Portable X-Ray Fluorescence as a Tool for Urban Soil Contamination Analysis: Accuracy, Precision, and Practicality

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Abstract. Urban agriculture has become an essential component of urban sustainability, but it often faces the challenge of soil contamination with heavy metal(loid)s like lead (Pb), arsenic (As), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), and zinc (Zn). Traditional laboratory methods for detecting these contaminants, such as atomic absorption spectroscopy (AAS) and inductively coupled plasma techniques (ICP-MS, ICP-OES, ICP-AES), are accurate but can be costly, time-consuming, and require extensive sample preparation. Portable X-ray fluorescence (PXRF) presents a promising alternative, offering rapid, in situ analysis with minimal sample preparation. The study reviews literature on PXRF analyzers to determine their accuracy and precision in analyzing heavy metal(loid)s in urban soils, with the goal of optimizing sampling, reducing laboratory costs and time, and identifying priority metal contamination hotspots. A literature review was conducted using Web of Science and Google Scholar, focusing on studies that validated PXRF measurements with alternate laboratory methods or certified reference materials (CRMs). This study reviews 67 publications to evaluate the accuracy and precision of PXRF in analyzing heavy metal(loid)s in urban soils. The review covers instrument types, calibration methods, testing conditions, and sample preparation techniques. Results show that, when properly calibrated, particularly with CRMs, PXRF achieves reliable accuracy. *Ex situ* measurements tend to be more precise due to controlled conditions, although *in situ* measurements offer practical advantages in urban settings. Portable XRF emerges as a viable method for assessing urban soil contamination, balancing accuracy and practicality. Future research should focus on optimizing sample preparation and calibration to further enhance PXRF reliability in urban environments. This review highlights PXRF's potential to streamline soil testing, reduce costs, and identify contamination hotspots, contributing to safer urban agriculture and more precise soil survey and conservation efforts.

1 Introduction

Urban agriculture has gained importance as a sustainable approach to enhancing foo security, revitalizing green spaces, and improving community well-being in cities. However, urban soils often contain harmful levels of heavy metal(loid)s such as lead (Pb), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), zinc (Zn), manganese (Mn)and mercury (Hg), due to past industrial activities, vehicle emissions, and other anthropogenic sources (Adimalla et al., 2020; Chaney et al., 1984;

Chen et al., 2005; Cheng et al., 2015a; Hu et al., 2013; Kosheleva and Nikiforova, 2016; Mielke, 2016; Morel et al., 2015; Pouyat and Mcdonnell, 1991; Wei and Yang, 2010; Wilcke et al., 1998). These contaminants pose significant risks to a human

35   health, particularly in areas where urban agriculture is practiced (Dumat et al., 2019), making the survey of soil quality crucial.

Traditional laboratory analysis of heavy metal(loid)s in soil includes the use of atomic absorption spectroscopy (AAS) and inductively coupled plasma technology techniques such as mass spectrometry (ICP-MS), optical emission spectroscopy (ICP-OES), and atomic emission spectrometry (ICP-AES) (Margui Grabulosa, 2006; Paya-Perez et al., 1993; Shefsky, 1997; U.S. EPA., 1996; U.S. EPA, 1998). These methods, however, can be expensive and time-consuming, requiring extensive sample

40   preparation. They also involve acid digestion, which can be hazardous if handled inappropriately and result in the generation of acid waste, contributing to unsustainable practices. Additionally, these processes can completely alter and contaminate samples due to chemical reactions and the use of corrosive acids (Lee et al., 2016; U.S. EPA, 1996). Standard x-ray florescence instruments are also used to study heavy metal(loid)s, but they are stationary and therefore cannot be taken to the field (Guilherme et al., 2008).

45   Among these challenges, portable X-ray fluorescence (PXRF) has emerged as a rapid and cost-effective alternative for heavy metal(loid) detection and quantification in soil (Madden et al., 2022; Ravansari et al., 2020). X-ray fluorescence operates by utilizing X-rays generated by an X-ray tube within the portable handheld analyzer (Bruker Corporation, 2023). The emitted X-ray beam interacts with the atoms in the sample, causing the displacement of inner-shell electrons. This displacement is a consequence of the energy disparity between the primary X-ray beam and the binding energy holding electrons in their

50   respective orbital shells. Upon electron displacement, the atom becomes momentarily unstable, seeking to rectify this by filling the vacancies left behind. This process, known as fluorescence, involves electrons from higher orbits moving down to occupy lower orbits with vacancies. The energy lost during this transition is specific to the distance between the electron shells, which is unique for each element and can be harnessed for elemental identification. Consequently, by measuring the energies emitted, the XRF instrument can pinpoint the elements present in the sample. To ascertain the quantity of each element, the instrument

55   or associated software analyzes the proportions of individual energies detected. In essence, XRF enables a detailed elemental analysis of materials through the study of X-ray interactions with atomic structures (Bruker Corporation, 2023).

Portable XRF offers real-time results, requires minimal sample preparation compared to methods like acid digestion. According to Pham et al. (2020), the instrument detects approximately 20-23 chemical elements of concern simultaneously. Some others are not detectable due to their concentration being smaller than the limit of detection of the devices (Pham et al.,

60   2020). Portable XRF applications include laboratory use as well as *in situ* analysis of metal(loid)s in soils and sediments, thin films, paints, coatings, oils and liquids, and hazardous waste. It is a non-destructive analytical technique allowing both qualitative and quantitative analyses of sample composition (Kalnicky and Singhvi, 2001). As this method of soil analysis gains popularity, the range of associated instruments available and methodology used grows as well. While several studies (Butler et al., 2012; Cheng et al., 2015; Hu et al., 2014; McLaren et al., 2012; Landes et al., 2019; Romzaykina et al., 2024;

65   Zhu and Weindorf, 2009) have demonstrated the effectiveness of PXRF in measuring heavy metal(loid) contamination in urban soil, there are some limitations with the technology. This review paper aims to assess literature on PXRF analyzers to determine their accuracy and precision in analyzing heavy metal(loid)s in urban soils, with the goal of optimizing sampling, reducing laboratory costs and time, and identifying priority metal contamination hotspots to promote urban agriculture.

2 Overview of PXRF Instrumentation and Methodologies in Urban Soil Analysis

70   **2.1 Selection of source material**

For this study, Web of Science and Google Scholar were selected as the primary search engines due to their comprehensive coverage of scientific literature, particularly in the fields of soil science and environmental studies. These databases were purposefully searched for the following keywords and phrases in varying combinations: *(p)xrf, urban soil(s), trace element(s), heavy metal(loid), (p)XRF in situ vs. ex situ, trace metal(s), ICP comparison, and (p)xrf accuracy and precision.* The use of

75   these platforms ensured a broad and diverse range of sources, capturing both well-established and emerging research relevant to the application of PXRF in urban soil analysis. When narrowing down the sources available, focus was directed to peer-reviewed studies where there was either an alternate lab method or certified reference materials (CRMs) used to validate the PXRF measurements. These articles were able to provide details concerning the correlation of the results in juxtaposition to more traditional laboratory methods, which helped to convey the information needed to thoroughly determine the true accuracy

80   and precision of PXRF measurements in soil research applications. Articles that provided background information on the PXRF and heavy metal pollution was also used in this review.

We reviewed articles published from as early as 1990, which was the earliest relevant study available. During the search, there were articles that appeared via search engine - particularly on Google Scholar - that produced a number of articles that did not meet the criteria set and therefore was not relevant to the study. In Fig. 1, the large decrease in initial search results compared

85   to articles selected is clear. The search includes articles published up to March 2024. Lastly, repeated articles were disregarded. Ultimately, a total of 67 publications were used for the review. The literature review focused on journal publications instead of including book chapters to ensure a consistent analysis and to utilize sources with more rigorous peer review standards. Figure 2 shows the top 20 most cited articles used in this review.

In the sections below, we first review the instruments used, calibration methods, testing locations, homogenization methods,

90   testing containers, testing modes, and testing times used among the research reviewed. Further the accuracy and precision of the PXRF, and the ways sample preparation, calibration, and testing methods may have influenced the results are discussed. Finally, we conclude with the best methodology, strengths, and limitations of PXRF analysis.
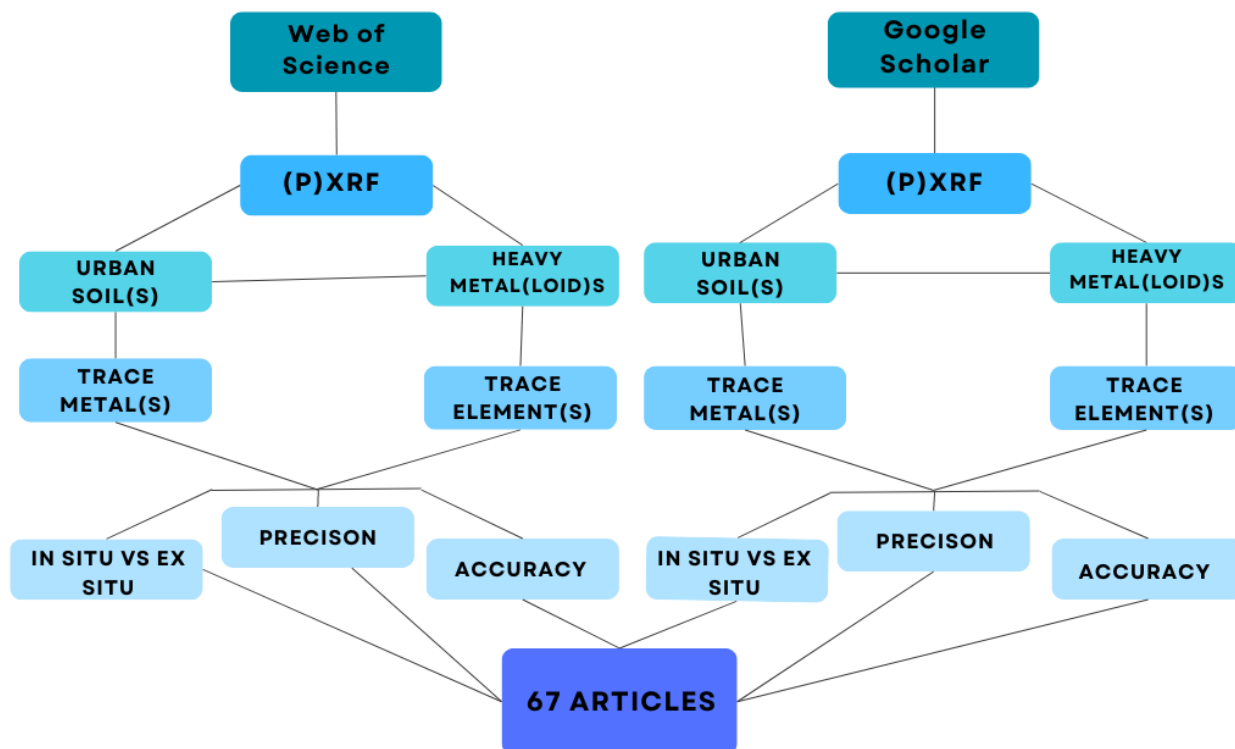
Figure 1: A flow chart portraying the process of selecting studies for this review.
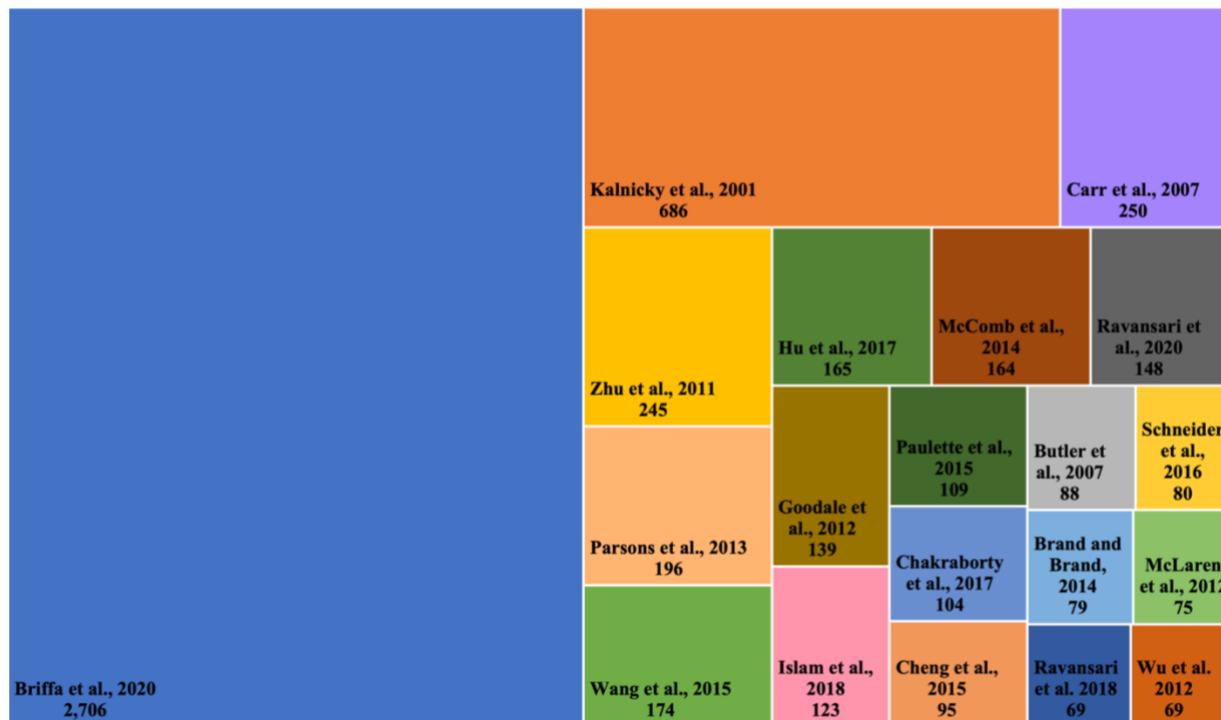
Figure 2: The 20 most cited articles used in this literature review (up to July 2024), followed by the number of citations, according to Google Scholar.

2.2 Instrument type

120   Portable XRF instruments have become a popular tool for assessing heavy metal(loid) contamination in soil, with various instruments used in studies around the world. For example, the Niton XL3t by Thermo Scientific (2002) was used by Yang et al. (2015) to assess heavy metal(loid) contamination in soil from an industrial site in China. The Niton XL3t GOLDD+ by Thermo Scientific (2010) was applied to Li et al. (2021) experiment to analyze soils from a city in China. Islam et al. (2018) used the Niton XL3t 950 GOLDD+ by Thermo Scientific (2010) to measure heavy metal(loid)s in Bangladesh. The X-

125   MET7000 by Oxford (2011) was applied to research by Xia et al. (2022) to assess soil contamination from a variety of sites.

McLaren et al. (2012) utilized the Bruker Tracer III-V (2012) in testing contaminated vertosol soils in Australia. An Olympus Innov-X instrument was used by Zhu et al. (2011) to study soils in the U.S. This popular PXRF was also used to measure elements in Chinese soils in collaborative research with Zhu and Weindorf (2009) as well as in work by Carr et al. (2007) in Ireland. Radu et al. (2013) worked with the Niton XLp (2015) for their own study of Irish soils. Walser et al. (2022) measured

130   Pb in urban areas using the X-MET8000 by Oxford Instruments.

The most popular brand of instrument used amongst the urban soil research reviewed is the Olympus Innov-X Systems PXRF, used in twenty-four studies. It was followed closely by Thermo-Scientific Niton instruments, used in 22 of the studies reviewed. SciAps PXRF was used three times. The Oxford X-MET was used twice. The Bruker instrument was used once as well as the Explorer 9000 and Eclipse III. These numbers account for the fact that Brand and Brand (2014) used both the Olympus and Niton instruments in one study, as well as the fact that Xia et al. (2022) used the Olympus, Explorer 9000, and the Oxford X-Met in one study. Seventeen of the articles reviewed had no mention of a particular PXRF instrument. These instrumentation examples are a small representation of the extensive research that is available on soil studies using PXRF. The choice of instrument often depends on specific constraints of the study, such as equipment availability and the instrument's cost. The age of the instrument is not necessarily an indicator of its accuracy or precision. In general, the accuracy and precision of the PXRF instrument depends on several factors, including the instrument calibration and measurement conditions. Therefore, the type of instrument has no clear impact on the accuracy and precision of PXRF readings.

2.3 Instrument calibration

Calibrating PXRF instruments is a crucial step in accurately measuring heavy metal(loid) concentrations in soil samples, and various calibration methods have been explored in recent studies. Several studies have used Certified Reference Materials (CRMs) or soil standards to calibrate PXRF instruments. For example, in a study conducted by Qu et al. (2020) in Wuhan City, China, researchers verified the instrument by scanning the CRM GSS 3 seven times to calculate the relative standard deviation, which was found to be 6.51%. Another study used three National Institute of Standards and Technology (NIST) reference materials: 2709 San Joaquin soil, TILL-4p soil, and 2710 Montana Soil (Schmidt et al., 2024). Romzaykina et al. (2024) calibrated their PXRF using the enclosed standard 2711A. Kim et al. (2019) utilized both a 316-alloy chip, blank samples, and NIST reference material 2710 Montana Soil.

Alloy chip, clip, or coin calibration were quite common among research available. This involves the use of small discs or chips made of the same alloy or metal(loid) as the sample being analyzed. The discs or chips are measured by the PXRF to establish a calibration curve for the specific alloy or metal(loid) (Pîrnău et al., 2020; Wang et al., 2015; Weindorf et al., 2016). This works similarly to the use of any other CRM. A study by Pîrnău et al. (2020) used alloy coins to calibrate a PXRF for the analysis of heavy metal(loid)s in soil samples from Romania. The PXRF was operated in laboratory based on manufacturer calibration and a factory pre-calibrated alloy coin (Alloy 316) was used to standardize the instrument before scanning. The use of the thorough calibration process, as evidenced by the diverse methods and approaches documented in numerous studies, is fundamental to the integrity and validity of both *ex situ* and *in situ* PXRF soil analyses across different environmental settings.

2.4 Testing location

Soil analysis through PXRF has been widely used in research, with *ex situ* measurements being the most common approach. Although most studies have only utilized *ex situ* measurements (Al Maliki et al., 2017; Kazimoto et al., 2018; Mukhopadhyay et al., 2020; Suh et al., 2016), which involves taking soil samples to the laboratory for analysis measurements, some have

incorporated both field and laboratory PXRF measurements in their research (Lee et al., 2016; McStay et al., 2022; Urrutia-Goyes et al., 2017; Zhang et al., 2022). On the other hand, however, several studies consisted of measurements occurring
165 strictly *in situ* (in the field) such as Jean-Soro et al. (2015), Paulette et al. (2015), Radu et al. (2013), Udeigwe et al. (2015), and Zhu and Weindorf (2009). The samples used in the studies we reviewed were taken from various locations such as residential areas, old and present mining sites, near roads, industrial areas, landfills, green houses, parks, and community gardens. In a study by Romzaykina et al. (2024) however, researchers used artificially contaminated soils to represent the diversity of soils in Moscow.

2.5 Homogenization

According to Schumacher et al. (1990), the need for sample homogeneity prior to laboratory analyses has been long recognized by geologists, chemists, and members of other scientific disciplines. Homogeneity is the degree that the material under investigation is mixed resulting in the random distribution of all particles in the sample. Scientists must strive to obtain a homogenous sample to obtain data exhibiting minimal error attributable to sample heterogeneity. It is especially important for
175 elements such as Pb due to the inherent heterogeneity of soil Pb in a contaminated sample (Wharton et al., 2012). Among these, sieving and grinding are the most common techniques for achieving a uniform particle size distribution of soil samples. For instance, Williams et al. (2020) sieved the soil samples through a 2-mm sieve and then homogenized them using a ball mill. Similarly, Ravansari and Lemke (2018) homogenized the soil samples using a ball mill. Another commonly used homogenization method is grinding the soil samples using either a mortar and pestle or a mechanical grinder (Markey et al.,
180 2008). Most authors used a combination of sieving through a 2-mm sieve and a grinding method to homogenize the soil samples. During laboratory tests, the mortar and pestle method was the most popular, with evidence of soil milling, mechanical grinding, being far less common. In some articles the homogenization method was not specified.

2.6 Testing container

When conducting PXRF measurements, various factors can influence the accuracy and precision of the results, including the
185 type of container material used, as demonstrated in a study by Zambito et al. (2022) which found that the use of glass containers for soil samples resulted in elemental interferences compared to plastic containers. In one study, soil samples undergoing the XRF technique were analyzed through zip-locked plastic bags. The soil samples were measured according to an empty plastic bag analyzed as a blank sample and all sample measurements were blank-corrected (Wu, 2012). In another study, PXRF screenings were made in plastic Olympus cuvettes and covered with a "special" film (Romzaykina et al., 2024).

190 In a study by Laperche and Lemière (2020), several types of plastic films and plastic bags were tested for their effects on PXRF measurements. It was discovered that the use of certain types of plastic bags, such as polyethylene or polypropylene, can produce a significant interference signal that leads to inaccurate measurements. Taking measurements at different places on a sample bag was proposed to control sample homogeneity. The authors investigated several types of plastic bags commonly used such as low-density polyethylene (LDPE) bags, a proprietary type of bag, and Prolene film on cups. Laperche and Lemière

195 (2020) concluded a minor effect on heavier elements, and observable and major effects on elements like potassium, calcium, and silicon. Their research further showed that plastic material could also contain some metal(loid)s. This suggests that LDPE is more suitable than high-density polyethylene, due to a lower number of additives. A variable number of layers of polyethylene film were tested against adsorption and reported a linear correlation with the number of layers. Ultimately, the authors recommended the use of low-density polyethylene bags as well as polypropylene testing films, as they produced the

200 most accurate results with minimal interference.

Parsons et al. (2011) research suggests that external films and windows, such as Kapton and Mylar, that are used to protect the instrument may attenuate and scatter radiation, affecting analysis. For lighter elements like potassium and calcium, which emit lower energy radiation, attenuation effects by protective films can be significant due to the fact that the absorbance of low-energy X-rays is higher, which affects lighter elements more than heavier ones.

205 **2.7 Testing mode**

A "soil mode" is a specific testing mode in PXRF instruments that is designed for the analysis of soil samples. It uses a soil, sediment, and dust-specific calibration model and parameters (Lemière, 2018). This was the most popular mode used in the research analyzed in this review. According to Lemière (2018), the soil and mining modes were introduced in PXRF instruments to improve the accuracy of the analysis for different types of matrices. The soil mode is designed to provide

210 analysis of light elements and to reduce the effect of heavy matrix elements on the analysis. In other words, a "soil mode" offers broad and easy coverage of low concentrations and is often used for scanning and detection (Lemière, 2018).

In contrast, a "mining mode" is optimized for heavy elements and is suitable for the analysis of geological samples, such as ores, concentrates, rocks, soils, and other geological materials typically associated with mining and mineral exploration. Therefore, the best approach for high concentrations and quantification is user calibration with the "mining mode" (Lemière,

215 2018). It is characterized by a higher voltage and lower current than the "soil mode", which enables the instrument to detect elements at higher concentrations (Goodale et al., 2012). The most popular factory testing mode used was a "soil mode", but in some articles, the mode was not specified. As a result, it was difficult to determine the effect of these modes on the results obtained from multiple studies. Thus, it would be beneficial for researchers to explore this further.

2.8 Testing Time

220 Studies have reported using analysis times ranging from 20 seconds to 5 minutes per sample. Jeong et al. (2021) used the average readings of three 60 second PXRF readings. In a study conducted by Li et al. (2018), researchers analyzed 74 compost samples from with measurement times of 180 seconds per sample, but discovered the measurement time could be shortened to 90 seconds per sample by using a "soil mode" calibration rather than a "mining mode." Similarly, Xia et al. (2022) measured for 60 seconds per sample in a "soil mode." Liu et al. (2022) tested 88 samples for 60 seconds each (30 seconds per beam).

225 Authors claimed that the longer measurement time was necessary due to the low concentrations of heavy metal(loid)s in their

samples. Qu et al. (2020) tested the 93 samples used in their research for 90 seconds each. Another study of artificially spiked soils found that exposure times of 120 and 180 seconds yielded nearly identical readings for Cu, Pb, Ni, and Zn, while a 90-second exposure showed significant deviations, especially at lower concentrations (Romzaykina et al., 2024). Overall, the average time for PXRF testing was 90 seconds, most often followed by two repetitions per sample. When using a "soil mode",

230   90 seconds should provide a thorough reading for elements within a detectable limit.

3 PXRF vs. Lab Analysis: A Comparative Perspective in Soil Testing

3.1 Comparison of PXRF and laboratory methods

Most of the studies that include *ex situ* measurements validate their results using AAS, ICP-MS, ICP-OES, and ICP-AES, as well as by comparing PXRF results to certified values. Several studies produced accurate and precise measurements. In the

235   reviewed articles, the correlation coefficient (r) values between the PXRF results and laboratory analysis results for heavy metal(loid)s varied depending on the specific metal(loid). In a study conducted in Australia, McLaren et al. (2012) found that the PXRF measurements for As, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Pb, Si, Ti, and Zn were highly correlated with the laboratory measurements, with correlations ranging from 0.82 to 0.98. Butler et al. (2007) found that PXRF measurements of Pb in soil samples had a correlation coefficient of 0.6 and 0.9 when compared to laboratory analysis using ICP-MS, indicating a strong

240   positive relationship between the two methods. Cheng et al. (2015) found a positive correlation of 0.94 between two sets of Pb concentration data (ICP-MS and XRF screening results on air-dried samples measured through Ziploc bags). These positive correlation coefficients display how PXRF results can obtain similar measurements to more traditional forms of heavy metal analysis.

Gonzalez et al. (2021) conducted a study where they compared Pb measurements of a set of soil samples between PXRF and

245   ICP-MS as well as between PXRF and two separate ICP-OES measurements, one following nitric acid extraction and the other following the relative bioaccessibility leaching procedure. They then calculated the relationship between the methods using the Berry-Mielke's Universal R test. An R value of 0.832 was the result of the PXRF vs. ICP-MS measurements. The R-value was 0.765 and 0.522 between the PXRF and both ICP-OES measurements, respectively. Note that the p-value for all aforementioned measurements was <0.0001. Therefore, ICP-MS was shown to have the strongest agreement with the tool.

250   Some studies found slightly weaker correlations, such as the study by McStay et al. (2022), which reported r^2 values ranging from 0.03 to 0.89 for Pb, Cu, and Zn, Mn, and As in urban soils. Alternatively, research by Gutiérrez-Ginés et al. (2013) on abandoned mines and landfills found that PXRF measurements had high R^2 values of As, Ca, Cd, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, Sr, Ti, V and Zn when compared to certified standards, ranging from 0.744 to 0.999. According to research by Kim et al. (2019), when comparing PXRF measurements with ICP-AES analysis, PXRF tended to underestimate Pb and As

255   concentrations, although a significant correlation between the two methods suggested that PXRF data can be used as a secondary variable despite its lower accuracy.

In a study conducted along a polluted river (Wu et al., 2012), researchers conducted pairwise comparisons between PXRF and ICP-AES measurements. The study found that for elements such as Ni, Cu, Zn, and Pb, the PXRF measurements generally agreed well with ICP-AES results. However, for Cd, Cr, Hg, and As, the XRF measurements showed poor accuracy and 260 diverged significantly from the ICP-AES results. These findings were further supported by statistical analyses, including regression slopes and correlation coefficients. Researchers concluded that while XRF measurements can be reliable for certain elements like Pb, Ni, Zn, and Cu, they may not be as accurate for elements like Hg, Cd, Cr, and As, as shown in Table 1. The importance of verifying and calibrating analytical methodologies was emphasized.

Table 1: Adapted from Wu et al. (2012), summarizing soil contamination from runoff in Tainan City based on 60 samples collected 265 **and analyzed.**

Element	Method	Mean (mg/kg)	R^2	Relative Proximity (%)
Pb	ICP-AES	2306.92	0.6689	85.17
	XRF	1371.6		
Zn	ICP-AES	12184.91	0.7281	80.0
	XRF	24187.79		
Ni	ICP-AES	444.05		50.0
	XRF	1590.92		
Cu	ICP-AES	3988.1		35.42
	XRF	4055.38		
As	ICP-AES	9.11	0.3449	25.0
	XRF	66.13		
Cr	ICP-AES	78.38	0.1504	16.67
	XRF	495.13		
Cd	ICP-AES	1.24	0.07823	5.77
	XRF	31.43		
Hg	ICP-AES	0.7	0.01143	2.3
	XRF	44.10		

Burlakovs et al. (2015) also compared data from PXRF analysis with AAS and ICP-MS for 48 topsoil samples collected from the Kudjape Landfill in Estonia. Results showed a strong correlation between PXRF and AAS, as demonstrated by an R^2 value of 0.8915, indicating that PXRF provides reliable concentration estimates, especially for metals like Cu and Mn, which closely 270 aligned with AAS measurements. However, some variability was noted for elements like Pb and Cr. Moisture content and organic matter were identified as factors influencing element concentrations in waste samples, and moisture correction was applied to PXRF raw data to mitigate these effects. While AAS and ICP-MS offer higher precision, PXRF was found to be satisfactory for screening purposes, offering significant time and resource savings in landfill management. For specific

elements or higher precision, AAS or ICP-MS may still be necessary, and careful planning and sample preparation are essential

275 for ensuring reliable PXRF results.

In Gutierrez-Gines et al. (2013) research, Zn, Pb, Ni, and As exhibit relatively stable PXRF/Standard ratios across their concentration ranges, with only minor fluctuations observed. In contrast, Cr and Cu show the largest variability, particularly at higher concentrations, indicating potential inconsistencies in PXRF measurements for these elements. Meanwhile, Cd and Mn demonstrate more stable ratios over smaller concentration ranges, with Cd showing a slightly increasing trend at higher

280 concentrations. Figure 3, created based on Gutierrez-Gines et al. (2013) data, highlights these trends across varying concentration ranges, showing the relationship between PXRF measurements and certified values for each element.
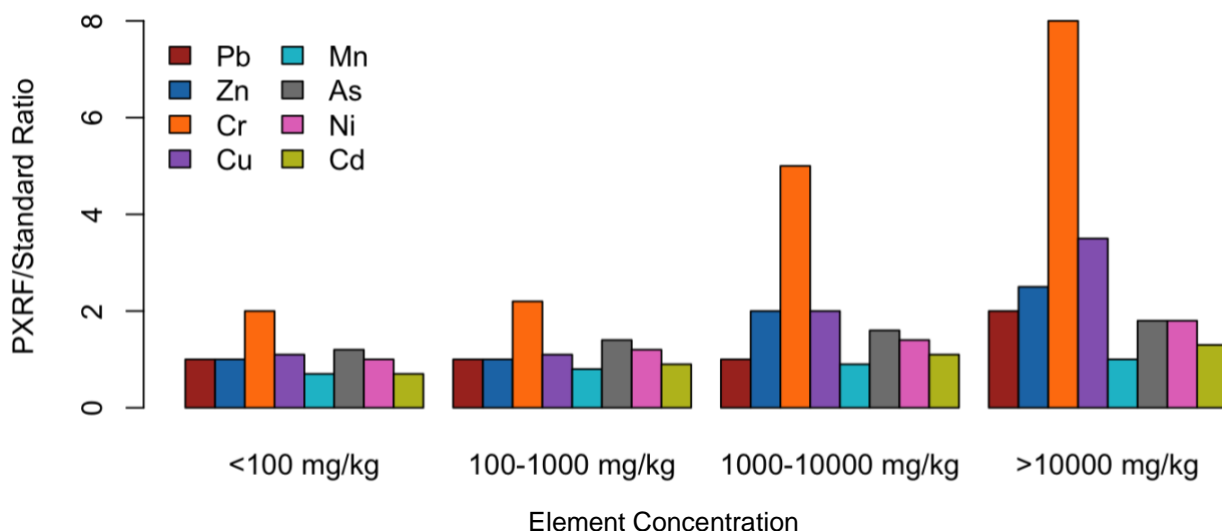
Figure 3: Comparison of PXRF/Standard ratios for various elements (Pb, Zn, Cr, Cu, Mn, As, Ni, Cd) across different concentration

285 **ranges. This figure was created based on the data presented in Gutierrez-Gines et al. (2013), showing the relationship between PXRF measurements and certified values.**

The coefficient of variation for ICP-MS Pb measurements in Qu et al. (2020) study was lower at 30.07% compared to the one for *in situ* PXRF, which stood at 38.71%. This discrepancy in variability suggests that factors beyond Pb concentration contribute to the variation observed in PXRF measurements, such as soil water content, organic matter, and particle size.

290 Despite these variations, both methods yielded average Pb concentrations slightly below the background level of 35 mg kg^{-1} in China. Interestingly, the average concentration of Pb measured by ICP-MS exceeded that of *in situ* PXRF, indicating the

influence of other soil factors on PXRF analysis. This discrepancy underscores the necessity of correcting *in situ* PXRF measurements before utilizing them for spatial simulations of soil Pb contamination.

A study conducted by Pozza et al. (2020) combined the use of PXRF and visible near-infrared technology. They first performed
295   Cubist modelling, which helped them obtain predictions of the results. The resulting data exhibited high skewness, with the PXRF having higher values for Lin's Concordance correlation coefficient. However, the most accurate results were achieved by incorporating both visible near infrared principal components and PXRF Compton-normalized values through a generalized regression analysis model. Since model averaging of visible near infrared and PXRF predictions outperformed individual methods, integrating the two improved Pb prediction accuracy in this case (Pozza, et al., 2020).

300   The results obtained in research conducted by Schmidt et al. (2024) indicated that PXRF technology tended to overestimate As concentrations and underestimate Pb concentrations in soil samples compared to ICP-MS analysis. However, before applying any correction factors, there was a strong positive correlation between the calibrated PXRF values and the corresponding ICP-MS data for both As and Pb, with Spearman coefficients of 0.850 and 0.981, respectively. The application of a ratio correction factor improved the accuracy of PXRF measurements for As and Pb.

305   Elements with larger atomic masses (e.g., Pb) show higher accuracy, while those with smaller atomic masses (e.g., Ni) exhibit lower accuracy in a study by Romzaykina et al. (2024). Lead, Cu, Zn, and Cd were considered reliable for PXRF readings above certain concentration thresholds, while Ni showed reliability only at higher concentrations. Portable XRF readings generally aligned well with ICP-OES measurements, with slight overestimation observed. Discrepancies, however, were noted for some elements, particularly Cd, further indicating limitations in PXRF accuracy for certain contaminants. Overall, the
310   reviewed studies suggest that PXRF analysis can provide a reliable and efficient alternative to laboratory analysis for heavy metal(loid) contamination assessment in urban soils, with high correlation coefficients reported for varying elements when appropriate correction factors are applied. Specific values, however, may vary depending on the soil characteristics and analytical protocols used, highlighting the importance of careful calibration instruments for accurate results.

3.2 *In Situ* vs. *Ex Situ*: accuracy and precision of PXRF measurements

315   Portable XRF allows for both *in situ* and *ex situ* measurements, offering rapid results with minimal preparation. *In situ* measurements, however, are affected by environmental factors such as moisture and organic matter, which can compromise accuracy. By contrast, *ex situ* measurements, performed in controlled conditions, provide better precision. Schumacher et al. (1990) underscored the need for homogenous samples to reduce errors from sample heterogeneity. Interferences such as water and large organic/inorganic matter can further degrade *in situ* accuracy. Hu et al. (2014) found that *in situ* PXRF measurements
320   were less accurate and precise compared to *ex situ*, yet still reliable when compared with ICP-MS and atomic fluorescence spectrometry (AFS) results (Table 2). For example, As measurements using *in situ* and *ex situ* PXRF were 13% and 31% higher than AFS results, while Pb and Zn values were 38% and 17% lower than ICP-MS values. Copper results showed a 10%

lower reading with *in situ* PXRF and a 15% higher reading with *ex situ* PXRF compared to ICP-MS, with accuracy generally improving from *in situ* to *ex situ* (Hu et al., 2014). Tian et al. (2018) reported, however, poor agreement between *in situ* and

325   *ex situ* PXRF measurements compared to ICP-MS after acid digestion (Table 2). Romzaykina et al. (2024) found high R² values for Pb (0.94), Cu (0.95), and Zn (0.95) with PXRF, which improved with calibration based on ICP-OES. Nickel showed lower accuracy (R² = 0.68), suggesting PXRF is less reliable for some metals. The study also emphasized the influence of soil matrix, such as organic matter, on PXRF accuracy, reinforcing the need for calibration in urban environments (Table 2).

Table 2: Comparison of *in situ* and *ex situ* PXRF measurements of heavy metal(loid) concentrations and R² values in urban soil
330   **studies. Concentration data for Pb, Cu, and Zn from 47 soil samples collected in Nanjing City, China from Hu et al. (2014), R² values from 30 samples collected from greenhouse farms in Shouguang, China, additional R² values from 83 samples collected from three green areas in Moscow, Russia, from Romzaykina et al. (2024) using ICP-OES for calibration. The table highlights differences in accuracy between field and laboratory measurements.**

Element	Nanjing			Shouguang			Moscow
(mg/kg)	*In situ,* concentration	*Ex situ,* concentration	ICP-MS, concentration	*In situ,* R²	*Ex situ,* R²	Sieved, R²	(R²)
Pb	22	34.2	35.4	0.04	0.13	0.30	0.94
Cu	41.6	52.7	46	0.63	0.58	0.83	0.95
Zn	98	110.9	118	0.85	0.86	0.98	0.95
As	-	-	-	0.18	0.13	0.30	-
Ni	-	-	-	0.26	0.32	0.23	0.68
Mn	-	-	-	0.47	0.48	0.91	-

To investigate the impact of sample preparation methods on measurements, Gutierrez-Gines et al. (2013) tested soil samples
335   from landfills and abandoned mines. The samples were analyzed using PXRF after two different preparation methods: drying and further grinding and pressing (referred to as "pressed" soil samples). Analyzing fresh samples closely resembled *in situ* determinations, allowing for comparison with prepared samples. Grinding and pressing represented the standard laboratory preparation method for this system, while drying and sieving served as an intermediate step. Comparing measurements on fresh samples with those on dried samples showed high comparability. Notably, the soils in these sites, characterized by a
340   Mediterranean climate, were relatively dry during the sampling period (late spring), with a maximum soil moisture content of about 10%. Given the limited number of urban studies examining both field and lab PXRF measurements, researchers would benefit from further investigations focusing on this comparison.

3.3 Optimizing sample preparation for PXRF: homogenization, calibration, and measurement techniques

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It is difficult to determine which homogenization method produced the most accurate results, as it can vary depending on the specific samples and the elements being analyzed. In a study by Hu et al. (2014), however, it was observed that grinding and sieving samples before analysis did improve accuracy and precision of results, though for Tian et al. (2018), it only significantly improved accuracy of results for Cu, Mn, and Zn. From examination of results, it can be assumed that there isn't a notable

350 difference between results obtained from grinding soil with a mortar and pestle vs. any form of mechanical grinding. The "soil mode" has been shown to be effective in measuring heavy metal(loid) contamination in urban soils. However, it is important to note that the accuracy of the "soil mode" can vary depending on the specific instrument used and the calibration model applied.

The accuracy and precision of PXRF measurements can be influenced by several factors, including drying methods,

355 measurement times, and metal(loid) concentrations. Schneider et al. (2016) found that varying measurement times at intervals of 60, 90, 120, 180, and 240 seconds had no significant effect on PXRF accuracy or precision. Tests conducted on four reference materials showed consistent results across different time intervals, with a Friedman test revealing no significant differences in concentrations of 11 elements across the five measurement times at a 5% significance level. Based on these findings, a count time of 60 seconds was deemed sufficient for most analyses.

360 The type and concentration of metal(loid)s being measured, however, can affect the required testing times. Gutierrez-Gines et al. (2013) demonstrated that longer measurement times improve PXRF accuracy and precision, especially for low metal concentrations. While high metal concentrations produced consistent results even with shorter times, low concentrations required extended measurement times to enhance detection limits. Additionally, their study highlighted that higher metal concentrations in processed soil samples led to greater accuracy and precision, particularly when longer measurement times

365 were applied.

On the other hand, sample drying methods also play a role in PXRF accuracy. Paulette et al. (2015) found that oven-dried samples yielded moderately more accurate results compared to air-dried samples, possibly due to insufficient drying time for air-dried soils. This suggests that proper sample preparation is essential to improving the reliability of PXRF results.

Optimal analytical conditions for PXRF analysis involve several key factors. Al Maliki et al. (2017) recommended a sample

370 layer thickness of 2 mm, use of special containers (e.g., 6.4 cm Chemplex containers) with plastic films (e.g., 3.6 mm Mylar Polyester), and a moisture content of 0.5% in both the samples and standards. Ensuring a uniform grain size is also crucial for accuracy. The study also noted that various types of sample containers, such as Ziploc bags, can be used effectively as long as consistency is maintained between the standards and the samples. Future research should focus on optimizing the balance between sample bulk density, mineralogy, moisture content, and instrument settings to further enhance PXRF performance.

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3.4 Advantages and applications of PXRF in urban soil analysis: efficiency, accuracy, and spatial interpolation techniques

The innovative use of PXRF has significantly advanced the field of soil analysis, offering new insights and efficiencies in environmental studies. According to Chakraborty et al. (2017), the portability, inexpensiveness, and accuracy of the PXRF

380 spectrometer offer formidable advantages over traditional laboratory based chemical analyses. In their research, 131 points were scanned and beyond identifying those levels, the optimized spatial variability interpolations were plotted using spherical and exponential kriging models. These interpolations, laid over contemporary high-resolution imagery, allowed him to quickly delineate exactly which areas across the city of Baia Mare exceeded limits for elemental concentrations. Portable XRF reported values clearly identified the pollution hotspots which needed further attention. The primary benefit of this approach is that all

385 described procedures can be conducted on-site within one to two days, allowing for the generation and mapping of results using only a laptop (Chakraborty et al., 2017). Finally, many of the inter-elemental correlations established in this research further corroborate the findings of two earlier studies which used PXRF for elemental characterization in Romania (Paulette et al., 2015). In summary, PXRF analysis coupled with spatial visualization of interpolations provide a straightforward approach for delineating soils that are a hazard to the public.

390 Portable XRF is effective and economic for accurately assessing the ecological risk of soils and can provide useful information for fast and detailed risk assessment of polluted soil. With careful consideration of many factors that may affect the effectiveness of PXRF, such as soil heterogeneity, instrument stability during analysis, sample thickness/width, and detector resolution, PXRF can provide highly accurate results and its use in soil science should be encouraged (Ravansari et al., 2020). Its ability to provide rapid on-site analysis is particularly useful when studying soils in areas where sample collection is

395 challenging, such as in densely populated urban environments or in contaminated areas where sampling may be restricted. Additionally, it can provide multi-element analysis, allowing for simultaneous measurement of multiple heavy metal(loid)s in a single soil sample (McComb et al., 2014). This can save time and resources compared to analyzing samples for each heavy metal individually using traditional laboratory methods.

In Romzaykina et al. (2023) study of potentially toxic metals in Moscow's greenspaces, the use of correction factors

400 significantly improved the reliability of contamination maps interpolated from point measurements. These maps were evaluated by comparing them to reference maps based on ICP-OES data. The application of correction factors reduced the areas with significant deviations (>30%) on the potentially toxic metal maps and increased the fraction of non-deviated areas (±10% from ICP-OES values) by 2 to 6 times, depending on the metal and location. For example, on the Cu map of the RUDN University campus, areas with significant deviations dropped from nearly 40% on the PXRF-based map to less than 5% on the

405 PXRF × k-based map, as shown in Fig. 4. These deviations were linked to different vegetation patches or soil properties, with

hotspots in areas with high soil organic content that interfered with Cu detection by PXRF. Non-deviated areas for Cu, Pb, and
Ni increased to 50-70% on adjusted maps (Romzaykina et al., 2023).
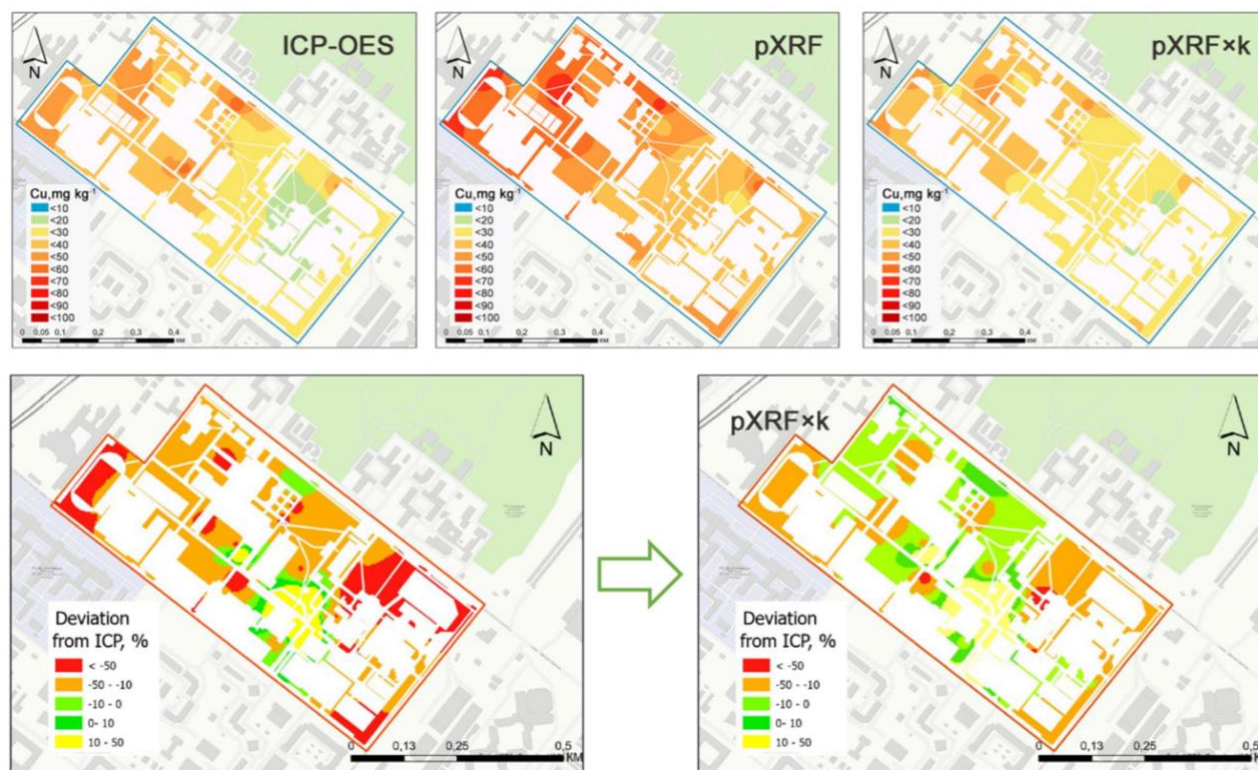
Figure 4: Maps created by Romzaykina et al. (2024) that show the spatial distribution of deviations in proximal assessments of Cu
410 **concentrations from the ICP-OES reference, comparing pXRF without correction factors (left) and with correction factors (right).**

Portable XRF analysis can provide accurate and precise results when used appropriately, as demonstrated by the strong
correlation observed in several studies. This suggests that PXRF analysis can be a reliable and cost-effective alternative to
traditional laboratory methods for measuring heavy metal contamination in urban soils (Table 3). While ICP and AAS are
415 highly accurate analytical techniques that can detect minute levels of trace substances within a sample, the techniques are
complicated, must be carried out by specialists, and the delicate equipment requires regular calibration and maintenance.
Alternatively, due to the PXRF's non-destructive nature, samples tested can be reused, preserved, or safely shipped off for
further analysis using other methods. In many cases, PXRF analysis is a viable alternative to either replace the aforementioned
equipment completely, or act as a backup when it is out of action (Hu et al., 2017).

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Table 3. Summary of the most common XRF instruments, calibration methods, and testing locations used in urban soil studies.

	PXRF Instruments		
	Thermo Scientific Niton	**Olympus Innov-X**	**Bruker Tracer III-V**
Pros	Widely used, reliable	High precision, versatile	Good for specific applications
Cons	Expensive	Requires proper handling	Less common
Applications	Urban soil, industrial sites	Agricultural soil, contaminated land	Specific soil types
	Calibration Methods		
	Certified Reference Materials	**Alloy Chip/Clip**	**Regression Models**
Pros	High accuracy	Cost-effective, easy to use	High precision with statistical analysis
Cons	Expensive	May require frequent calibration	Complex to set up
Applications	Various soil types	Metal(loid) specific studies	Detailed contamination analysis
	Testing Locations		
	***In Situ* (Field)**	***Ex Situ* (Lab)**	**Both**
Pros	Rapid results, no sample prep	Controlled conditions, high accuracy	Flexibility in application
Cons	Affected by environmental factors	Time-consuming	May require duplicate analysis
Applications	Urban areas, quick assessment	Laboratory research, detailed analysis	Field and lab studies

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3.5 Limitations of PXRF analysis: soil heterogeneity, moisture, and organic matter interference

Factors affecting discrepancies between PXRF measurements of soil standards and their certified values are largely attributed to sample heterogeneity and soil matrix interference. For instance, organic materials generally led to overestimation of potentially toxic metals, while mineral substrates yielded more accurate results, with sand being the most accurate substrate

430 (Romzaykina et al., 2024). Results demonstrated that PXRF measurements are affected by the presence of water and organic matter (Ravansari and Lemke, 2018). For example, it was discovered that increasing water content resulted in decreased recorded concentrations for all elements. This finding highlights the importance of considering soil moisture effects. Soil moisture can cause errors in PXRF analysis due to increased absorption and scattering (Parsons et al., 2012). The US

Environmental Protection Agency reported that soil samples with more than 15% moisture content lead to elemental
435 measurements that are lower than the actual concentration (Simmons, 2023).

A study by Rosin et al. (2022) used a control group as well as a manipulated one to investigate the specific effects of water
and organic matter content on the PXRF measurements. It was concluded that since the attenuation of X-rays by water is higher
than that of air due to greater density of the latter, greater sample moisture leads to lower net peak areas of characteristic X-
rays that constitute the sample, which results in lower precision, accuracy, and detection limits. The presence of moisture
440 particularly impacts the accuracy of detecting elements with atomic numbers below 30, including Mg, Al, and Si (Rosin et al.,
2022). This study also determined that as the amount of organic matter in a soil sample decreases, the precision and detection
limit of the PXRF increases.

Moreover, results demonstrate that the PXRF measurement response is elementally dependent. Ravansari and Lemke (2018)
wrote that although the experiments in their study were carefully controlled, they were conducted with a limited number of
445 samples using a single instrument - a Niton XL3t + 950 PXRF in soil analysis mode. Therefore, results should be considered
preliminary until they can be verified with a larger number of soils containing a wider range of organic matter fractions, ideally
with PXRF analyzers from additional manufacturers (Ravansari and Lemke, 2018).

The presence of other elements in the soil can interfere with the accuracy of PXRF analysis, leading to inaccurate readings.
Due to this background noise caused by the soil matrix, Nawar et al. (2019) pointed out that the PXRF can be improved through
450 the spectral data analysis coupled with random forest machine learning method for low-Z elements which have spectral overlap
and low fluorescence yield at low concentration (K, P, Ca, and Mg). Furthermore, regular calibration and maintenance of
PXRF analyzers is necessary to ensure accurate and precise measurements. Drift in instrument performance over time can lead
to errors in readings (Brand and Brand, 2014).

The particle size of the soil can also affect the accuracy of PXRF measurements, which can prove as a barrier in the field.
455 Additionally, PXRF analyzers can only measure heavy metal concentrations in the top few millimeters of soil, further limiting
their usefulness in the field at locations that require measurements at greater depths. Heavy metal(loid) contamination in urban
soils is often heterogeneous, with hotspots of contamination occurring at specific locations. Portable XRF measurements may
not capture the full extent of heavy metal(loid) contamination in such cases.

4 Conclusions

460 Portable XRF analyzers have emerged as a valuable tool for assessing heavy metal(loid) contamination in heterogeneous urban
soil. In this literature review, we aimed to evaluate the accuracy and precision of PXRF analyzers in relation to heavy
metal(loid) contamination and provide insights into their limitations and reliable methodological applications. The use of
PXRF analyzers offers several advantages, including real-time results, minimal sample preparation requirements, and the

ability to detect multiple elements simultaneously. These features make PXRF an attractive option for on-site soil analysis,
particularly in urban agricultural settings where rapid and cost-effective techniques are needed.

This review highlighted the importance of instrument calibration in achieving accurate measurements. Various calibration methods were explored, including the use of CRMs, regression models, alloy calibration, statistical calibration, and pure silica standards. The use of certified standards was found to improve the accuracy and precision of PXRF measurements compared to other calibration methods. Additionally, the choice of instrumentation varied across studies, with different PXRF models being utilized based on equipment availability and cost considerations. The age of the instrument did not necessarily indicate its accuracy or precision. The reliability of PXRF measurements depends on factors such as instrument calibration and measurement conditions.

The testing location and homogenization methods used in PXRF analysis were also discussed. *Ex situ* measurements, where soil samples are taken to the laboratory, were the most common approach. Some studies, however, incorporated both field and laboratory measurements, which suggested that the PXRF is sufficient at taking accurate and precise field measurements. More research is recommended to further compare the accuracy and precision of both *in situ* and *ex situ* measurements. Sieving and grinding were the most employed techniques for soil homogenization. Furthermore, the choice of testing container material was found to influence the accuracy and precision of PXRF measurements, with evidence suggesting that glass containers may introduce elemental interferences. Lastly, the soil mode in PXRF instruments, specifically designed for soil analysis, was the most popular testing mode used in research. This mode utilizes a soil-specific calibration model and parameters to improve the accuracy of analysis for different types of matrices.

Overall, while PXRF analyzers demonstrate promise in assessing heavy metal(loid) contamination in heterogeneous urban soil, there are still limitations and considerations to be addressed. Future research should continue to explore calibration methods, optimize sample preparation techniques, and validate PXRF measurements against traditional laboratory techniques. This will contribute to advancing soil survey and conservation planning, reducing costs and time associated with site assessments as well as identifying metal(loid) contamination hotspots to ensure the health and safety of urban agricultural practices and communities.

Competing interests

The contact author has declared that none of the authors has any competing interests.

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Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors used ChatGPT to improve readability and language of the manuscript. After using this service, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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Author contributions

Eriell Jenkins: Data curation, Formal analysis, Visualization, Writing – original draft; Anna Paltseva: Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – review and editing; John Galbraith: Writing – review and editing.

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Data statement

Since this is a review paper, no original research data is presented.

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