Application of portable X-ray fluorescence spectrometry in environmental investigation of heavy metal-contaminated sites and comparison with laboratory analysis

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Abstract. In this study, portable X-ray fluorescence spectrometry (pXRF) was used to measure the heavy metal contents of As, Cu, Cr, Ni, Pb and Zn in the soils of heavy metal-contaminated sites. The precision, accuracy and system errors of pXRF were evaluated and compared with traditional laboratory methods to examine the suitability of in situ pXRF. The results show that the pXRF analysis achieved satisfactory accuracy and precision in measuring As, Cr, Cu, Ni, Pb, and Zn in soils, and meets the requirements of the relevant detection technology specifications. For the certified reference soil samples, the pXRF results of As, Cr, Cu, Ni, Pb, and Zn show good linear relationships and coefficients of determination with the values measured using the reference analysis methods; with the exception of Ni, all the measured values were within the 95% confidence level. In the soil samples, the coefficients of determination between Cu, Zn, Pb, and Ni concentrations measured laboratory pXRF and the values measured with laboratory analysis all reach 0.9, showing a good linear relationship; however, there were large deviations between methods for Cr and As. This study provides reference data and scientific support for rapid detection of heavy metals in soils using pXRF in site investigation, which can better guide the practical application of pXRF.

1. Introduction

The outlook for soil environmental conditions is not optimistic in China, and environmental pollution caused by toxic heavy metals has received increasing research attention [1]. Simple, rapid, and efficient measurement of heavy metal concentrations in the soil is of great importance in the determination of site contamination, the guidance of on-site sampling, and the assessment of remediation success [2].

The main traditional methods of measuring heavy metals in the soil are atomic fluorescence spectrometry (AFS) [3], atomic absorption spectrometry (AAS) [4], and inductively coupled plasma–atomic emission spectroscopy (ICP-AES) [5]. Although these methods produce accurate results, their operations are complicated and the analysis cycle is long, making them time-consuming and laborious. These methods are therefore only suitable for laboratory analysis. In comparison, X-ray fluorescence spectrometry (XRF) enables simultaneous multi-element analysis and has many associated advantages such as simple sample preparation, low signal interference, wide analysis range, and reliable results. Thus, XRF has become an efficient technique for heavy metal analysis [6]. Consistent with the technological development of instrument miniaturization, the portable XRF analyzer (pXRF) has been developed for portability and in situ analysis. The pXRF has extensive uses in geological exploration,
mining, ore-dressing, smelting, and environmental monitoring fields [7-11] and its adoption has greatly improved the efficiency of detection of heavy metals.

In this study, we collected hundreds of soil samples from multiple plots potentially contaminated with heavy metals in Jiangsu Province, China. Heavy metal concentrations were measured using in situ pXRF (soil samples collected on-site), laboratory pXRF (soil samples after drying and grinding), and AAS/AFS, to evaluate the data quality of values measured using pXRF and validate the feasibility of field application of pXRF. This study will provide reference and guidance for the rapid diagnosis and evaluation of soils potentially contaminated with heavy metals.

2. Materials and methods

2.1. Experimental instruments

The analyses were conducted using a pXRF analyzer (Niton XL3t 960), atomic absorption spectrophotometer (Agilent 240FS and Agilent 240Z), and atomic fluorescence spectrophotometer (AFS-230E).

2.2. Soil sampling

Reference soil materials were manufactured by the Institute of Geophysical and Geochemical Exploration, Ministry of Land and Resources of the People’s Republic of China (No.: GBW07403, GBW07404, GBW07405, GBW07407, GBW07408, GBW07444, GBW07445, and GBW07451).

The about 400 test soil samples were collected from tens of sites potentially contaminated with heavy metal in Jiangsu, China. All samples were dried in air and stones, plant roots and stems, and other impurities were removed. The samples were ground, passed through 10-mesh and 100-mesh nylon sieves sequentially, and then stored in zipper-lock bags until required for analysis.

2.3. Analytical methods

(1) pXRF measurement

Prior to measurement, the instrument was calibrated using the reference samples equipped with the instrument. Three replicates were measured for each sample, all for 120s per sample. The measured data were exported in Excel format.

Measurement of certified reference materials: The heavy metal concentrations in certified reference materials for soil composition analysis were directly measured using pXRF.

In situ measurement of soil samples (in situ pXRF method): The zipper-lock bags containing soil samples were placed at the emission port of the pXRF instrument in the sampling sites, and the heavy metal concentrations in samples were directly measured.

Ex situ measurement of soil samples (laboratory pXRF method): After air-drying, grinding, and passing through nylon sieves, the soil samples were analyzed using pXRF in the laboratory to measure heavy metal concentrations.

(2) Laboratory analysis (AAS/AFS method): The methods of measuring the six heavy metals (As, Cu, Cr, Ni, Pb and Zn) in the soil are listed in Table 1.

2.4. Evaluation methods

To test the reliability of pXRF measurement results, we analyzed the precision and accuracy of pXRF and verified the instrument accuracy and precision. According to the reference methods proposed by the US Environmental Protection Agency, we selected the relative standard deviation and the relative error to evaluate the accuracy and precision of the instrument. This approach complies with the principle that the evaluation indices should be as simple as possible [12]. The equations (Eq. 1 and Eq. 2) used for this calculation are as follows:
where \( X_i \) (mg/kg) is the value measured using pXRF, \( \bar{X} \) (mg/kg) is the mean value of total samples measured using pXRF, \( N \) is the number of samples analyzed, \( SD \) (mg/kg) is the standard deviation of samples analyzed, and \( RSD \) is the relative standard deviation of samples analyzed.

\[
RSD = \frac{SD}{\bar{X}} \times 100\% = \frac{\sqrt{\sum_{i=1}^{N} (X_i - \bar{X})^2 / (N - 1)}}{\bar{X}} \times 100\% \tag{1}
\]

\[
RPD = \frac{C_x - C_k}{C_k} \times 100\% \tag{2}
\]

where \( C_k \) (mg/kg) is the certified value in the certified reference material, \( C_x \) (mg/kg) is the value in the certified reference material measured using pXRF, and \( RPD \) is the relative error between the above two results, and the closer the RPD to 0, the higher the degree of fit. In addition, the closer the data points to the 1:1 line, the higher the degree of fit. We also conducted correlation analysis on the data using Origin 9.0 to obtain the coefficient of determination of the correlations between heavy metal concentrations measured using pXRF and traditional AAS/AFS laboratory analysis. In correlation analysis, a coefficient of determination of >0.70 is generally considered to indicate a significant correlation [13,14].

3. Results and discussions

3.1. Precision and accuracy of pXRF

The stability index (precision) and the accuracy index (accuracy) can be used to evaluate the reliability of the method. The accuracy, precision, and applicability of the pXRF method can be validated by analyzing the difference between the heavy metal concentrations of the certified reference materials and the values measured using pXRF [15]. When tested with the

| No. | Heavy metal | Analytical method | Instrument |
|-----|-------------|-------------------|------------|
| 1   | Copper (Cu) | Soil quality - Determination of copper and zinc - Flame atomic absorption spectrophotometry (GB/T 17138-1997) | Agilent 240FS |
| 2   | Zinc (Zn)   | Soil quality - Determination of lead and cadmium - Graphite furnace atomic absorption spectrophotometry (GB/T 17141-1997) | Agilent 240Z |
| 3   | Lead (Pb)   | Soil quality - Determination of total chromium - Flame atomic absorption spectrophotometry (HJ/T 491-2009) | Agilent 240FS |
| 4   | Chromium (Cr) | Soil quality - Determination of nickel - Flame atomic absorption spectrophotometry (GB/T 17139-1997) | Agilent 240FS |
| 5   | Nickel (Ni) | Soil quality - Determination of total mercury, total arsenic, and total lead - Atomic fluorescence spectrometry - Part 2: Determination of total arsenic in soil (GB/T 22105.2-2008) | AFS-230E |
| 6   | Arsenic (As) | Soil quality - Determination of total mercury, total arsenic, and total lead - Atomic fluorescence spectrometry - Part 2: Determination of total arsenic in soil (GB/T 22105.2-2008) | AFS-230E |
certified reference material (GBW07407) for soil composition analysis, the mean values of As, Ni, and Zn measured using pXRF were slightly lower than the certified values. In contrast, the mean values of Cr, Cu, and Pb measured using pXRF were slightly higher than the certified values (Table 2). The accuracy (RPD) was between 0.6% and 19.8%, while the precision (RSD) was between 3.7% and 10.8%. Both the RPD and RSD values were within ±20%. These results indicate that pXRF achieves satisfactory accuracy and precision in measuring As, Cr, Cu, Ni, Pb, and Zn in soils [16,17], and meets the accuracy and precision requirements of instrument detection as specified by the US Environmental Protection Agency and the Technical Specification for Soil Environmental Quality Monitoring in Farmland in China.

Table 2. Comparison of heavy metal concentrations certified in the certified reference material (GBW07407) and the values measured using pXRF.

| Heavy metal | Certified value | pXRF | RPD (%) | RSD (%) |
|-------------|----------------|------|---------|---------|
|             | Mean (mg/kg)   | Standard deviation | Mean (mg/kg) | Standard deviation |
| As          | 4.8            | 1.3  | 4.6     | 0.5     | 4.2   | 9.8 |
| Cr          | 410            | 23   | 491.1   | 19.9    | 19.8  | 4.1 |
| Cu          | 97             | 6    | 97.6    | 9.5     | 0.6   | 9.7 |
| Ni          | 276            | 15   | 266.3   | 23.6    | 3.5   | 8.9 |
| Pb          | 14             | 3    | 15.8    | 1.7     | 12.9  | 10.8 |
| Zn          | 142            | 11   | 131.4   | 4.9     | 7.5   | 3.7 |

3.2. System error of pXRF
To verify the results of pXRF measurement based on linear correlation equations, we selected seven certified reference materials for soil composition analysis with known concentrations of heavy metals as the dependent variables and the values measured using pXRF as independent variables (Figure 1). Correlation analysis showed that the certified values (CV) of soil As, Cr, Cu, Ni, Pb, and Zn concentrations were significantly positively correlated with the values measured using pXRF ($P < 0.001, n = 7$); the coefficients of determination ($R^2$) were 0.994, 0.943, 0.971, 0.732, 0.994, and 0.996, respectively. The values measured using pXRF (except for soil Ni concentration) and certified values in the certified reference materials were statistically within a 95% confidence level [16]. In addition, within the concentration range of mg/kg, As, Cu, and Zn had a slope of greater than 1, indicating the values measured using pXRF were generally lower than those measured using the standard analytical methods. In contrast, Cr and Ni had a slope of less than 1, indicating the values measured using pXRF were generally higher. Finally, the slope of Pb was 1.044, indicating that the values measured using pXRF were generally consistent with those measured using the standard analytical method.
Figure 1. Correlations between heavy metal concentrations certified in the certified reference material and the values measured using pXRF.
Figure 2. Correlations between the concentrations of six heavy metals in soil measured in situ and ex situ using pXRF and the values measured using AAS/AFS.
3.3. Comparison of pXRF and AAS/AFS measurements results

Based on the measurement results of soil samples, we applied linear correlation to fit the values measured in situ and ex situ using pXRF to the values measured by the laboratory reference methods (Figure 2). All linear parameters (including linear equation, coefficient of determination $R^2$, and sample size $N$) are shown in Table 3. Compared with the values measured in situ using pXRF, the values measured ex situ using pXRF show better linear correlations with the values measured using laboratory analysis. In particular, the coefficients of determination reached 0.9 between the Cu, Zn, Pb, and Ni concentrations measured ex situ using pXRF and the values measured with laboratory analysis, indicating good linear relationships. However, the linear relationship was not significant for Cr and As, indicating a large deviation in measuring these two metals in soil using pXRF. Overall, the soil samples after grinding, drying, and sieving are characterized by small particle size, low water content, and high uniformity, enhancing their suitability for measurement with pXRF. The measurement results from these samples therefore show stronger correlations with the results of laboratory analysis.

Table 3. Correlations between the values of in situ and ex situ pXRF measurements and laboratory analysis.

| Heavy metal | Values of in situ pXRF measurement and laboratory analysis | Values of ex situ pXRF measurement and laboratory analysis |
|-------------|----------------------------------------------------------|----------------------------------------------------------|
|             | Linear equation | Coefficient of determination ($R^2$) | Sample size ($N$) | Linear equation | Coefficient of determination ($R^2$) | Sample size ($N$) |
| As          | Y=1.328X        | /                                      | 203               | Y=1.17X         | /                                      | 203               |
| Cu          | Y=0.543X        | /                                      | 342               | Y=0.98X         | 0.900                                  | 342               |
| Cr          | Y=0.247X        | 0.397                                  | 350               | Y=0.256X        | 0.426                                  | 350               |
| Ni          | Y=0.35X         | 0.117                                  | 248               | Y=0.786X        | 0.940                                  | 248               |
| Pb          | Y=0.047X        | 0.201                                  | 373               | Y=0.909X        | 0.984                                  | 373               |
| Zn          | Y=1.37X         | 0.828                                  | 430               | Y=2.06X         | 0.931                                  | 430               |

The results between the in situ pXRF measurement and laboratory reference analysis methods have a certain credibility. Using the results of laboratory analysis as the true values of the samples, we calculated the relative errors and the cumulative frequencies of relative errors in the values measured in situ and ex situ using pXRF (Figure 3). According to the accuracy requirement for laboratory quality control in the “Technical Specifications for Soil Environmental Monitoring” (HJ/T 166-2004), we selected 30% as the evaluation criterion for relative error between methods. That is, the result is acceptable when the relative error between different laboratories is no greater than 30% for the measurement result of heavy metals in the same soil sample. The As values measured in situ with pXRF in 88.8% of the soil samples and 93.8% of the As values measured ex situ are within the selected range. Similarly, Cr, Cu, Ni, Pb, and Zn account for 74.1%/82.6% (A/B, A: cumulative frequency of relative errors between the values measured with in situ pXRF and those measured using laboratory analysis, B: cumulative frequency of relative errors between the values measured with laboratory pXRF and those measured using AAS/AFS, the same below), 73.9%/91.4%,...
59.7%/38.9%, 64.7%/84.5%, and 74.8%/95.8%, respectively. For all studied heavy metals except Ni, there was a higher cumulative frequency of relative errors in the values measured ex situ using pXRF than those measured in situ using pXRF, indicating a higher accuracy. The high relative errors may have occurred for the following reasons: (1) the water content, particle size, and uniformity of soil samples collected on-site could not fully meet the requirements of pXRF for sample measurement [18]; (2) in situ and ex situ measurements using pXRF and laboratory analysis have inherent errors, and; (3) the concentrations of six heavy metals in the hundreds of soil samples collected in this study have larger distribution ranges. The pXRF measurement has upper detection limits and thus the accuracy of the measurement results for high-concentration samples cannot be guaranteed [19].

4. Conclusions
The precision and accuracy of pXRF generally meet the basic requirements of environmental site investigation. In addition to eliminating the tedious procedure of traditional laboratory measurement, pXRF is a simple, rapid, and efficient method that greatly improves the efficiency of detection of heavy metals in soils. The heavy metal concentrations of As, Cr, Cu, Ni, Pb, and Zn in soils measured using pXRF show good correlation with the values measured using laboratory reference analysis methods. pXRF has good applicability and meets the requirements of rapid detection. Combined with the validation using laboratory analysis methods, pXRF can be used for rapid detection of heavy metals in soil and to achieve on-site screening of pollutants. On the basis of this study, we will further investigate the effects of soil particle size, water content, and pre-treatment methods on the results of pXRF measurement to provide data support and a scientific basis for this technique in the investigation of soil heavy metal pollution.

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Figure 3. Relative errors and their cumulative frequency between the concentrations of six heavy metals measured in situ and ex situ using pXRF and the values measured by AAS/AFS (● Relative error in the in situ measurement using pXRF, ○ Relative error in the ex situ measurement using pXRF, cumulative frequency of relative error in the in situ measurement using pXRF, and   cumulative frequency of relative error in the ex situ measurement using pXRF).
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