result is superior to all the other seven elements. Excellent

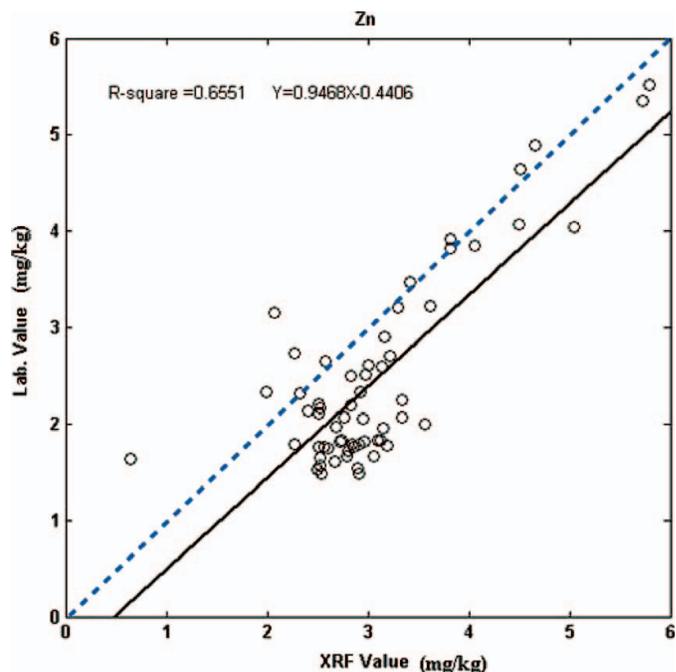


Figure 9. Graph of x-ray fluorescence (XRF) versus inductively coupled plasma atomic emission spectrometer (ICP-AES) (Zn). (color figure available online.)

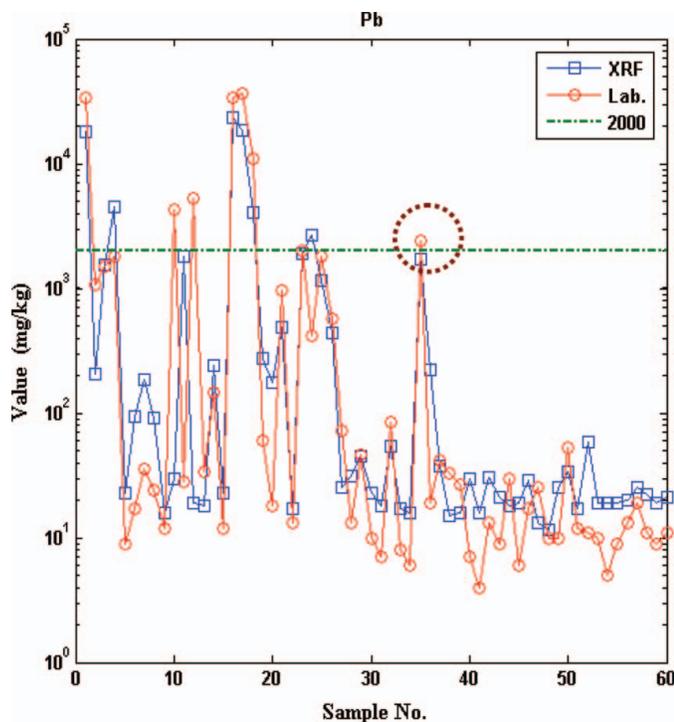


Figure 10. Graph of x-ray fluorescence (XRF) versus inductively coupled plasma atomic emission spectrometer (ICP-AES) (Pb: PTL is 2000 mg/kg). (color figure available online.)

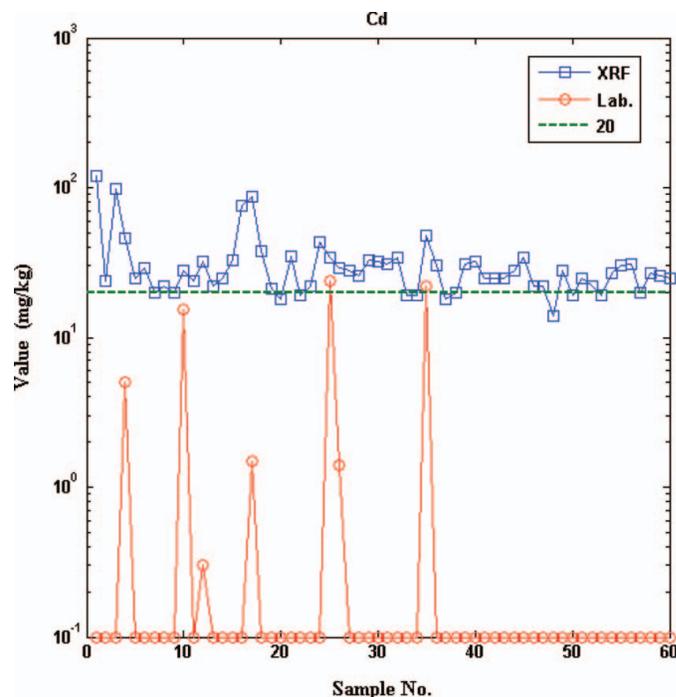


Figure 12. Graph of x-ray fluorescence (XRF) versus inductively coupled plasma atomic emission spectrometer (ICP-AES) (Cd: PTL is 20 mg/kg). (color figure available online.)

sensitivity and accuracy of detecting Pb allow a very small potential for interference by other factors, unless a very unique situation would occur. High screened measurement values of the above information indicate a considerable degree of reliability.

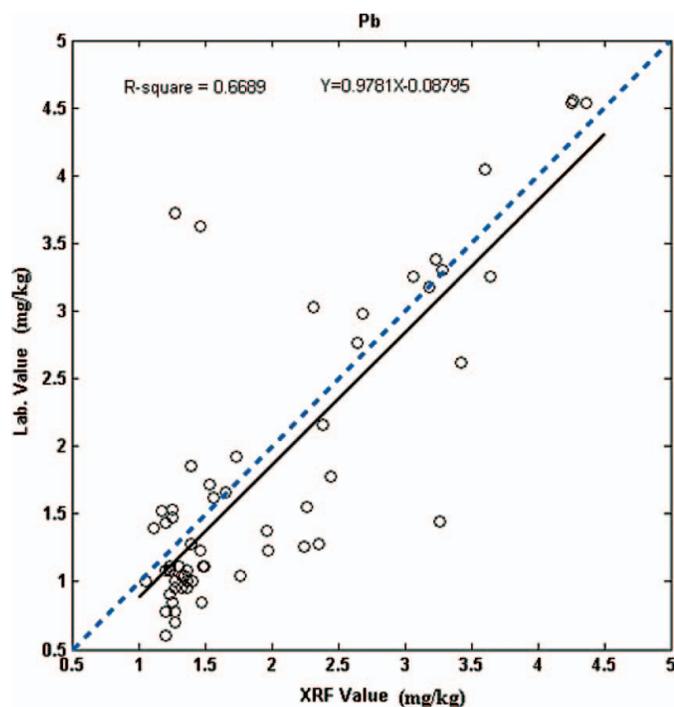


Figure 11. Graph of x-ray fluorescence (XRF) versus inductively coupled plasma atomic emission spectrometer (ICP-AES) (Pb). (color figure available online.)

Element cadmium (Cd)

Cd shows poor accuracy. There is no significant relationship between the XRF measurements and the ICP-AES experiments (Figure 12). As can be seen in Figure 12, the XRF measurements are all higher than the ICP-AES experiments. The RP is only 5.77% (Tables 4 and 5). The regression line with a slope of 0.9106 and R^2 value of 0.07823 diverges greatly from the 1:1 line that the 1:1 line lies outside the scope of the figure (Figure 13).

Element chromium (Cr)

Cr presents poor accuracy. There is a parallel gap of the XRF measurements below the PTL compared with the ICP-AES experiment results (Figure 14). Most of the XRF measurements are all higher than the results of the ICP-AES experiments. The RP is only 16.67% (Tables 4 and 5). The regression line with a slope of 0.5778 and R^2 value of 0.1504 diverges from the 1:1 line extensively that the 1:1 line lies outside the range of the figure (Figure 15).

Element mercury (Hg)

Similar to Cr, Hg presents poor accuracy. The XRF measurements parallelly shift away from the ICP-AES experiment results

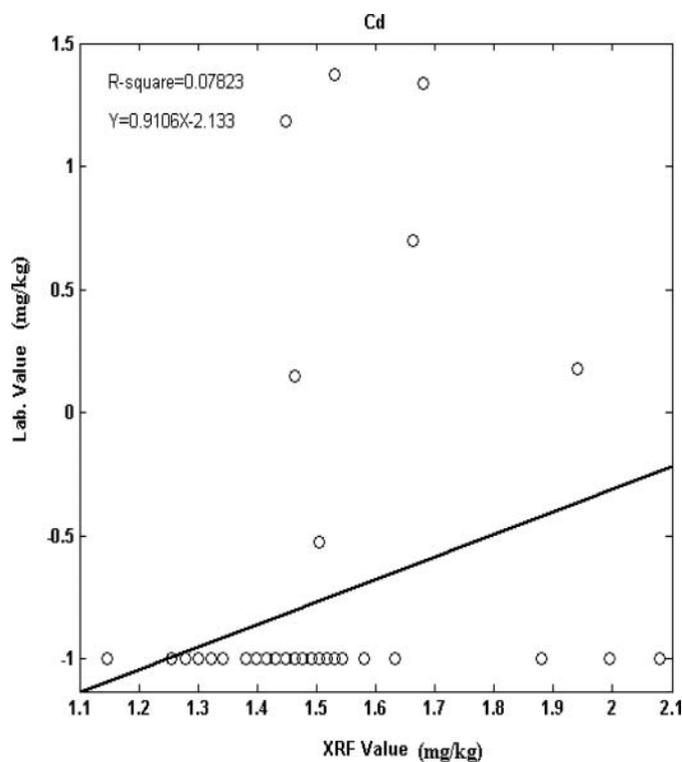


Figure 13. Graph of x-ray fluorescence (XRF) versus inductively coupled plasma atomic emission spectrometer (ICP-AES) (Cd).

(Figure 16). As can be seen in Figure 16, the XRF measurements are all higher than the results of the ICP-AES experiments. The RP is only 2.30% (Tables 4 and 5). The regression line with a slope of 0.1076 and R^2 value of 0.01143 totally diverges from the 1:1 line and lies outside the scope of Figure 17. This sample of the screen test data for Hg shows uncertainty regarding other factors which may cause serious interference. In the case where the Hg screening test shows abnormality without any special performance of the other elements, this information can be useful as a basis for choosing sampling sites.

Table 5. The numbers over the pollution threshold limit (PTL) for x-ray fluorescence (XRF) and inductively coupled plasma atomic emission spectrometer (ICP-AES) samples

Element	XRF No. over PTL [†]	ICP-AES No. over PTL	Relative Proximity (RP) [‡] (%)	R^2
Pb	7	6	85.71	0.6689
Zn	15	12	80.00	0.6551
Ni	20	10	50.00	0.7281
Cu	48	17	35.42	0.4095
As	12	3	25.00	0.3449
Cr	30	5	16.67	0.1504
Cd	52	3	5.77	0.07823
Hg	43	1	2.30	0.01143

[†]PTL (Table 3)

[‡]RP: Number of detected field samples of the ICP-AES results over the PTL divided by the number of detected field samples of the XRF results over the PTL

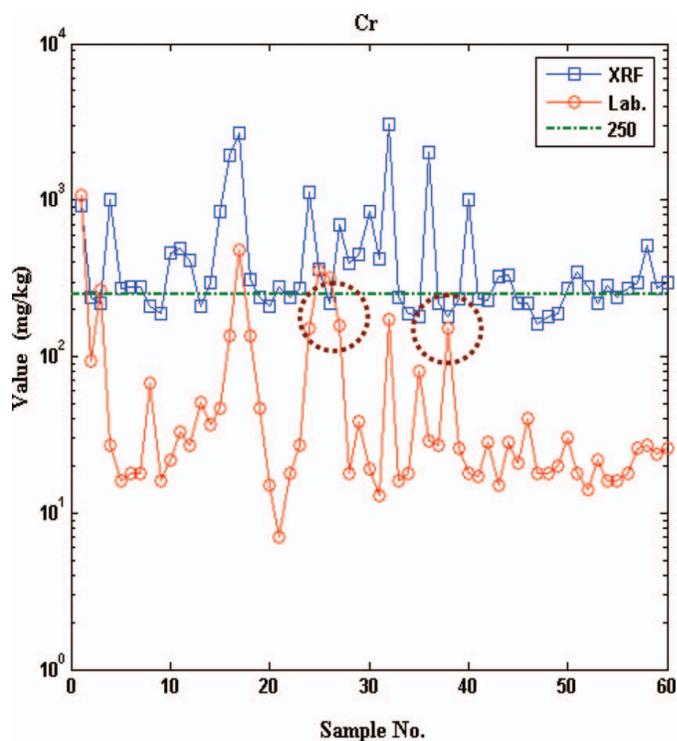


Figure 14. Graph of x-ray fluorescence (XRF) versus inductively coupled plasma atomic emission spectrometer (ICP-AES) (Cr: PTL is 250 mg/kg). (color figure available online.)

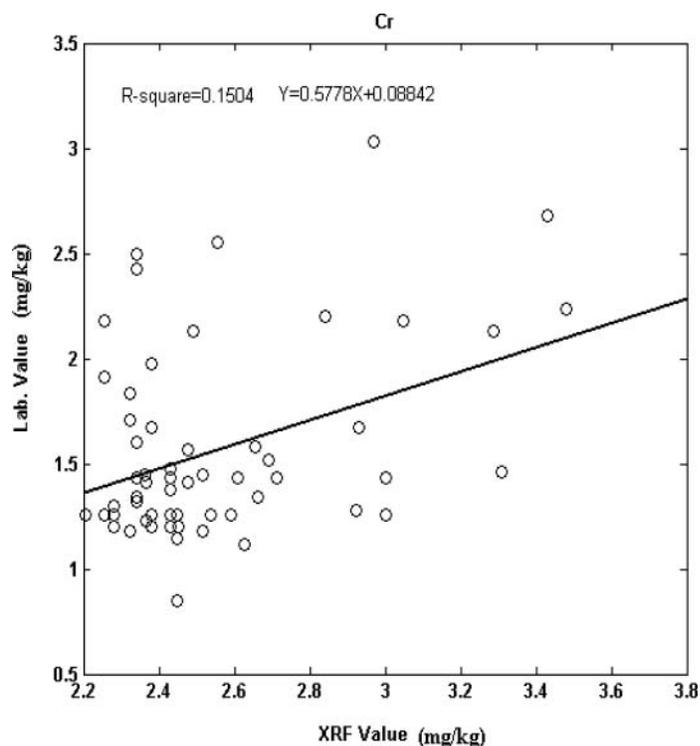


Figure 15. Graph of x-ray fluorescence (XRF) versus inductively coupled plasma atomic emission spectrometer (ICP-AES) (Cr).

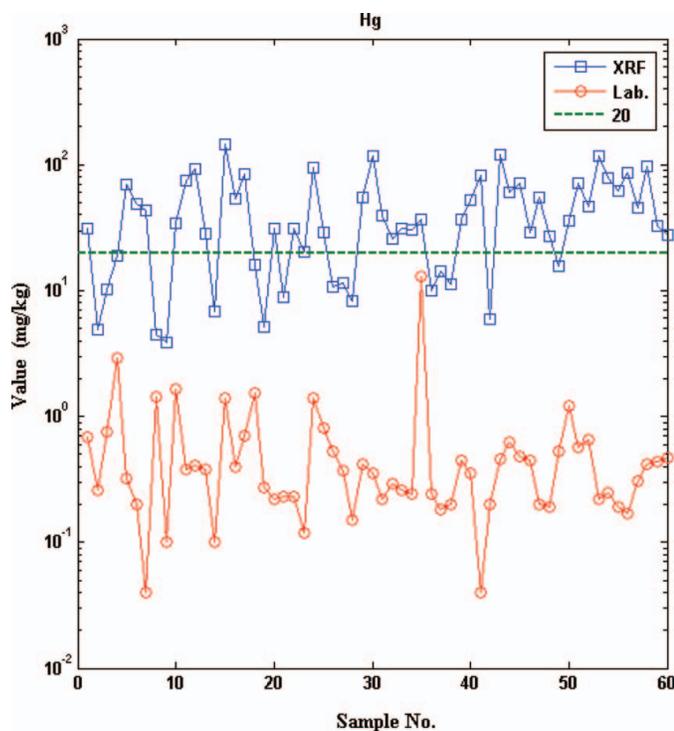


Figure 16. Graph of x-ray fluorescence (XRF) versus inductively coupled plasma atomic emission spectrometer (ICP-AES) (Hg: PTL is 20 mg/kg). (color figure available online.)

Element arsenic (As)

Similar to Cr and Hg, the trend of element As parallels for both the XRF measurements and the ICP-AES exper-

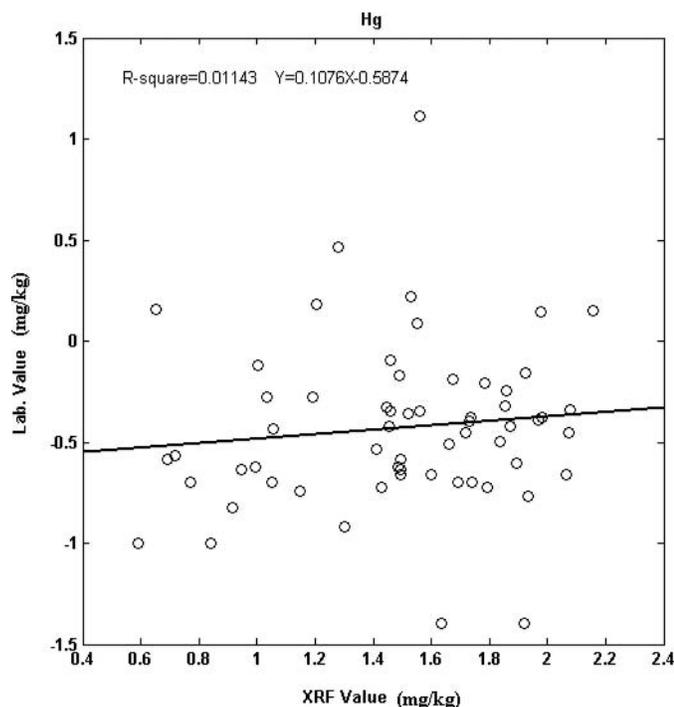


Figure 17. Graph of x-ray fluorescence (XRF) versus inductively coupled plasma atomic emission spectrometer (ICP-AES) (Hg).

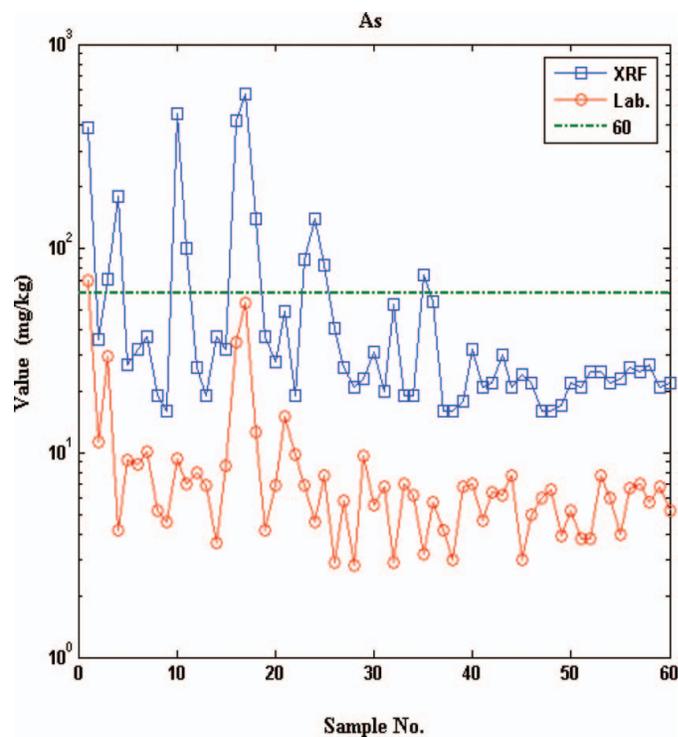


Figure 18. Graph of x-ray fluorescence (XRF) versus inductively coupled plasma atomic emission spectrometer (ICP-AES) (As: PTL is 60 mg/kg). (color figure available online.)

iment results. As can be seen in Figure 18, the XRF measurements are all higher than the results of the ICP-AES experiments. The sensitivity and accuracy of detecting As compared with the existing laws and regulations are not satisfied (Figure 18), and 25.00% of the data are in close proximity to each other (Tables 4 and 5). The regression line, with a slope of 0.4208 and R^2 value of 0.3449, turns greatly away from the 1:1 line and, thus, lies outside the range of the figure (Figure 19).

Comprehensive Interpretation

Comprehensive interpretation was carried out by overall evaluations of both the raw data of XRF versus ICP-AES and their regression lines. Table 4 presents the summary of eight elements measured by the XRF method and the results obtained from the ICP-AES experiments for 60 samples from the Erren River watershed.

Based on the interpretation of the individual elements and the summary table (Table 4), the eight heavy metal elements can be approximately divided into two groups (Table 5). The first group includes Pb, Zn, Ni, and Cu, which the XRF measurements show to have better agreement with the ICP-AES experiment results. The order of reliability by the XRF measurements is $Pb > Zn > Ni > Cu$. The second group includes As, Cr, Cd, and Hg. The order of reliability by the XRF measurements is $As > Cr > Cd > Hg$. Table 5 shows that the first group Cu, Ni, Zn, and Pb measured values have good correlation (RP ranges from

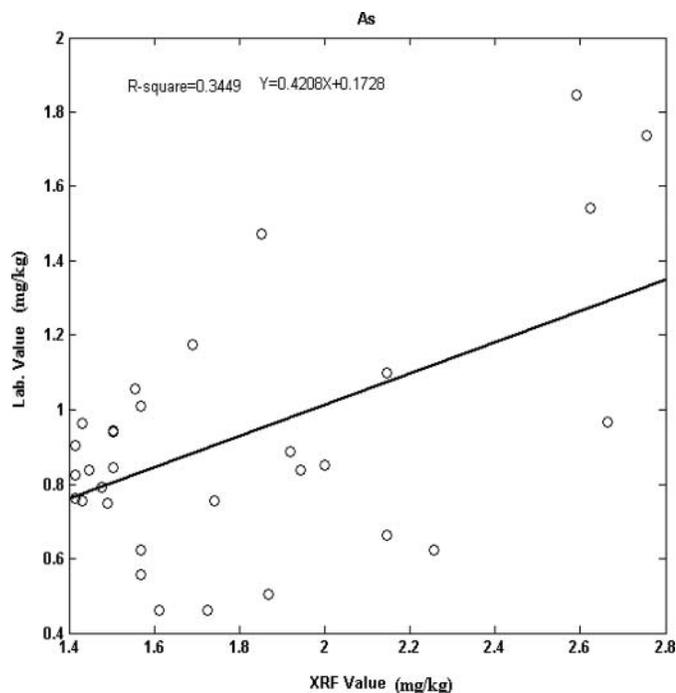


Figure 19. Graph of x-ray fluorescence (XRF) versus inductively plasma atomic emission spectrometer (ICP-AES) (As).

35.42%–85.71%). The second group, which includes Hg, Cd, Cr, and As, shows poor correlation (RP ranges from 2.3%–25%). In contrast, the R^2 values of the regression line range from 0.4095–0.7281 for the first group and from 0.01143–0.3349 for the second group.

Also observed is that the XRF results are able to sensitively and accurately detect the first group of elements (Pb, Zn, Ni, and Cu), especially, for those values above the PTL. However, in some cases, the values which are below the PTL do not always mean that the ICP-AES results will be below the PTL also. For example, in Figure 10 and Figure 14 (brown-dotted-circle), the values obtained by the ICP-AES experiments are above the PTL, while the values obtained by the XRF measurements are below the PTL.

Conclusions

The XRF instrument is a powerful tool that can be very effective in the validation of both the absence and presence of certain metal elements. In principle, this instrument could be employed to provide rapid in situ detection of the presence of toxic metals such as Pb, Ni, As, Cr, Cd, Cu, Zn, and Hg in soil samples (Radu and Diamond, 2009). Data presented in this paper suggest that XRF measurements can be used as a screening technique and are highly reliable in detecting samples where the first group of element (Pb, Zn, Ni, and Cu) concentrations is well in excess of the PTLs (Shrivastava et al., 2005). The order of reliability by the XRF measurement for metals is Pb > Zn > Ni > Cu. However, the second group of elements that include Hg, Cd,

Cr, and As shows poor correlation between the XRF measurements and the ICP-AES experiments. Due to the limitations of the XRF and ICP-AES analytical test methods, the most effective methodology needs to be verified and calibrated via the supplier's specifications (Shrivastava et al., 2005).

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