

# Use of portable X-ray fluorescence spectrometry for environmental quality assessment of peri-urban agriculture

David C. Weindorf · Yuanda Zhu ·  
Somsubhra Chakraborty · Noura Bakr ·  
Biao Huang

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**Abstract** Urban expansion into traditional agricultural lands has augmented the potential for heavy metal contamination of soils. This study examined the utility of field portable X-ray fluorescence (PXRF) spectrometry for evaluating the environmental quality of sugarcane fields near two industrial complexes in Louisiana, USA. Results indicated that PXRF provided quality results of heavy metal levels comparable to traditional laboratory analysis. When coupled with global positioning system technology, the use of PXRF allows for on-site interpolation of heavy metal levels in a matter of minutes. Field portable XRF was shown to be an effective tool for rapid assessment of heavy metals in soils of peri-urban agricultural areas.

**Keywords** X-ray fluorescence spectrometry · Heavy metals · Agriculture

## Introduction

In recent years, increases in global population have led to urban expansion into previously rural areas. Also, an emphasis on urban sustainability has encouraged peri-urban farming via community gardens and green roofs. While these concepts are ecologically sound, questions remain about the safety of growing food crops in close proximity to urban environments fraught with pollution. The Food and Agriculture Organization (FAO) of the United Nations (1999) estimated that 800 million urban residents worldwide either earn income from urban farming practices, or use the food grown in urban environments to feed themselves. However, farming in such areas also has potential risks.

The FAO (1999) identified many potential risks in urban farming including: excessive use of pesticides, nitrogen, and raw organic matter containing heavy metals. Furthermore, the most viable source of water for peri-urban farming is often recycled wastewater which can potentially be laden with heavy metals from nearby industry. Air pollution and particulate matter offer another source of potential pollutant input to urban or peri-urban farming. Zhao et al. (2007) studied the spatial distribution of heavy metals in agricultural soils of peri-urban areas of Wuxi, China, and found elevated levels of As, Hg, Cu, Cd, Cr, Zn, and Pb. They associated these elevated levels with nearby

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D. C. Weindorf (✉) · Y. Zhu · S. Chakraborty ·  
N. Bakr  
School of Plant, Environmental, and Soil Sciences,  
LSU AgCenter, 307 MB Sturgis Hall, Baton Rouge,  
LA, 70803 USA  
e-mail: dweindorf@agcenter.lsu.edu

B. Huang  
Institute of Soil Science—Chinese Academy  
of Sciences, P.O. Box 821, Nanjing,  
210008 People's Republic China

metallurgy, electroplating, and steel-making industries. Similarly, Hu et al. (2006) studied soils on the outskirts of Beijing, China, and found elevated levels of similar metals. They noted that Cd levels exceeded the critical value of the national soil quality standard. Hao et al. (2009) investigated heavy metal concentrations in both soil and vegetables from a peri-urban area in Jiangsu Province, China, and identified some samples that exceeded the Chinese Soil Environmental Quality Standard II for Cu and Zn. However, in all of these studies, traditional laboratory techniques were used for metal quantification (inductively coupled plasma atomic emission spectroscopy or lab-based X-ray fluorescence spectrometry).

Outside of China, Dia et al. (2009) found elevated levels of Pb, Mn, and Zn associated with roadside soils in Texas. Stehouwer et al. (2006) studied mine reclamation with municipal biosolids in Pennsylvania. They found that Al, Mn, Cu, Ni, Pb, and Zn were mobilized under acidic conditions and could threaten vadose zone water quality. Similar mobility of Cd was reported by Ingwersen and Streck (2006) on sandy soils irrigated with metal-laden municipal wastewater in Germany. In Louisiana, several studies have documented extensive heavy metal contamination (e.g., Welt et al. 2003; Devall et al. 2006). The EPA's Superfund Information System lists 15 sites in Louisiana where metal contamination has been or is currently being addressed. Such facilities include utilities, an ammunition plant, petrochemical refineries, foundries, and shipbuilders.

Spatial variability of heavy metals can be addressed by linking sampling location (latitude and longitude) with elemental concentrations. In a spatial distribution study of heavy metals in a rapid development region of China (Guangdong province), Zhang et al. (2008) concluded that soil parent material and pedogenesis are the primary factors influencing heavy metal spatial variability, but anthropogenic activities are the second most important factor. However, Li et al. (2008) found that high concentrations of Zn, Cu, Pb, Cd, Hg, and As in agricultural fields adjacent to a petrochemical complex in Guangzhou, China, decreased with depth and were tied to industrial pollution. They used GIS mapping to identify "hot-spots" in agricultural fields which should be

avoided or remediated prior to further agronomic production.

Common among all these studies are: (1) knowing the spatial location of heavy metal contamination, and (2) rapidly quantifying metal concentrations so that management decisions can be made to protect human health and environmental quality. Unfortunately, current monitoring of heavy metals is often accomplished via traditional soil sampling, with samples sent to laboratories for inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis. While this technique is highly accurate, it requires the collection of extensive soil samples and laboratory preparation/analysis. This approach is severely limited by both the high costs of analysis and time used in laboratory processing. As such, field portable X-ray fluorescence (PXRF) spectrometry was employed in the present study to allow for higher intensity soil analysis in the field with results obtained and spatially modeled on-site.

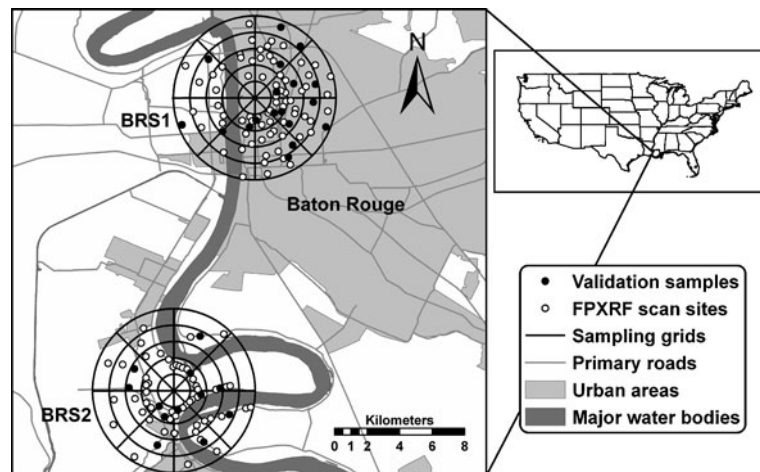
Two peri-urban sites near Baton Rouge, Louisiana, were evaluated using the PXRF to quantify soil contamination from nearby petrochemical plants. The objectives of this study were to: (1) evaluate the effectiveness of using PXRF for quantifying peri-urban heavy metal contamination (As, Co, Cr, Cu, Fe, Mn, Pb, and Zn) in agricultural soils; (2) validate the results obtained from the PXRF using traditional ICP-AES lab analysis; and (3) develop on-site maps of contamination using geospatial interpolation.

## Materials and methods

### Site description and sampling scheme

Two sites were evaluated in May, 2010, in Baton Rouge, Louisiana, USA (Fig. 1). Site 1 (BRS1) is centered by a large petroleum refinery, including areas of downtown Baton Rouge, residential areas, and sugarcane (*Saccharum* spp.) fields across the Mississippi River. The refinery is immediately north of the city of Baton Rouge. Site 2 (BRS2) was just south of Baton Rouge and centered by an active chemical production plant. The sampled/scanned fields were actively being used for sugarcane production. Soil textures ranged from

**Fig. 1** Location of sampling sites BRS1 and BRS2 in Louisiana, USA



clay to sandy loam. Soil parent materials were mostly thick loess for the eastern half of BRS1 and recent alluvium for the western half of BRS1 and all of BRS2. A conditioned Latin hypercube sampling scheme was employed to develop sampling sites for BRS1 and BRS2 (Minasny and McBratney 2006). Input factors of directional aspect and distance from the industrial site were used as the controlling variables. Higher density sampling was proportionally weighted toward areas closer to the industrial plant and at directional aspects supportive of documented wind patterns. The sampling scheme was designed in ArcGIS 9.3 (ESRI, Redlands, CA, USA). Sampling points were uploaded into an e-Trex global positioning system (GPS) receiver and geo-located in the field for scanning/sampling.

#### Field measurements with portable X-ray fluorescence

A battery operated Omega Xpress PXRf (Innov-X Systems, Inc., Woburn, MA, USA) with Ag anode X-ray tube operated at 40 keV was used in this study. Fluorescence detection was accomplished via ultra-high resolution (<165 eV) silicon drift detector. Factory standardization was accomplished via a stainless steel ‘316’ alloy clip containing 16.130% Cr, 1.780% Mn, 68.760% Fe, 10.420% Ni, 0.200% Cu, and 2.100% Mo, and was fitted tightly over the aperture. The instrument was operated in a two-beam light element

analysis program (LEAP) mode engaged under a proprietary standard configuration known as *soil mode*. Soil mode uses a scatter normalization algorithm for soil, liquids, and powders allowing for sequential analysis via K-line and L-line electron fluorescence (Environmental Protection Agency 2010). Utilization of LEAP mode provides optimized tube excitation for increased performance on lighter elements. Samples were scanned for 60 s through the ~2 cm aperture. A total of 67 and 91 scans were performed at BRS1 and BRS2, respectively. Data was collected and processed in the on-board computer. Elemental concentration and standard error were reported on an individual element basis for each scan. The limit of detection (LOD) is defined as three times the standard error for each element. Logged data was then exported to MS Excel for further analysis and preparation for import into ArcGIS. The LOD varies by element, with higher atomic numbered elements generally allowing for lower detection limits. For example, lighter elements such as P, S, Cl, and Ar have LODs of 10,000–50,000 mg kg<sup>-1</sup>, elements such as K and Ca have LODs of 250–2,500 mg kg<sup>-1</sup>, and heavier elements such as Fe, Cu, and Zn have LODs of 5–100 mg kg<sup>-1</sup>.

#### Validation

Validation of PXRf total elemental concentrations was achieved by randomly collecting samples at ~35% of scan sites. A total number of

55 samples were collected for validation by lab analysis. A portion of each sample was used for determination of the moisture content based on weight loss at 105°C. Validation samples were then air-dried, ground, and passed through a 2-mm sieve. Subsamples of approximately 1 g were oven dried, manually ground to <100 µm and subjected to aqua regia digestion per Method 04.12-B via HNO<sub>3</sub>, HCl, and H<sub>2</sub>O<sub>2</sub>. Validation quantification was accomplished using a Ciros model inductively coupled plasma atomic emission spectrometer (Spectro Analytical Instruments, Marlboro, MA, USA) (US Composting Council 2002; Soil Survey Staff 2004). NIST standard reference materials 1646 (estuarine sediment), 2704 (Buffalo River sediment), and 2711 (Montana soil) were also scanned by PXRF and NIST SRM 1646 in triplicate and measured via ICP-AES after digestion for accuracy checking.

Data analysis

Descriptive statistics and principal component analysis (PCA) were conducted using MYS-TAT 12 package. Interpolation of elemental spatial variability was performed using ArcGIS 9.3 (ESRI, The Redlands, CA, USA). Ordinary kriging was employed as an appropriate technique for modeling the distribution of heavy metals (Largueche 2006; Weber and Englund 1994).

Results and discussion

Recovery rates of PXRF

As shown in Table 1, a reasonable agreement was found between PXRF readings and certified values for most of the elements studied. However, PXRF readings were one or two orders of magnitude higher than certified values for Cd, Co, and Hg. Specifically, certified Cd and Hg contents of the NIST standards were lower than LODs of PXRF, which may have led to the abnormal readings. The abnormally high readings of Co by PXRF may be due to the well-recognized inter-element effects among Zn, Co, and Fe (Bartkiewicz and Hammatt 1964). For the other elements (As, Ba, Cr, Cu, Fe, Mn, Ni, Pb,

Table 1 Recovery rates of the certified elements on NIST Standard reference materials 1646, 2711, and 2704 using PXRF and digestion-ICP method

Element	NIST SRM 1646—estuarine sediment				NIST SRM 2711—Montana soil				NIST SRM 2704—Buffalo soil					
	Certified (mg/kg)	PXRF (mg/kg)	Recovery (%)	Digestion-ICP (mg/kg)	Recovery (%)	Certified (mg/kg)	PXRF (mg/kg)	Recovery (%)	Certified (mg/kg)	PXRF (mg/kg)	Recovery (%)	Certified (mg/kg)	PXRF (mg/kg)	Recovery (%)
As	11.6 ± 1.3	11 ± 2	94.8	5.40 ± 0.02	46.6	105 ± 8	96 ± 8	91.4	23.4 ± 0.8	12 ± 3	51.3	23.4 ± 0.8	12 ± 3	51.3
Ba	-	513 ± 27	-	35.67 ± 0.56	-	726 ± 38	373 ± 16	51.4	414 ± 12	313 ± 19	75.6	414 ± 12	313 ± 19	75.6
Cd	0.36 ± 0.07	4 ± 5	1,111.1	-	-	41.7 ± 0.25	54 ± 8	129.5	3.45 ± 0.22	1 ± 7	29.0	3.45 ± 0.22	1 ± 7	29.0
Co	10.5 ± 1.3	575 ± 44	5,476.1	7.61 ± 0.25	72.5	10 ± ?	563 ± 34	5,630.0	14 ± 0.6	679 ± 40	4,850.0	14 ± 0.6	679 ± 40	4,850.0
Cr	76 ± 3	59 ± 5	77.6	32.1 ± 1.6	42.2	47 ± ?	34 ± 5	72.3	135 ± 5	97 ± 6	71.9	135 ± 5	97 ± 6	71.9
Cu	18 ± 3	22 ± 3	122.2	8.6 ± 0.4	47.8	114 ± 2	137 ± 6	120.2	98.6 ± 5	92 ± 5	93.3	98.6 ± 5	92 ± 5	93.3
Fe	33,500 ± 1,000	29,922 ± 195	89.3	21,678 ± 1,320	64.7	28,900 ± 600	27,195 ± 207	94.1	41,100 ± 1,000	39,700 ± 308	96.9	41,100 ± 1,000	39,700 ± 308	96.9
Hg	0.063 ± 0.012	2 ± 2	3,174.6	-	-	6.25 ± 0.19	19 ± 3	304.0	1.44 ± 0.07	13 ± 2	902.8	1.44 ± 0.07	13 ± 2	902.8
Mn	375 ± 20	318 ± 8	84.8	170.8 ± 8.5	45.5	638 ± 28	669 ± 10	104.9	555 ± 19	568 ± 10	102.3	555 ± 19	568 ± 10	102.3
Ni	32 ± 3	16.3 ± 9	50.9	26.0 ± 0.7	81.3	20.6 ± 1.1	10 ± 9	48.5	44.1 ± 3	24 ± 9	54.4	44.1 ± 3	24 ± 9	54.4
Pb	28.2 ± 1.8	29 ± 2	102.8	36.5 ± 1.4	129.4	1,162 ± 31	1,375 ± 13	118.3	161 ± 17	141 ± 4	87.6	161 ± 17	141 ± 4	87.6
Ti	5,100 ± ?	5,092 ± 88	99.8	-	-	3,060 ± 23	3,155 ± 61	103.1	4,570 ± 18	5,037 ± 79	110.2	4,570 ± 18	5,037 ± 79	110.2
Zn	138 ± 6	127 ± 4	92.0	77.2 ± 4.3	55.9	350.4 ± 4.8	382 ± 7	109.0	438 ± 12	326 ± 6	74.4	438 ± 12	326 ± 6	74.4

Ti, and Zn), the PXRF recovery rates ranged from 48.5% to 122.2%.

Recovery rates of the aqua regia digestion–ICP method

NIST SRM 1646 (estuarine sediment) was the only reference material used to check the recovery rates of the aqua regia digestion–ICP method used in this study (Table 1). The recovery rates of the digestion–ICP method varied from 42.2% to 129.4%. It is noteworthy that five out of nine elements had a recovery rate lower than 56%. The method used is not a total digestion technique but is designed for elements that are “environmentally available” (Environmental Protection Agency 1996). Generally, it has reasonably high recovery rates for most elements. Delgado et al. (2010) found the recovery rates ranged from 78.5% to 105% for their studied elements (Al, As, Cd, Co, Cr, Cu, Fe, Cu, Ni, Pb, and Zn), justified by two standard materials. The reason for the low recovery rates from the NIST SRM 1646 remains uncertain. However, many studies have reported high correlations between the results based on both aqua regia digestion and total digestion methods, particularly for soil with relatively low heterogeneity (e.g., Ma and Chen 1998). Measurements based on aqua regia digestion method are therefore still helpful in evaluating the accuracy of PXRF measurements.

Correction of ICP data with moisture content

Although soil moisture is not considered to have a significant effect on PXRF accuracy (Innov-X

Systems 2010), the dilution effect of moisture in the soil may cause discrepancies with laboratory results. Since ICP results are based on dry soil sample weights, corrections with original moisture contents are necessary to represent the field conditions under which the PXRF scans were performed.

Table 2 shows the fitting parameters between PXRF readings and ICP data with and without correction. Overall, the moisture-corrected ICP data (adjusted to represent field conditions) matched better with the PXRF readings than the non-corrected data, as indicated by improved fitted slope performance (closer to 1, except for Zn), enhanced  $R^2$  values, and reduced root mean square errors (RMSEs; except for Mn). As such, PXRF measurements may represent the true field conditions more closely than conventional ICP data.

PXRF–corrected ICP data comparison

PXRF measurements matched reasonably well with the corrected ICP data for the majority of the studied trace elements (As, Co, Cu, Fe, Mn, Pb, and Zn, except for Ba and Cr) in terms of the coefficients of determination ( $R^2$  values, Table 2). Even for Ba and Cr, the poor match between the two datasets is mainly due to a few outliers and a close relationship can clearly be identified for the majority of the samples (Fig. 2).

PXRF readings provided higher concentrations than the ICP data for almost all the elements, except for Zn, as evidenced by the slopes of the fitting line which were less than 1 (Table 2). Considering the low recovery rates of ICP data

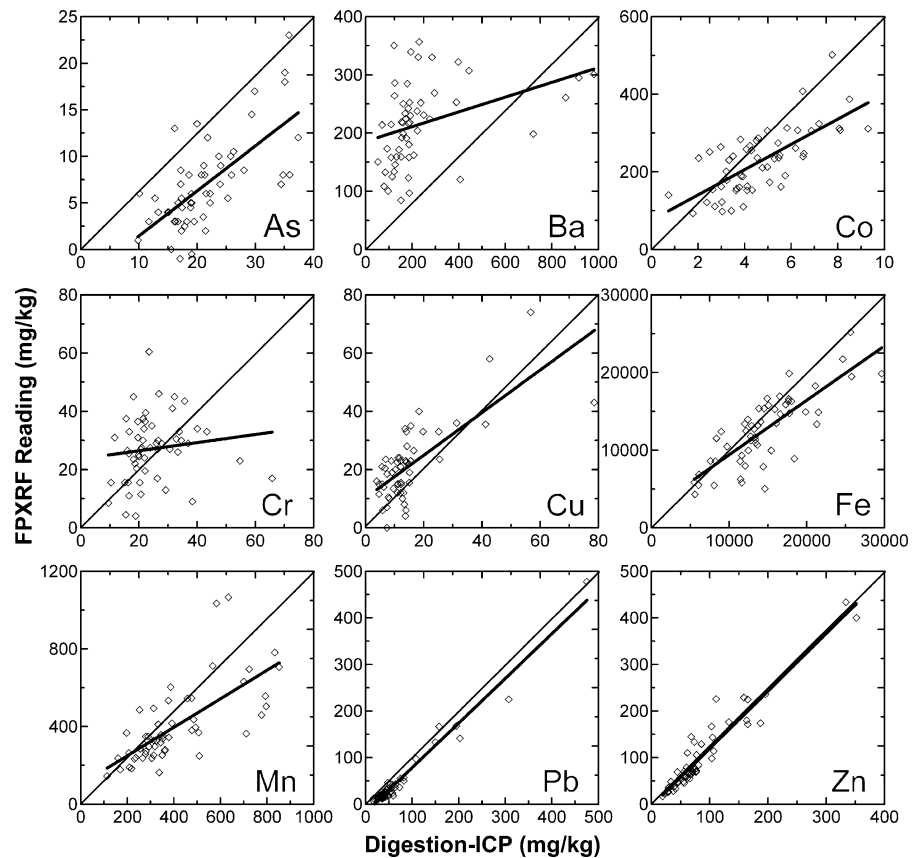
**Table 2** Parameters of fitting lines between PXRF readings and digestion–ICP results with and without field moisture correction

Parameter	Correction	As	Ba	Co	Cr	Cu	Fe	Mn	Pb	Zn
Slope	No	0.322	0.091	20.586	−0.055	0.635	0.486	0.549	0.900	1.094
	Yes	0.483	0.127	35.522	0.140	0.731	0.701	0.735	0.957	1.234
$R^2$	No	0.348 <sup>a</sup>	0.074	0.356 <sup>b</sup>	0.004	0.481 <sup>b</sup>	0.454 <sup>b</sup>	0.526 <sup>b</sup>	0.955 <sup>b</sup>	0.859 <sup>b</sup>
	Yes	0.462 <sup>b</sup>	0.129	0.503 <sup>b</sup>	0.016	0.541 <sup>b</sup>	0.637 <sup>b</sup>	0.490 <sup>b</sup>	0.968 <sup>b</sup>	0.912 <sup>b</sup>
RMSE	No	16.05	4,629.92	4,514.12	127.97	88.45	11,460,000	18,828.9	254.11	1,022.04
	Yes	13.25	4,352.41	3,485.71	126.31	78.22	7,631,980	20,245.6	181.78	637.16

<sup>a</sup>Significant at level of significance  $\alpha = 0.05$  (two-tailed test)

<sup>b</sup>Significant at level of significance  $\alpha = 0.01$  (two-tailed test)

**Fig. 2** Correlation between PXRF readings and aqua regia digestion–ICP results (with correction of field moisture contents) for the studied soil elements at two sites in Louisiana, USA



on NIST SRM 1646, the PXRF readings may be closer to the “true” total concentrations. It is noteworthy that the PXRF readings of Co were two orders of magnitude higher than the ICP data while those of all the other elements were of the same magnitude. Still, the PXRF readings and the ICP data for Co are highly correlated, suggesting that a modification of the internal factory calibrations may be required to obtain better results.

#### Descriptive statistics of in situ PXRF readings

As previously mentioned, PXRF readings may represent the true field conditions more accurately than the ICP data given the complicating factors of moisture dilution effect and recovery rates.

The results of two-sample *t* test assuming unequal variances indicated that the mean concen-

trations of all elements differ between BRS1 and BRS2 (Table 3). However, the elements may be divided into two groups based on a closer evaluation of the means and medians: the first group consists of the elements with average concentrations that are of the same order of magnitude in both BRS1 and BRS2 (As, Ba, Co, Cr, Cu, and Fe), and the second includes the elements that have much higher means and medians in BRS1 than in BRS2 (Mn, Pb, and Zn).

Elemental contents in BRS1 were highly positively skewed for almost all elements, while BRS2 exhibited a lower level of variability (Table 3). The trace elements in BRS1 also had a wider range than those in BRS2. Since the majority of the BRS1 is in urban area and BRS2 is dominated by rural areas (Fig. 1), more human activities (e.g., traffic and residential construction) in BRS1 may be the cause of the higher trace element means.

**Table 3** Descriptive statistical parameters of trace elements and geochemical background for two study sites in Louisiana, USA

Parameter	As	Ba	Co	Cr	Cu	Fe	Mn	Pb	Zn
BRS1, N = 91									
Mean	5.4 <sup>a</sup>	237.1 <sup>a</sup>	233.3 <sup>a</sup>	47.2 <sup>a</sup>	29.8 <sup>a</sup>	13,376.0 <sup>a</sup>	712.3 <sup>a</sup>	105.0 <sup>a</sup>	170.8 <sup>a</sup>
Median	4.5	216.0	206.0	27.5	21.0	11,500.5	354.5	48.5	110.0
Min.	-4.5	41.5	64.0	-2.5	6.0	3,017.5	124.5	10.5	32.0
Max.	24.0	1,073.5	1,603.5	1,195.0	188.5	83,113.0	15,902.0	966.5	1,030.5
Kurtosis	2.9	19.5	31.5	55.2	14.6	28.6	57.5	18.4	9.4
Skewness	1.2	3.5	5.2	7.3	3.6	4.9	7.3	3.7	2.7
BRS2, N = 67									
Mean	8.7 <sup>b</sup>	266.5 <sup>b</sup>	253.4 <sup>b</sup>	28.6 <sup>b</sup>	21.3 <sup>b</sup>	15,134.0 <sup>b</sup>	346.3 <sup>b</sup>	22.5 <sup>b</sup>	79.6 <sup>b</sup>
Median	7.5	266.0	237.0	28.5	20.0	13,907.0	322.5	16.5	70.0
Min.	2.0	94.0	100.0	8.0	3.0	4,712.5	143.0	6.5	34.5
Max.	53.0	386.5	501.5	43.5	73.5	28,100.0	1,377.5	252.0	267.0
Kurtosis	25.9	0.3	0.7	-0.1	11.2	0.3	22.0	41.0	7.1
Skewness	4.3	-0.3	0.9	-0.4	2.4	0.6	3.8	6.1	2.4
Geochemical background <sup>a</sup>									
Mean	6.6	-	13	65	18	27,000	900	33	82
Median	5.3	-	14	75	20	28,000	900	33	94
Min.	0.5	-	3	9	2	3,000	200	3	4
Max.	21.5	-	23	93	26	43,000	1,600	52	122

Superscripts a and b denote the results of two-sample *t* test assuming unequal variances,  $\alpha = 0.01$  (two-tailed test)

<sup>a</sup>Data from Horowitz et al. (1991)

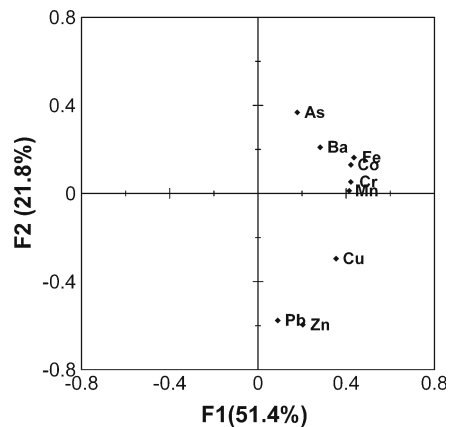
Relationships among variables using PCA

Principal component analyses were performed for the datasets of BRS1 only, BRS2 only, and BRS1 and BRS2 together. The PCA results are very similar for the three datasets, implying that the sources of the trace elements are likely the same for the two study sites (Fig. 3).

Significant high correlation coefficients were obtained among As, Ba, Co, Cr, Cu, and Fe. Similarly, close correlations were identified among Cu, Zn, and Pb (Table 4).

PCA results showed that approximately 73% of the total variability was explained by the first two factors, with ~51% and ~22% linked to components 1 and 2, respectively (Fig. 4). Specifically, As, Ba, Co, Cr, Mn, and Fe were positively loaded in component 1, and Cu, Pb, and Zn were positively loaded in component 2. The two components may provide information regarding the sources of the trace elements, as suggested by other researchers (e.g., Loska and Wiechula 2003; Delgado et al. 2010; Sollitto et al. 2010). The natural origin of the related elements may be considered in component 1, while component 2 can

be linked to the contaminants from anthropogenic activities. Note that the concentrations of As were positively loaded in component 1. This implies that As identified in the study area is associated with geochemical background concentrations only or has a very low contamination level for the study area, indicated by a low mean concentration (Table 3).



**Fig. 3** Principal component analysis for all samples from sites BRS1 and BRS2 in Louisiana, USA

**Table 4** Pearson correlation matrix for evaluated soil elements of all PXRF scans for two study sites in Louisiana, USA

	As	Ba	Co	Cr	Cu	Fe	Mn	Pb	Zn
As	1								
Ba	0.374 <sup>b</sup>	1							
Co	0.354 <sup>b</sup>	0.564 <sup>b</sup>	1						
Cr	0.259 <sup>b</sup>	0.387 <sup>b</sup>	0.798 <sup>b</sup>	1					
Cu	0.144	0.349 <sup>b</sup>	0.586 <sup>b</sup>	0.573 <sup>b</sup>	1				
Fe	0.427 <sup>b</sup>	0.627 <sup>b</sup>	0.936 <sup>b</sup>	0.836 <sup>b</sup>	0.583 <sup>b</sup>	1			
Mn	0.226 <sup>a</sup>	0.355 <sup>b</sup>	0.745 <sup>b</sup>	0.974 <sup>b</sup>	0.598 <sup>b</sup>	0.797 <sup>b</sup>	1		
Pb	-0.136	-0.010	0.058	0.037	0.374 <sup>b</sup>	0.039	0.051	1	
Zn	-0.183	0.063	0.201	0.313 <sup>b</sup>	0.680 <sup>b</sup>	0.187	0.363 <sup>b</sup>	0.688 <sup>b</sup>	1

<sup>a</sup>Significant at level of significance  $\alpha = 0.05$  (two-tailed test)

<sup>b</sup>Significant at level of significance  $\alpha = 0.01$  (two-tailed test)

### Enrichment factors

Because FRXRF scans were performed only on the soil surface, which normally has lower trace element concentrations than the subsoils due to pedogenesis (leaching) except for those elements that are extremely immobile (e.g., Pb), normalization is required prior to the calculation of enrichment factors. A number of elements including Al, Cs, Li, and Fe have been suggested as normalizing elements by previous studies (e.g., Sharman et al. 1984; Loring 1991; Herut et al. 1993; Grousset et al. 1995; Delgado et al. 2010). Due to robust data availability, Fe was selected as the normalizing element. The enrichment factor was calculated as (1):

$$EF = [C_{ij}/C_{ni}] / [C_{ib}/C_{nb}] \tag{1}$$

where  $C_i$  is the PXRF reading of the  $i$ th element of the  $j$ th sample,  $C_{nj}$  is the PXRF reading of the normalizing element (Fe) of the  $j$ th sample,  $C_{ib}$  is the geochemical background mean of the  $i$ th element, and  $C_{nb}$  is the geochemical background mean of the normalizing element (Fe). The available geochemical background values for the study area are listed in Table 3.

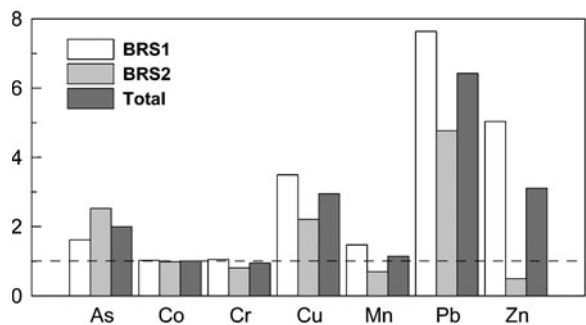
Figure 4 shows the enrichment factors of each studied element for BRS1, BRS2, and the two sites together. Overall, six out of seven elements (except for As) have higher enrichment factors in BRS1 than in BRS2, reflecting stronger anthro-

pogenic influences in urban areas. Specifically, As at BRS2, Cu and Pb at both sites, and Zn at BRS1 are highly enriched in the surface soils, given a critical enrichment factor of 1.5. The elevated level of As is likely associated with the use of agricultural herbicides and pesticides as BRS2 is mostly agricultural land.

### Spatial distribution of the studied elements

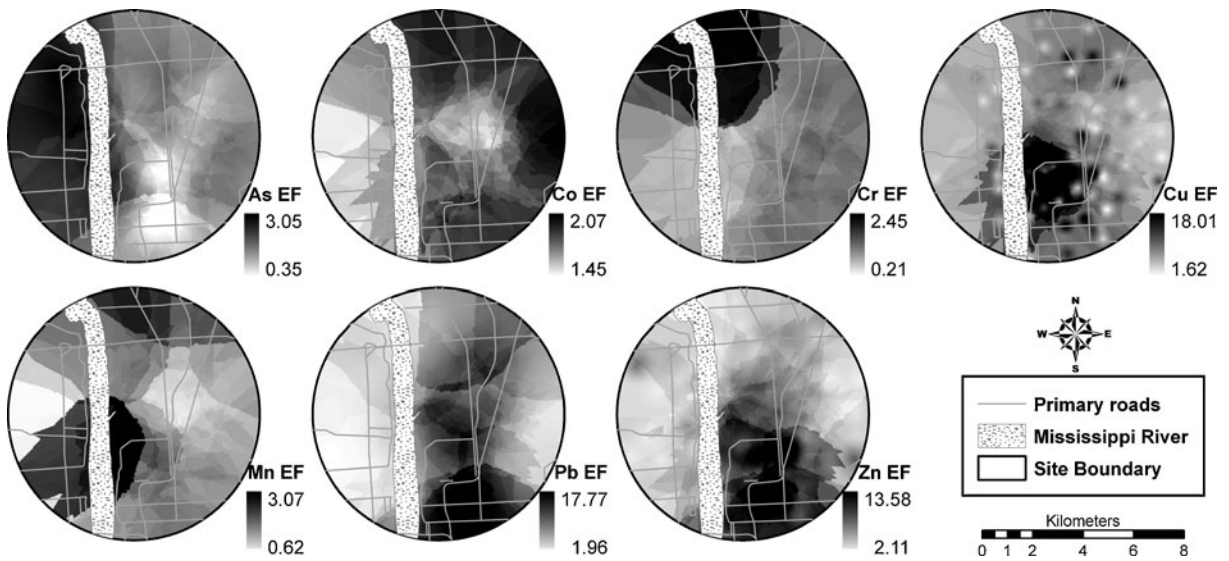
The major advantage of PXRF application is that the elemental concentrations can be obtained on site in a very short period of time, i.e., generally less than 2 min. Coupled with GPS, spatial distribution maps can be readily generated and incorporated into environmental quality assessment.

Figures 5 and 6 show the spatial distribution maps of the EF of the studied elements for BRS1



**Fig. 4** Averaged enrichment factors for elemental soil data from the sample sets of BRS1, BRS2, and BRS1 and BRS2 together from Louisiana, USA



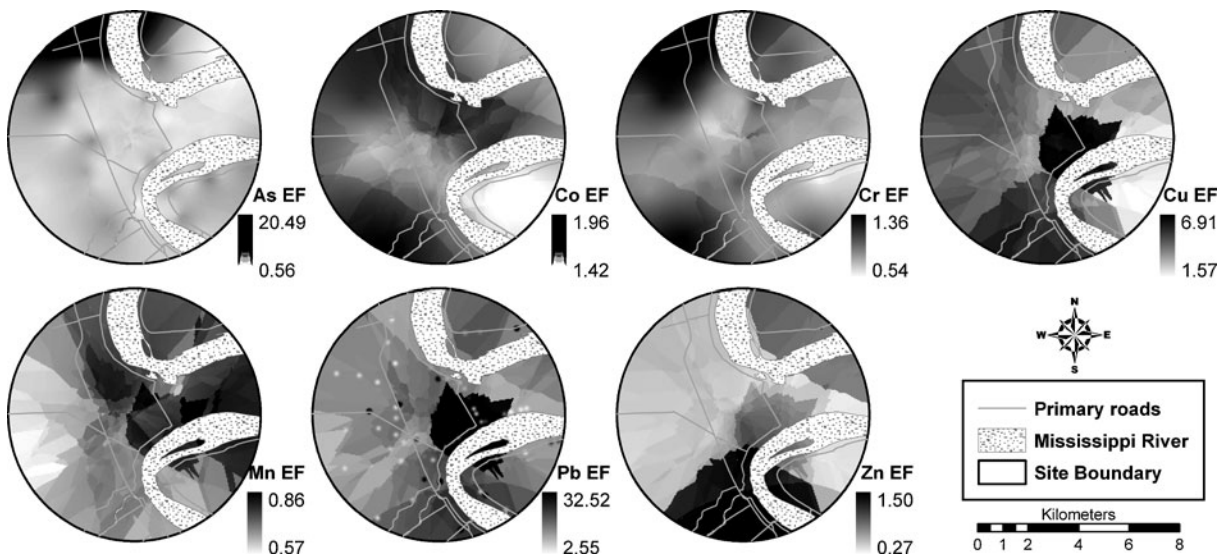


**Fig. 5** Interpolated enrichment factor maps for selected elements at site BRS1 (Louisiana, USA) using ordinary kriging

and BRS2, respectively. Again, BRS1 is centered by a petroleum refinery and BRS2 is centered by a chemical plant, respectively. According to the interpolated maps of both sites, As, Co, and Cr showed noticeable depletion, while other elements (Cu, Mn, Pb, and Zn) exhibited a substantial degree of enrichment in the center. This is likely associated with frequent production activity and

transportation associated with the refinery and chemical plant.

Specifically, Cu and Mn for both sites and Pb for BRS2 had significantly higher concentrations in the center. The highest degrees of enrichment of Pb and Zn for BRS1 were found in the area of the south part of the sampling circle, which has Interstate 10 and other major local roads with high



**Fig. 6** Interpolated enrichment factor maps for selected elements at site BRS2 (Louisiana, USA) using ordinary kriging

traffic volume. Although the average enrichment factor of Zn for BRS2 is lower than 1 (Fig. 4), the enrichment in the center and the lower part of the sampling circle can be detected according to the map (Fig. 6). The distribution maps provided additional information not readily identified solely by PCA. When interpolation and PCA results are considered together, the origins of the elements at each site can be interpreted in greater detail.

## Conclusions

Rapid urbanization and the increasing popularity of peri-urban agriculture have raised concerns about heavy metal contamination. A rapid, on-site approach would be more effective than the time-consuming and cost-prohibitive traditional methods for assessing environmental quality. This study examined the feasibility of utilizing portable XRF in environmental quality assessment for the two study sites in Baton Rouge, Louisiana, USA (BRS1 and BRS2).

Elements quantified via PXRF for NIST standards matched the certified value quite well for most elements (except for Co and Hg). Furthermore, PXRF showed better recovery rates than aqua regia digestion/ICP quantification. Overall, reasonable correlation between PXRF readings and certified NIST standards indicated that PXRF can be used to accurately identify most heavy metals in soils.

Validation samples (~35% of the scan sites) showed that PXRF readings closely correlated with aqua regia digestion/ICP quantification. Furthermore, the correlation was improved by correcting ICP results for field moisture content. This proved that field moisture conditions have a dilution effect on laboratory ICP results. As such, PXRF readings likely represent true field elemental concentrations better than ICP data.

Principal component analysis indicated that for both study sites, grouping Cu, Pb, and Zn together was appropriate and the elevated elemental concentrations of these three elements are likely attributed to anthropogenic activities. Concentrations of the other elements studied are related to their natural geologic origins.

Interpolation maps of enrichment factors (converted from geo-referenced PXRF readings) explicitly revealed the spatial distribution patterns of the studied elements. The interpolation patterns matched the PCA results quite well but also provided more details. The results indicate that the petroleum refinery and chemical plant did elevate the concentrations of some trace elements (Cu, Mn, Pb, and Zn) but intensified anthropogenic activities (e.g., traffic and residential construction) associated with urbanization play a more important role in increasing the concentrations of some trace elements (specifically Pb and Zn).

In summary, the study showed that PXRF has considerable promise as an appropriate field quantification tool for assessing trace element concentration as an indicator of environmental quality. Linked with GPS, the spatial distribution patterns of the trace elements can be readily obtained with PXRF in the field, in minutes.

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