

Dear Editor and Reviewers,

We sincerely thank you for your constructive feedback and the opportunity to revise our manuscript. In response to the reviewer comments, we have made several significant improvements that enhance both the depth and clarity of the paper:

- We increased the number of reviewed studies from 67 to 84, broadening the evidence base and strengthening the conclusions.
- A new summary of PXRF instrument brand usage has been added, highlighting Olympus and Thermo Scientific as the most commonly applied, offering practical insight into tool selection.
- We now provide clearer guidance on calibration practices (e.g., use of CRMs), optimal measurement conditions, and testing time with corresponding new figures to support real-world application.
- The revised version concludes with specific research needs, including the lack of urban-specific calibration protocols and the need for integrated spatial methods in future PXRF research.
- Figures and tables have been reorganized (and even some of them were removed) to better communicate key findings, including a refined literature search flowchart and frequency distribution of PXRF instruments.
- We refined the language throughout and restructured sections for better flow, including a clearly stated research question, improved synthesis of results across studies, and stronger integration of practical implications.

Collectively, these changes significantly improve the manuscript's clarity, structure, and practical value, aligning with the goals of both reviewers. We hope the revised version meets your expectations and offers a meaningful contribution to the field of urban soil research.

Sincerely,

Anna Paltseva

RC1: '[Comment on egusphere-2024-3101](#)', Anonymous Referee #1, 28 Nov 2024

The manuscript addresses the review of an interesting topic, however, it lacks the necessary depth to warrant publication.

- **We thank the reviewer for recognizing the significance of our review topic. To address concerns about depth, we have expanded the literature base, incorporating a broader and more detailed comparative analysis. We've enhanced methodological discussions, explicitly clarified PXRF limitations, and improved practical recommendations. Additionally, visual aids have been revised to provide clearer data presentations, significantly deepening the manuscript's analytical rigor and practical utility.**

While the title and objectives clearly indicate a focus on urban soils, the manuscript does not provide a sufficient justification for limiting the review exclusively to urban soils. Why is the method under review only applicable to urban soils, and would it also be suitable for agricultural soils? The rationale for restricting the review to XRF studies conducted in urban soils is not clearly explained.

- **We agree with the reviewer on the importance of clearly articulating our rationale. In the revised manuscript, we explicitly emphasize the unique challenges associated with urban soils, such as significant heterogeneity, complex land-use histories, and contamination from diverse anthropogenic sources like industrial residues, traffic emissions, and urban waste. These factors particularly influence PXRF accuracy and precision, making it distinctly suitable for rapid assessment in urban contexts. We now clearly explain that while PXRF can indeed be used in agricultural soils, the specific focus and value of our review lie in addressing these distinctive urban characteristics, thereby providing targeted insights for urban soil management.**

The introduction sets up expectations for the reader, but the conclusion essentially restates what can already be found in the individual studies reviewed.

- **In the updated manuscript, we restructured the conclusions to clearly synthesize comparative insights drawn across reviewed studies, moving beyond mere restatements. We specifically highlight novel insights into optimal methodological approaches, practical limitations, and effective strategies for deploying PXRF in urban soil contexts. Additionally, we've explicitly identified existing research gaps—such as the need for region-specific calibration models and standardized methodological protocols tailored to urban soils—thus offering original guidance for future research and practical applications.**

Therefore, as it is currently presented, the manuscript does not offer significant new insights into the limitations and advantages of the method.

The information in Section 2 could be better organized and presented in a more reader-friendly format, such as tables or graphs, to enhance the clarity and accessibility of the bibliographic review results.

**We appreciate the reviewer's suggestion and have substantially revised Section 2 to improve organization, clarity, and data accessibility. In the updated version:**

- **We have updated a literature search flowchart (Figure 1), now including 84 reviewed studies.**
- **We have replaced the prior citation-based figure with a bar graph (Figure 5) showing the frequency of PXRF instrument brands across studies in section 3.1.**
- **To enhance accessibility of the review data, we included structured tables summarizing analytical parameters by element.**

To make the review more engaging and to strengthen its case for publication, I suggest the inclusion of the following:

1. A list of the chemical elements analyzed in the reviewed studies, along with their frequency of occurrence.
  2. A systematic presentation of  $R^2$  values, along with estimates of the accuracy for each element.
  3. The detection limits for each element, as reported in the reviewed studies.
- **We agree with this suggestion a comprehensive table summarizing the correlation coefficients ( $R^2$ ) clearly comparing PXRF and laboratory methods (ICP-MS, ICP-OES, ICP-AES) across reviewed studies, categorized by element. We also have added a summarized analysis of PXRF measurements across different studies, highlighting which elements consistently exhibit reliable measurements and under which conditions accuracy significantly decreases (Table 2 and 3).**

Including these details would make the review more informative and comprehensive, offering additional value to the scientific community.

- **Thank you very much for your thoughtful review. The manuscript has been revised according to your suggestions, providing a more substantial rationale, improved clarity, and comprehensive insights that align closely with the manuscript's objectives and research question.**

**RC2:** '[Comment on egusphere-2024-3101](#)', Anonymous Referee #2, 07 Feb 2025

This study is relevant and necessary as it provides insight into the performance of portable X-ray devices. However, the article would benefit from a clearer structure and a well-defined research question to better guide the reader.

- **We appreciate this valuable feedback. To enhance clarity, we have defined the main research question at the end of the Introduction section, clearly stating: *"What is the accuracy, precision, and practical applicability of portable X-ray fluorescence (PXRF) in evaluating metal contamination specifically within urban soils, and under what conditions does its performance vary?"* We have also reorganized the manuscript structure, clearly linking each subsequent section back to this central research question.**

Currently, the inclusion of numerous individual studies makes it difficult to follow, especially since they are not always synthesized or compared to one another—which should be a key objective of a review.

- **We fully agree, and have significantly revised the manuscript to better synthesize and compare findings across studies. Specifically, we have:**
  - **Introduced summary tables presenting R<sup>2</sup> values, analytical methods across elements and instruments (Table 2).**
  - **Highlighted cross-study patterns and discrepancies, including conditions where PXRF yields reliable results versus where it underperforms.**
  - **Added interpretive commentary throughout, particularly in Sections 3 to draw out key themes, methodological contrasts, and practical implications.**

Additionally, the study lacks detail on the choice of the urban setting, which could have a significant impact on the findings.

- **We acknowledge this critical point. We have clearly stated that urban soils present specific analytical challenges due to their heterogeneous nature, history of anthropogenic contamination, and complex land-use patterns.**

Besides, the authors tend to write several times some information for instance about the soil moisture/OM or mode choice importance. This makes the paper hard to read and without any clear conclusion while such study could have been helpful for choice in measurement technique.

- **We agree with this observation. We have revised the manuscript to the best of our capacity significantly improving its readability and coherence.**

Finally, I'm not convinced about the "performance status" the authors accepted. In some cases there is a factor 2 to 3 between ICP and PXRF measurement which seems quite high.

**In the revised manuscript, we have addressed this concern by:**

- **Clarifying acceptable thresholds for PXRF deviations based on regulatory and peer-reviewed sources (e.g., U.S. EPA Method 6200, which allows up to  $\pm 30\%$  for screening-level comparability).**

- Explicitly discussing cases where PXRF deviates from ICP results—especially for elements with lower atomic mass, or under challenging field conditions.
- Providing detailed Tables 2 showing  $R^2$  values and methods and Table 3 used to help readers assess which metals and conditions yield reliable PXRF results.
- New Figures 2 and 3 illustrate how increasing PXRF measurement time significantly lowers detection limits. As shown in Figure 2, elements like Pb, Hg, Cd, and As exhibit up to an ~80% reduction in detection limits when extending scan time from 15 to 480 seconds. Figure 3 further confirms this trend, demonstrating a Poisson-based inverse square root relationship between measurement time and detection limit across ten metals (Kalnicky & Singhvi, 2001). These results emphasize the critical role of count time in improving PXRF sensitivity and analytical precision.

Other comments,

\*L. 29 I think a “d” is missing in “foo security”

- **The typo was corrected from "foo security" to "food security".**

\*L. 80 “Articles that provided background information on the PXRF and heavy metal pollution l. 82 was also used in this review.” I think it’s were instead of was.

- **The sentence was revised accordingly.**

\* L.82 “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 stud” sentence not clear

- **We have rewritten this sentence for greater clarity as follows: "During the literature search, particularly on Google Scholar, a number of retrieved articles did not meet the predefined inclusion criteria and thus were excluded from the review."**

\* Figure 1 : not sure about the relevance of 1 flow chart for Wos and 1 for google scholar when the words searched are the same. The horizontal line between urban soil and HM in the WOS flow chart is not horizontal. Please complete the lines or the legend by “and” or “or” or any other logical link they represent.

- **We appreciate this suggestion for improving Figure 1 and incorporated the changes.**

\*Fig. 2 Not sure about the relevance of Fig.2. Maybe a chart with number of studies employing each type of XRF or at least each type of XRF with different specificity as described in paragraph 2.2 would be better?

- **To address this, we have replaced Figure 2 with a clear bar chart illustrating the number of reviewed studies employing each PXRF instrument type and integrated it in section 3.1. We have eliminated section 2.2 to avoid redundancy and lists.**

\*L. 262 “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, “ same sentence than l. 258 ;

- **We thank the reviewer for pointing out this redundancy. We have revised the text accordingly.**

\* I’m a bit confused about the conclusion for table 1. You mentioned that Ni measurements with ICP and XRF are in close proximity while there is a factor 3 and no R2 ; same for Pb and Zn with a factor 2 between ICP and XRF.

- **Thank you for highlighting this. The Table 1 was corrected to address the discrepancies.**

\* L. 280 “with Cd showing a slightly increasing trend at higher concentrations” Isn’t that Cu rather than Cr?

- **Thank you for identifying this. We have corrected this statement.**

\* L. 294 “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” please define or explain “cubist modelling” and “lin’s concordance”

- **In the revised manuscript, we briefly defined and explained these terms:**
  - **Cubist modelling: A statistical machine-learning method used for predicting continuous numeric outcomes from large datasets by creating predictive rule-based models.**
  - **Lin’s Concordance correlation coefficient (CCC): A statistical measure that quantifies agreement between two measurement methods, indicating both accuracy and precision simultaneously.**

\* L.300 “ The results obtained in research conducted by Schmidt et al. (2024) [...] PXRF measurements for As and Pb”, this look like a list of studies that performed or not ... I’m not sure about the relevance of this paragraph after the table and fig.3. Maybe rephrase or complete to highlight the interest of detailing this study? Besides, l.263 the author wrote that method does not perform well for As ....

- **We agree with your concern. This paragraph was rewritten.**

\* Table 2 not sure about “in situ r2” and “ex situ r2” is it the r2 between PXRF and ICP for in -situ (or ex situ) measurements? please detail the legend

- **We have removed Table 2 for the manuscript.**

\* Is paragraph 3.3 a “conclusion” about how to perform measurements ?

- **Paragraph 3.3 was moved to 3.5 section and provides recommendations and practical considerations based on the reviewed studies rather than a formal conclusion.**

\* I. 390 “Portable XRF is effective and economic [...] for each heavy metal individually using traditional laboratory methods.” Is that a concluding paragraph ? why an other paragraph of example after this one

- **We acknowledge this confusion and reorganized these sections clearly to separate our concluding statements from specific illustrative examples.**

\* L.430 and 432 comments about the moisture and organic matter content have been wrote before

- **Thank you for highlighting this redundancy. We have made changes in the text to avoid redundancy.**