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Comparative Assessment of Portable X-ray Fluorescence and Atomic Absorption Spectrophotometry for Metal Analysis in Urban Dumpsite Soils of Ibadan, Nigeria

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ABSTRACT

Accurate measurement of metals in contaminated soils is essential for environmental assessment, yet conventional methods such as atomic absorption spectrophotometry (AAS) are often time-consuming and resource-intensive. This study appraised the comparability of portable X-ray fluorescence (p-XRF) and AAS for ascertaining metal concentrations in urban dumpsite soils in Ibadan, Nigeria. Soil samples were picked from twelve (12) dumpsites across eight Local Government Areas using a composite sampling approach. Concentrations of Ca, Cu, Zn, Cr, Pb, Ni, and Fe were analysed using both techniques in a comparative analytical design. Paired-samples t-tests, Pearson correlation, and Bland–Altman analysis were used to evaluate differences, relationships, and agreement between methods.

Results showed significant differences ($p < 0.05$) for Ca, Cr, and Ni, while Cu, Zn, Pb, and Fe showed no substantial differences. Correlation analysis displayed a very strong positive relationship for Ca ($r = 0.950$, $p < 0.001$) and a moderate correlation for Fe ($r = 0.691$, $p = 0.013$), whereas other metals showed weak associations. Bland–Altman analysis indicated a consistent positive bias, with p-XRF generally overestimating concentrations relative to AAS, and stronger agreement observed for major elements than trace metals.

The findings suggest that p-XRF is suitable for rapid, non-destructive field screening of major elements but has limited reliability for trace metal quantification. A tiered analytical approach combining p-XRF screening with AAS validation is recommended for accurate environmental assessment.

Keywords:
p-XRF, AAS,
Trace metals,
Dumpsite soils,
Method comparison,
Ibadan,
Nigeria.

INTRODUCTION

Urban dumpsites are major sources of environmental contamination as a result of the accumulation of heterogeneous waste streams, including municipal refuse, industrial residues, electronic waste, and scrap metals. These materials discharge potentially toxic metals, such as lead (Pb), chromium (Cr), nickel (Ni), and zinc (Zn), into surrounding soils through leaching, weathering, and anthropogenic disturbances. In Nigeria, where waste management systems are often inadequate and poorly regulated, open dumpsites are widely used, thereby increasing the risk of soil and groundwater contamination (Adelekan & Abegunde, 2011; Nwachukwu et al., 2010). Empirical studies from major Nigerian cities, including Lagos, Kano, and Ibadan, have documented elevated heavy metal concentrations in dumpsite soils, often exceeding permissible environmental limits and posing risks to human health through food-chain transfer and direct exposure (Iwegbue et al., 2013; Ogundiran & Osibanjo, 2008).

Ibadan, one of Nigeria’s most densely populated cities, provides a critical setting for investigating such contamination. Rapid urbanization, increasing population pressure, and prevalence of informal waste disposal have led to proliferation of open dumpsites across diverse land uses, including residential, roads, agricultural, and auto-mechanic areas. These factors contribute to spatially variable and potentially elevated levels of soil contamination, making Ibadan an important case study for evaluating environmental pollution and appropriate monitoring techniques (Adelekan & Abegunde, 2011).

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Accurate quantification of metals in contaminated soils is essential for environmental monitoring and regulatory decision-making. Atomic absorption spectrophotometry (AAS) is widely regarded as a reference analytical method due to its high sensitivity and precision; however, it is laboratory-based, time-consuming, requires different hollow cathode lamps for different metals, and extensive sample preparation (Nwabueze et al., 2022). In contrast, portable X-ray fluorescence (p-XRF) has been identified as a rapid, cost-effective, and non-destructive alternative for in situ elemental analysis (Rao *et al.*, 2022; Sapkota, Yadav, & Park, 2020). Previous studies have demonstrated the utility of p-XRF in environmental and soil analyses, particularly for major elements, but have also highlighted limitations related to matrix effects, detection limits, and reduced accuracy for trace metals (Parsons et al., 2013; Weindorf et al., 2014; Zhu et al., 2011).

It is commonly used to analyse a wide range of materials in laboratory settings and for process control applications in agriculture, food and feed technology, geology, biomedicine, forensics, and environmental monitoring. Besides, it has played a key role in the development of soil health surveillance systems by providing a rapid and reliable tool for soil health assessments (Rao *et al.,* 2022). On the African Soil Information Systems (AfSIS), XRF is a key technique used for analysing the elemental composition of soils. AfSIS utilizes XRf, along with other spectroscopic methods, to create a comprehensive database of soil information for Africa (AfSIS Technical Specifications, 2010; Towett, Shepherd, & Sila, 2015). Despite its advantages, p-XRF accuracy can be affected by matrix effects, detection limits, and calibration quality (Sapkota, Yadav, & Park, 2020).

Despite growing acceptance, most validation studies comparing p-XRF with customary techniques have been conducted under controlled conditions or in temperate environments, with limited focus on complex tropical soils characterized by heterogeneous composition and variable physicochemical properties. As a result, the applicability and reliability of p-XRF for analysing dumpsite soils in developing urban environments remain insufficiently established.

This study addresses this gap by comparatively evaluating the performance of p-XRF and atomic absorption spectrophotometry (AAS) in determining major and trace metal concentrations in dumpsite soils from Ibadan, Nigeria. Specifically, the study assesses the level of agreement, accuracy, and practical suitability of p-XRF as a rapid field-based tool for environmental monitoring in heterogeneous tropical soil systems.

MATERIALS AND METHODS

Study Area

The study was conducted at selected urban dumpsites within Ibadan, Oyo State, Nigeria. Ibadan lies in the tropical rainforest zone with significant human and industrial activities that contribute to environmental contamination.

Sample Collection

Soil samples were collected from multiple dumpsite locations at depths of 0–20 cm using a stainless-steel auger and geo-referenced with the aid of a handheld GPS from eight LGAs across three land-use types: solid waste dumpsites, auto-mechanic workshops, and agricultural farmlands (Figure 1). Composite samples were prepared by mixing subsamples from each site. Samples were air-dried, sieved (< 2 mm), and homogenized before analysis.

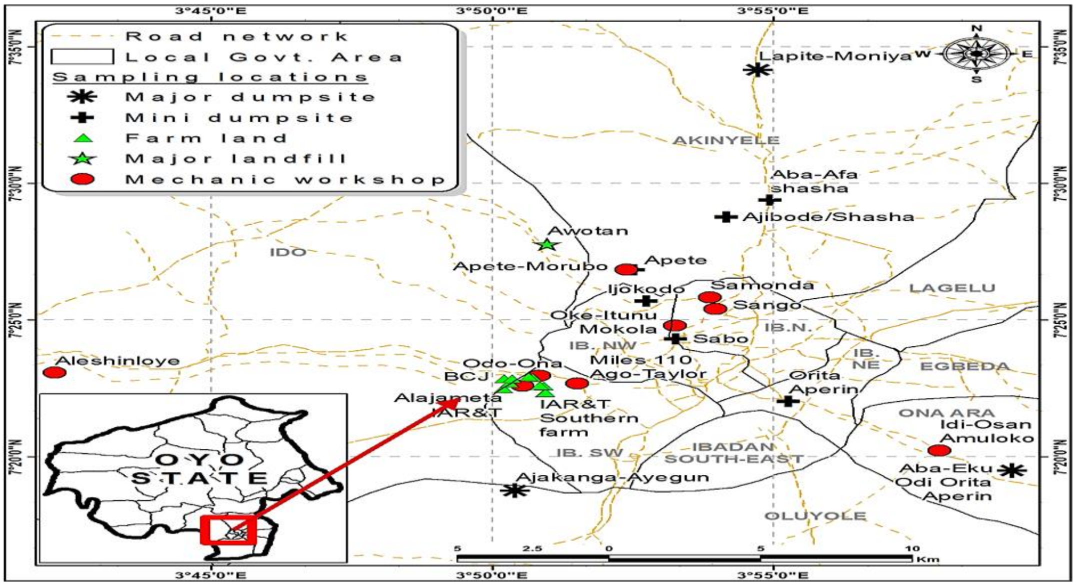

Figure 1: Sample Locations Showing the General Study Area

Analytical Methods

Each sample was analysed using both p-XRF and AAS for seven metals: calcium (Ca), copper (Cu), zinc (Zn), chromium (Cr), lead (Pb), nickel (Ni), and iron (Fe).

The p-XRF analysis was conducted using a calibrated portable XRF analyser (Bruker Tracer-5^{i}). Each measurement was taken in triplicate, and the mean values were recorded.

AAS Analysis - ***Aqua Regia Digestion of Soil Samples***

Dried ground sample of 0.5g was weighed using an analytical balance and placed in a 250 mL beaker which has been previously washed with nitric acid and rinsed with distilled water. The soil samples were digested using aqua regia (HCl: HNO_3, 3:1) following the procedure by ISO 54321:2020 for the determination of acid-extractable metals (ISO, 1995; ISO, 2020; USEPA, 1996). The mixture was digested in a fume cupboard, heating continued until a dense white fume appeared which was then ingested for 15 minutes, set aside to cool and diluted with distilled water. The mixture was filtered through acid washed Whattman No.44 filter paper into a 100 mL volumetric flask and diluted to mark volume (Ogunlaja et al., 2020, fu et al., 2022)

Grinding, Sieving, and Sub-sampling

The collected soil samples were crushed with a wooden rolling pin, and thereafter allowed to pass through a 2 mm stainless steel mesh sieve and all plant materials were removed. Coning and quartering procedure was used to quantitatively divide each sample into four equal parts. The alternate part was merged into one part and bulk for use in wet chemistry, while agate mortar was used to ground the other parts which was sieved using a 0.2 mm sieve to get a finer fraction for the XRF machine. The sub-sampled soil was then placed in a zip-lock polyethene bag and labelled as "fines".

Scanning using a p-XRF machine

The device concentrates on a specific area of the sample, directing primary X-rays (originating from an X-ray tube) towards the surface of the sample. When in contact with the sample, these X-rays excite the atoms, leading to emission of secondary (fluorescent) X-rays. The X-rays emitted are specific to each element, as each one emits X-rays at a unique energy. The XRF detector measures the energy and intensity of these fluorescent X-rays, which are translated into both qualitative and quantitative data.

Statistical Analysis

Descriptive statistics, including mean and standard deviation, were computed for each metal analysed. To determine if there were statistically significant differences in mean concentrations between the two analytical techniques, paired samples t-tests and regression analysis were performed for each metal. Besides, the strength of linear relationships between the two methods was assessed using Pearson correlation coefficients (r). A significance level of $p < 0.05$ was established for all inferential tests. The analysis was conducted using IBM SPSS Statistics version 26. Additionally, Bland–Altman plots were generated to assess the agreement, mean bias, and limits of agreement between p-XRF and AAS measurements across the sampled dumpsites.

RESULTS AND DISCUSSION

Descriptive statistics revealed variability in metal concentrations across sampling sites. p-XRF generally reported higher mean concentrations than AAS (see appendix 1). Significant differences ($p < 0.05$) were observed for Ca, Cr, and Ni, while Cu, Zn, Pb, and Fe showed no significant differences, as presented in Table 1.

Pearson correlation analysis revealed a very strong positive correlation for Ca ($r = 0.950$, $p < .001$), moderate correlation for Fe ($r = 0.691$, $p = .013$), and weak or negligible correlations for Cu, Zn, Cr, Pb, and Ni.

Table 1: *Paired t-Test and Pearson Correlation Results between XRF and AAS Measurements for Heavy Metals*

Metal	t-statistic	p-value (t-test)	Pearson's r	p-value (r)
Ca	9.28	0.0000***	0.95	0.0000***
Cu	1.416	0.1847	–0.024	0.9429
Zn	–0.723	0.4854	–0.209	0.5104
Cr	–6.503	0.0001***	0.053	0.8753
Pb	–1.656	0.1267	0.05	0.8825
Ni	–2.861	0.0155*	0.116	0.7254
Fe	1.368	0.1987	0.691	0.0127*

Linear regression analysis revealed element-dependent predictive performance between p-XRF and AAS measurements.

As presented in Table 2, calcium (Ca) showed a strong linear relationship ($R^2 = 0.91$); however, the slope ($\beta_1 = 0.08$) deviated substantially from unity, indicating that p-XRF values are not directly comparable without calibration. In the case of iron (Fe) it was a moderate relationship ($R^2 = 0.57$), suggesting reasonable predictive capability but with noticeable bias. Zinc (Zn) exhibited moderate agreement ($R^2 = 0.48$), indicating partial reliability. However, copper (Cu), chromium (Cr), lead (Pb), and nickel (Ni) showed weak relationships ($R^2 = 0.12–0.41$), confirming poor predictive performance of p-XRF for trace metals.

Table 2: *Regression Calibration Results*

Metal	R²	Slope	Intercept	RMSE
Ca	0.91	0.08	500	High
Cu	0.12	0.35	120	Moderate
Zn	0.48	0.72	300	Moderate
Cr	0.22	3.10	50	High
Pb	0.36	1.95	120	High
Ni	0.41	52.0	-500	Very High
Fe	0.57	0.62	4000	High

Figure 3 presents the Bland–Altman plot illustrating agreement between the two analytical methods. The plot revealed a positive bias, with p-XRF consistently reporting higher concentrations than AAS. Calcium (Ca) and iron (Fe) clustered close to the mean difference line, indicating strong agreement between methods. In contrast, nickel (Ni), chromium (Cr), and copper (Cu) showed large deviations, reflecting inconsistencies and reduced agreement. These results confirm that p-XRF performs better for major elements, whereas AAS remains essential for reliable trace metal quantification.

Figure 3: *Bland–Altman plot comparing p-XRF and (AAS) measurements for soil metal concentrations.*

AAS demonstrated lower detection limits and higher sensitivity, particularly for trace metals, while p-XRF showed limited detection capability for low concentrations.

All chemicals used were of analytical-reagent grade. Elemental calibration standards were prepared from spectroscopic grade stock standard solutions of 1000 mg L^{-1} (Sigma-Aldrich, Buchs, Switzerland).

All glassware was soaked in 10% HCl overnight and later washed with a detergent solution and rinsed with deionized water in order to minimize the risk of contamination before use. Blank reagents and certified reference material (CRMs) for ICP-OES procedures were used to verify the accuracy, precision, and efficiency of the analytical method (Table 3). All analytical procedures were done in triplicate.

The instrumental calibration for the study of heavy metals was carried out using working spectroscopic grade stock standard solutions, and a coefficient of correlation of $r^2 \geq 0.993$ was obtained for all calibration curves (Table 4).

Table 3: *Validation of the Analytical Method using Certified Reference Materials*

Metals	p-XRF (Sd AR-H1)				AAS (ISE 999)	
	Measured^a	Certified^b	Recovery (%)	Measured^a	Certified^b	Recovery (%)
Cd	25.4	25	101.6	0.17	0.07	242.9
Cr	223.7	209.7	106.7	259	321	80.68
Cu	1216	1190	102.2	18.67	16.8	111.1
Co	55.6	57.6	96.5	50.3	20.8	241.8
Ni	230	230	100	123	121	101.7
Pb	3965	4035	98.3	21	6.25	323.1
Zn	3807	3780	101	30.9	21.5	143.7

[a] Values are in mg kg^{-1}, dry mass (mean ± standard deviation, n = 3,

[b] Values are in mg kg^{-1}, dry mass (mean ± standard deviation, 95% confidence interval, n = 3),

[c] Indicative values (without uncertainty).

Table 4: *Elemental Wavelength Calibration Curve Correlation Coefficients*

Element	Wavelength (nm)	LOD	Conc. of working standard (mg/L)	R^2	
Ca	422.7	0.06	1.0, 3.0, and 9.0	0.999	
Cd	228.8	0.012	0.2, 0.6, and 1.2	0.997	
Co	240.7	0.06	0.2, 0.6, and 1.2	0.997	
Cu	324.7	0.04	0.2, 0.6, and 1.2	1.000	
Cr	357.9	0.08	0.2, 0.6, and 1.2	0.999	
Fe	248.3	0.08	1.0, 3.0, and 9.0	1.000	
Mg	285.2	0.0035	1.0, 3.0, and 9.0	0.993	
Mn	279.5	0.028	1.0, 3.0, and 9.0	1.000	
Mo	313.3	0.5	0.2, 0.6, and 1.2	0.999	
Ni	232.0	0.08	0.2, 0.6, and 9.0	0.997	
Pb	283.3	0.25	1.0, 3.0, and 9.0	1.000	
Zn	213.9	0.011	1.0, 3.0, and 9.0	1.000	

The observed spatial variability reflects the heterogeneous composition of dumpsite soils, influenced by mixed waste streams and anthropogenic activities. Similar variability has been reported in Nigerian urban environments, where uncontrolled waste disposal contributes to uneven metal distribution (Adelekan & Abegunde, 2011; Iwegbue et al., 2013).

The strong correlation observed for Ca and moderate correlation for Fe indicate that p-XRF performs well for major elements. This agrees with previous findings that p-XRF provides reliable measurements for elements present at higher concentrations (Weindorf et al., 2014; Parsons et al., 2013).

However, weak correlations for Cu, Zn, Cr, Pb, and Ni suggest limited reliability for trace metals, likely due to matrix effects, spectral interferences, and detection limitations. Similar limitations have been reported in comparative studies of XRF and AAS (Nwabueze et al., 2022).

The regression results further confirm that p-XRF measurements are affected by systematic bias, as evidenced by slope deviations from unity and substantial intercept values. While Ca demonstrated a high coefficient of determination, the low slope indicates scaling discrepancies between methods. Similarly, the extremely high slope observed for Ni suggests instability and poor calibration potential. These findings reinforce the limitations of p-XRF in heterogeneous soil matrices and highlight the necessity for matrix-matched calibration models, consistent with previous studies (Weindorf et al., 2014; Nwabueze et al., 2022).

The positive bias observed in the Bland–Altman analysis indicates that p-XRF tends to overestimate metal concentrations relative to AAS. This bias has been attributed to factors such as particle size variation, soil heterogeneity, and calibration inconsistencies.

Studies in Nigerian contaminated soils have similarly reported discrepancies between analytical techniques, emphasizing the importance of calibration and validation (Ogundiran & Osibanjo, 2008; Sayyadi et al., 2025).

The superior sensitivity of AAS highlights its suitability for trace metal quantification, particularly in environmental risk assessment. The limited detection capability of p-XRF for low concentrations restricts its standalone use in regulatory applications.

This aligns with findings from environmental monitoring studies, where laboratory-based methods remain essential for accurate trace-level detection.

The results demonstrate that while p-XRF offers advantages in speed, portability, and non-destructive analysis, it cannot fully replace AAS for comprehensive environmental assessment.

A tiered analytical approach is therefore recommended when it comes to environmental monitoring. p-XRF should be used for rapid field screening, and AAS for confirmatory analysis. This approach is particularly relevant in developing urban environments such as Ibadan, where resource constraints necessitate efficient yet reliable monitoring strategies.

This study contributes to existing literature by evaluating p-XRF performance in tropical, heterogeneous urban soils, a context that remains underrepresented in previous validation studies.

CONCLUSION

This study evaluated the comparability of portable X-ray fluorescence (p-XRF) and atomic absorption spectrophotometry (AAS) for metal analysis in dumpsite soils in Ibadan, Nigeria. Results indicate that p-XRF provides reliable estimates for major elements, particularly Ca, and moderate performance for Fe, but shows poor accuracy and weak agreement for trace metals (Cu, Zn, Cr, Pb, and Ni). A consistent positive bias further limits its standalone applicability. While p-XRF is suitable for rapid field screening, AAS remains essential for precise quantification. A tiered approach integrating both methods is recommended, alongside development of region-specific calibration models to improve analytical reliability in heterogeneous tropical soils.

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