

RESEARCH ARTICLE

Moisture, organic matter, and large particle correction for accurate Pb portable X-ray fluorescence assessment in urban soils

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Abstract

The need for accurate quantification of lead concentrations in urban centers around the world is turning attention towards rapid methods for contamination assessment. Portable X-ray Fluorescence (pXRF) has been recognized as a more accessible alternative to traditional digestion methods. This study was conducted to produce measurement corrections for in-situ pXRF measurements conducted on field soils under varying conditions of moisture, organic matter (OM) content, and particle size heterogeneity. Urban forest soils were analyzed for Pb under increasing soil moisture, OM, and coarse fraction contents with two different pXRF and the results were compared to reverse aqua regia digestions. While both instruments showed a strong correlation despite using different calibration methods, correction of pXRF data to digestion values improved accuracy but potentially underestimated Pb concentrations. We propose an empirical correction equation derived from the regression of variance between theoretical and observed concentrations to correct for moisture effects. OM and particle size heterogeneity did not produce a significant effect on Pb measurement and did not warrant correction. Our study confirms other work showing that pXRF provides an accurate and precise alternative to traditional digestion methods for Pb screening, provided that moisture is corrected.

KEYWORDS

contamination, correction equation, in-situ, pXRF, urban soil

1 | INTRODUCTION

Lead contamination in soil and water is a prevailing environmental justice and public health issue in aging cities

worldwide, where legacy Pb uses contribute to continuous Pb enrichment in residential soils.^{1,2} It is well documented that elevated concentrations of Pb in soils are an ongoing, widespread health issue in urban areas,³

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particularly as it is easily inhaled or ingested by children who are the most vulnerable to its neurotoxic effects. As a result, elevated concentrations of Pb in urban soils can negatively impact societal development,² as well as forest ecosystems,⁴ urban agriculture,⁵ and aquatic ecosystems.⁶ Across the world, varied guidelines for Pb soil monitoring have been put in place with the unique goal to identify contamination hotspots and targeting remediation efforts. In the USA, the US Environmental Protection Agency has set the soil screening level for Pb at 400 mg/kg in residential areas,⁷ based on a 5-points average sampling scheme. However, some individual states have set their own levels, such as, for example, California (80 mg/kg—⁸) or Vermont (41 mg/kg—⁹). For residential soils, the Canadian screening value is 140 mg/kg,¹⁰ in China it is 400 mg/kg (for “development land”, Li et al.¹¹), and in the Netherlands it is set at 530 mg/kg,¹² to cite only a few. While these values illustrate the wide variety of concentrations considered as action levels in the world, they also implicate the importance of screening soils for Pb levels in residential areas. As such, it is fundamental to have access to rapid, effective methods for soil metal assessment.

Most countries' environmental protection agencies have designed certified methods for Pb analysis in soils. The US EPA relies principally on acid digestion methods (EPA 3050B, 3051A) but allows the use of X-Ray fluorescence (pXRF) for screening values (EPA 6200). In Canada, CCME guidance advises to perform a pilot test where 15–20 site-specific samples are analyzed using both XRF and laboratory methods (typically spectroscopy post-digestion) if using XRF for soil screening. In China, the 2017 Technical Stipulation soil survey method requires the determination of Pb by inductively coupled plasma (ICP) or atomic absorption (AA) spectroscopy following complete acid digestion (cited in¹³). Because it is considered the most accurate and precise method for trace metal quantification, total and pseudo-total digestion prior to liquid-based analysis is therefore the gold standard for Pb assessment in soils. However, this process is performed *ex-situ*, time-consuming, costly (>\$50 per sample), and produces hazardous acid waste. In addition, the use of strong acids in complex methodologies to digest both environmentally available and silicate-locked Pb (hydrofluoric acid extraction) is prone to operating errors. Consequently, scores of studies have attempted to propose alternative acid-digestion methods for Pb screening.^{14,15,16} Such modified acid-digestion methods generally provide pseudo-total concentrations effective for measuring >85% of total Pb.¹⁷

Portable pXRF has been gaining recognition as an effective, alternate method for soil Pb assessment.^{18–20} Several studies have found strong linear correlations

between pXRF concentrations and those acquired through the digestion of soils.^{21–23} Rouillon and Taylor²⁰ suggested that the large quantity of data acquisition enabled by rapid *in-situ* pXRF analysis can minimize error, leading to increased confidence and better cost-effectiveness for contaminated site assessment on a large scale. However, previous investigations of pXRF as a means for assessing lower contaminant concentrations typically found in agricultural or urban soils have discerned limitations on pXRF accuracy and precision.²⁴

Previous work has identified soil moisture, organic matter (OM), and particle-size heterogeneity as major factors influencing the accuracy and precision of pXRF. For example,²⁵ observed a 15–20% decrease in recorded metal concentration at 30% soil moisture compared to dry soils. Similarly, Ravansari and Lemke²⁶ observed that pXRF trace metal concentrations decreased at a rate exceeding that expected from dilution with an increasing soil OM fraction. Underestimation of trace metals by pXRF under elevated soil moisture and in the presence of OM has been attributed to matrix attenuation effects.²⁷ Low atomic number elements such as carbon, oxygen, and hydrogen that are outside of the pXRF sensitivity range can contribute to a reduction of the apparent concentration of heavier analytes. This decrease is due to the closed-sum effect inherent to pXRF quantitative methods.²⁸ In addition to mass-based dilution, water can also cause soil swelling/shrinking, which in turn influences the fluorescence penetration depth.²⁷

Soil particle size heterogeneity has also been shown to exert a strong influence over pXRF accuracy.^{29,30} Certain elements are particularly prone to the so-called “nugget effect”, where an accessory mineral, enriched in the analyte of concern, is overrepresented within the analysis area. In addition, Rostron and Ramsey³⁰ noted that elements of lower atomic mass, with shallower critical depth and lower overall volume of analysis, are also susceptible to high analytical heterogeneity. While laboratory analysis via XRF typically employs grinding/sieving of soils to minimize heterogeneity issues, *in-situ* analysis necessitates repeated measurements to minimize the effects of heterogeneity (EPA method 6200).¹⁸

Measurement accuracy has been improved with varying success through the application of post-measurement corrections for the effects of moisture and OM on pXRF accuracy.^{25,26,31–34} One such correction proposed by Ge et al.³² for the correction of moisture effects was proven effective up to 20% moisture by mass. However, this correction is based upon the assessment of individual spectra. While most pXRF instruments output spectral data, this method is time-consuming and not practical for users without expert knowledge. Aside from theoretically based corrections, previously proposed empirical corrections

have typically been developed from a single pXRF instrument, often using a limited quantity of certified reference materials.^{26,35} pXRF performance across instruments has been investigated previously, comparing pXRF-assessed concentrations against each other and against traditional analytical methods. However, these investigations have been conducted on processed soils and therefore do not factor in, let alone correct for, the effects of field variables such as moisture, OM, and heterogeneity.^{36,37} In addition, it is necessary to evaluate the effect of these variables across varying soil types. For example, the shrink/swell capabilities of soil are likely to influence how drastically moisture will affect pXRF measurement due to volumetric changes.²⁷

We evaluated the effects of moisture, OM, and particle size heterogeneity on Pb concentrations, at environmental concentrations across multiple urban soils, as measured by two separate pXRF instruments. In an effort to produce corrections for these variables, we define three types of corrections: (1) fundamental corrections, based on particle behavior and fluorescence parameters such as Compton scattering, (2) theoretical corrections, based on estimations of the effects of physical parameters, principally in the form of dilution or concentration effects and (3) empirical corrections, based on experimental assessment of the parameter-based variances. Fundamental corrections require a complicated assessment of spectral results or rely upon assumptions that do not take unique sample behavior into account, while empirical corrections are far more accessible. Empirical corrections that have been previously proposed for the purpose of correcting soil matrix effects have not been evaluated for applicability across pXRF instruments and calibrations, nor across different urban soils.

Where applicable, we computed empirical pXRF correction equations that better reflect digestion values and/or compensate for moisture, OM, and grain size heterogeneity.

2 | MATERIALS AND METHODS

2.1 | Soil sample locations and collection

Urban forest soil samples were collected from Albany, NY; Burlington, VT; Springfield, MA; and Hartford, CT in the Fall of 2019. The sampling locations were chosen as representative soil materials for each city with moderately to elevated trace element concentrations.^{38,39} In each city, a sampling site with <5° slope, predominantly deciduous foliage cover, and located >2 m from impervious surfaces (e.g., roads, sidewalks) was selected. Approximately 2 kg of soil were collected from both A and B soil

horizons (except for the Albany, NY site, where no B horizon was identified) and subsequently oven dried at 70°C and sieved to <2 mm. The natural OM concentration of each soil was estimated by loss-on-ignition (LOI) at 550°C, and particle size distribution was analyzed with a Beckman Coulter LS 230 laser diffractometer.

In addition to the forest soil samples, 80 surface soil samples were collected from Hartford, CT. These samples were collected for the purpose of applying and evaluating the effectiveness of our correction equations. Publicly available GIS data for Hartford was downloaded from the Connecticut Department of Energy and Environmental Protection website, and the 'Create Fishnet' tool was used to generate an evenly spaced grid of approximately 150 sample sites across the city using ArcGIS (ESRI, Redlands, CA, USA). Once a sample site was identified the O-horizon material was scraped away, and at least 0.5 kg of soil was collected using an auger for the top 15 cm to capture surface contamination most relevant to plant uptake and dust generation. Samples were stored in airtight bags to maintain field moisture.

2.2 | Soil digestion and elemental analysis

Dried and sieved soil samples were digested to quantify the pseudo-total Pb concentrations. For the pseudo-total digestion, 1.0 g of soil was weighed into 50 ml centrifuge tubes. Next, a strong acid digestion following USEPA method 3050B,⁴⁰ using 5 ml of reverse aqua regia (9:1 ratio of 15 M HNO₃ + 10 M HCl, Trace Metal Grade, Fisher Scientific) heated to 70°C for 45 min using a hot plate. The digest was allowed to cool and diluted to 50 ml using 18.2 MΩ cm deionized water. For every 20 samples, a preparation blank and standard reference materials (NIST 2710 Montana Soil and NIST 2709a San Joaquin Soil) were included. Digests were analyzed on an Agilent 7700x ICP-MS (Agilent Technologies, Santa Clara CA, USA). Pseudo-total recovery rates for NIST 2710 and NIST 2709a were 91% and 94% for Pb. Blanks were <0.1 ng/L and the coefficient of variations were <4%.

2.3 | pXRF analysis of increasing organic matter, moisture, and heterogeneity

Moisture adjustment was performed by mixing 18.2 MΩ cm nanopure H₂O into the soil to reach mass ratios of 0 to ca. 30%. Confectioner's sugar was utilized as an OM surrogate and mixed with the soils to reach a range of OM fractions in the soils between in-situ, LOI-determined OM content and 20% OM content. To

simulate coarse particle fraction, 6 mm Supelco silicate beads were mixed in the soils to reach a range of 0 to 30% glass beads by mass. Approximately 30 g of dry soil was added to a pre-weighed HDPE bottle. Bottles were capped with Chemplex 2.5 μm X-ray transparent mylar film and homogenized with a tabletop vortex shaker before quadruplicate measurement by pXRF upon each consecutive addition of confectioner's sugar, water, or silicate beads. Each soil was analyzed in quadruplicate, using two different pXRF instruments. A Hitachi X-MET8000 was utilized with a factory-set fundamental parameters calibration for soil analysis, and a SciAps X-200 with a user-built empirical calibration of Compton normalized peaks (Supplementary Materials, Table S1). Both machines were set to a 60 s integrated measurement time.

The Hartford surface soils ($n = 80$) were analyzed in quadruplicate with each pXRF instrument at both field moist conditions as well as after drying soils at 70°C. Soil mass was recorded before and after drying to ascertain original moisture concentrations, for later use while applying moisture correction equations.

2.4 | Repeated measures ANOVA

Portable XRF trace metal concentrations were statistically analyzed by repeated measures ANOVA with a Greenhouse–Geisser correction within SPSS Statistics 27. This was performed to identify significant differences in analyte concentration across all soils as a result of increasing soil moisture, OM, or grain size heterogeneity. In addition, any significant interaction terms were distinguished within the repeated measures ANOVA. Interactions terms between the independent variable (moisture, OM, or silicate bead concentrations) and soil type or pXRF model were tested for significance. All statistical tests were conducted at the 95% significance level. Only trials with significant changes in analyte concentrations were considered for the development of a correction equation. In addition, the observed change in analyte concentration must not be significantly different between soil types nor pXRF instruments.

2.5 | Correction calculation

Lead concentrations measured on soils with artificially increased OM, moisture, or grain size heterogeneity were compared to theoretical concentrations. In the case of soil moisture, the theoretical concentration was considered to be equivalent to analyte concentrations measured on dry unaltered soils. OM and coarse particles contribute to the dry sample mass. Therefore, theoretical concentrations

($[\text{Pb}]_{\text{Theoret.}}$) were defined by the expected dilution of concentrations measured on dry unaltered soils ($[\text{Pb}]_{\text{Unalt.}}$). Equation (1) demonstrates how theoretical dilution concentrations were calculated for OM and grain size heterogeneity tests.

$$[\text{Pb}]_{\text{Theoret.}} = \frac{[\text{Pb}]_{\text{Unalt.}}}{1+x} \quad (1)$$

where x represents the % moisture/silicate beads content by mass. Correction equations were derived from the variance of observed concentrations ($[\text{X}]_{\text{Obs.}}$) from theoretical concentrations. To account for the varying average concentrations, measured concentrations were also normalized to concentrations measured on dry, unaltered soils. Equation (2) demonstrates the calculation of normalized variance between theoretical and observed concentrations.

Normalization of analyte variance from dry concentrations:

$$A = 1 - \frac{[\text{X}]_{\text{Obs.}}}{[\text{X}]_{\text{Theoret.}}} \quad (2)$$

where A represents the correction factor. Equation (2) was applied to all measurements taken on soils at each artificial increment of OM, moisture, or heterogeneity. All data points calculated from Equation (2) were subsequently regressed against moisture concentration. The regression equation (Equation 3) derived from these values provides a means of calculating a correction factor (A) for any given moisture concentration. Correction factors may then be utilized to correct the Pb concentration as measured on moist, organic rich, or heterogeneous soils.

Derivation of Correction Equations:

$$[\text{Pb}]_{\text{Theoret.}} = \frac{1}{1-A} [\text{Pb}]_{\text{Obs.}} \quad (3)$$

3 | RESULTS

3.1 | Soil characteristics

Except for the Albany site (loamy sand), all soils were classified as silty loams (Supplementary Materials, Figure S1). Percent OM was variable, ranging from 1.51% for the Albany sandy loam to 22.6% for the A horizon at Springfield, with all other soils around 6% to 8% OM (Supplementary Materials, Table S2). Urban forests, where these soils were sampled from, typically represent background levels of trace metals for urban soils.

Concentrations of Pb ranged between 25.1 and 127.6 mg/kg, as determined by pseudo-total digestion.

3.2 | Correction to digestion values

We assessed the accuracy of pXRF to traditional digestion by comparing the pXRF results on dry, sieved soils

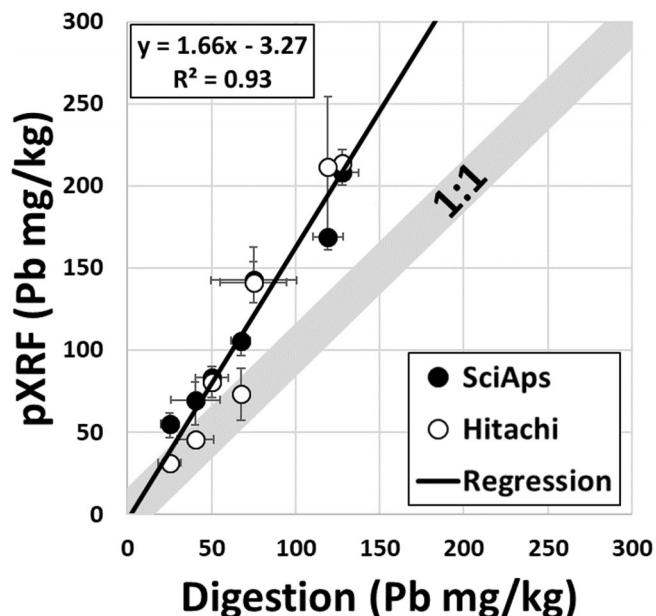


FIGURE 1 pXRF concentrations as a function of digestion concentrations for the seven study soils, as measured by both the Hitachi (open circles) and SciAps (closed circles) pXRF instruments. A gray reference line demonstrates the 1:1 ratio. Error bars represent 1 standard deviation of quadruplicate measurements for pXRF and triplicate for digestion.

against digestion values (Figure 1) using the Hitachi XMET8000. A linear relationship was determined between the concentrations measured by pXRF and digestion. The coefficient of determination (R^2) was 0.93 (Figure 1). Pseudo-total concentrations were generally lower than pXRF concentrations. With a regression slope of 0.56, Pb displayed a greater dependence on analyte concentration for the degree of disparity between pXRF and digestion concentrations (Figure 1). We used these data to provide an empirical correction of pXRF values to better mirror digestion values, displayed in Figure 1, which may be used to adjust pXRF concentrations measured on dry, sieved soils.

To test the correction equation, we applied it to pXRF measurements taken on the dried Hartford, CT surface soils. Each soil ($n = 80$) was analyzed by both pXRF instruments. Only data points within the range of metal concentrations used to derive correction equations were assessed, resulting in a n value of 145 (two measures per samples, minus measures outside of the range). Analyte concentrations determined by the two different instruments were in good agreement (Figure 2) with a coefficient of correlation of 0.96.

When the linear correction equations determined above (Figure 1) were applied to the pXRF measurements, the intercept value of the correlation equation improved significantly from 3.92 to 2.74. Regression of instrument-specific pXRF concentrations as a function of digestion concentrations before and after correction (Figure 2 and Supplementary Materials, Table S3) provides a means of assessing the ability of corrected pXRF measurements to reflect digestion values. Uncorrected pXRF concentrations were invariably higher than those of the digestion (Figures 2b,c) while coefficients of

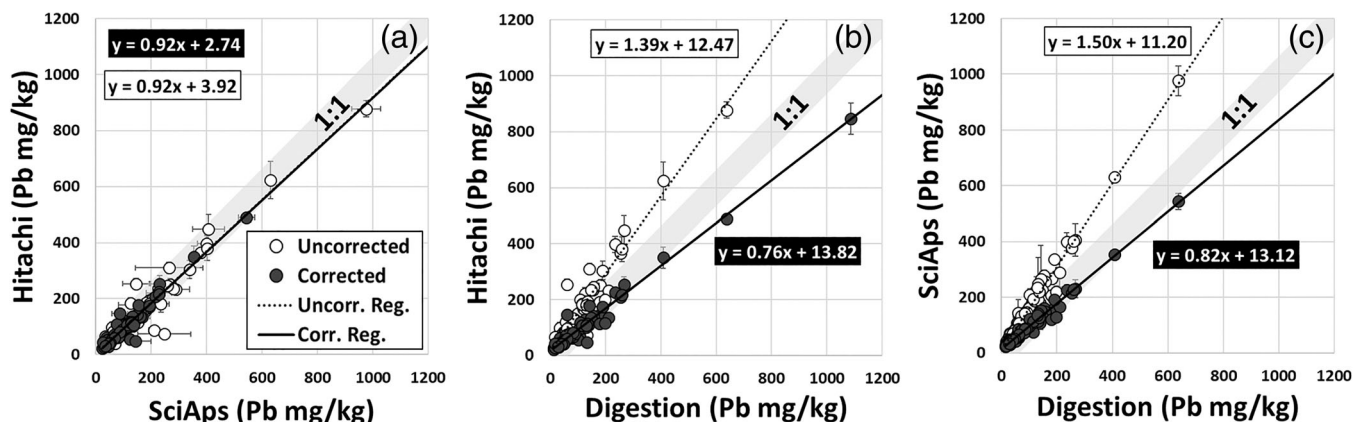


FIGURE 2 (a) Comparison of XRF analysis across devices. (b) Digestion-derived concentrations as a function of pXRF concentration acquired on the Hitachi for field-moist surface soil samples collected in Hartford, CT. (c) Digestion-derived concentrations as a function of pXRF concentration acquired on the SciAps for field-moist surface soil samples collected in Hartford, CT. Soils are represented both before correction (open circles) and after being corrected with the equations described in table 1 (closed circles). Each point represents the average of quadruplicates. The 1:1 line is represented for ease of interpretation

correlation revealed a good correlation (0.94, Supplementary Materials, Table S3). Applying the correction equations to the pXRF measurements improved their correspondence to the digestion values, as illustrated by the lower chi-squared values of 15% error after correction (Supplementary Materials, Table S3).

3.3 | Effect of moisture on pXRF accuracy

Repeated soil Pb quantification upon the addition of moisture up to 42% showed a general decrease in the measured Pb concentrations. Unsurprisingly, that decrease was more pronounced the higher the Pb content (Supplementary Materials, Figure S2). Repeated measures ANOVA with Greenhouse–Geisser correction (Supplementary Materials, Table S4), used to test the significance of the decrease, shows that there was a significant effect of soil moisture on Pb ($F_{(5,65)} = 8.00$, $p = 0.001$). While moisture led to an apparent decrease in detected concentrations (Supplementary Materials, Figure S2) by as much as 20% decrease at 30% moisture (Figure 3a), it did not produce a significant difference between the Hitachi and SciAps ($F_{(5,60)} = 0.96$, $p = 0.41$). The interaction between moisture and soil type also proved insignificant ($F_{(30,35)} = 1.73$, $p = 0.15$).

Data points displayed in Figure 3a were calculated with Equation (2), in which each point is the normalized variance between measurements taken on moist and dry soils, regressed as a function of moisture concentration. The resulting regression equation was subsequently substituted into Equation (3) as variable A to produce a specific correction equation (Equation 4). The correction equation was developed from data measured on both pXRF instruments and all soils, as the goal was to evaluate the efficacy of a universal equation across instruments and soils.

$$[\text{Pb}]_{\text{Theor.}} = \frac{[\text{Pb}]_{\text{Obs.}}}{1 - (0.0061 * x)} \quad (4)$$

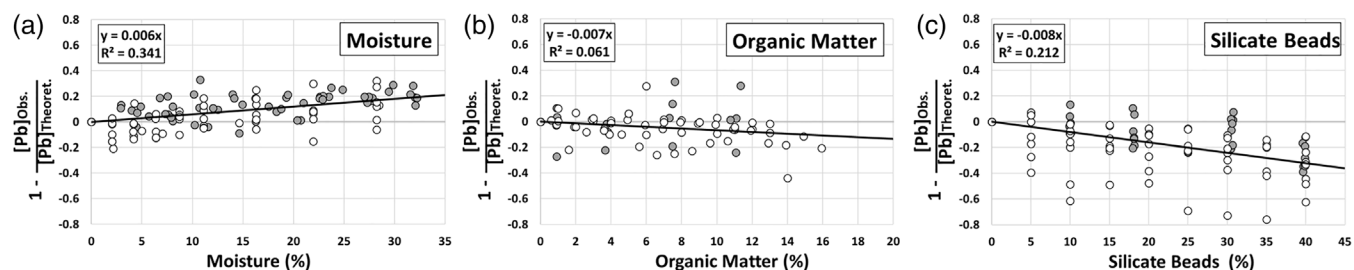


FIGURE 3 Variance between theoretical and observed concentrations, normalized to concentrations measured on dry, unaltered soils, as a function of moisture (a), organic matter (b), or silicate bead concentration (c). Linear regressions correspond to the entire dataset for each graph, forced to the origin

Equation (4) above shows that each percent moisture (x) decreases the Pb concentration by 0.61%.

3.4 | Effect of organic matter on pXRF accuracy

Precision in Pb analysis as a function of OM content was generally good across replicates except for the soil with the highest concentration (Supplementary Materials, Figure S2) and, in agreement with the limited changes in Pb concentrations with increased OM content (Supplementary Materials, Figure S2), the repeated measures ANOVA with Greenhouse–Geisser correction (Supplementary Materials, Table S4) showed no significant main effect of soil OM content on Pb ($F_{(1,27,8,91)} = 0.55$, $p = 0.52$). Because the OM content of Springfield A horizon, Albany, and Hartford A horizon soils (26%, 13%, 16%, respectively) was too close to the upper limit of the testing range, these soils were excluded from the statistical analysis. A lack of consistency in the response of metal concentrations to increasing OM content (Supplementary Materials, Figure S2) was reflected in the low proportion concentration variance that may be explained by OM concentration ($R^2 = 0.06$; Figure 3b). This lack of a consistent change in observed analyte concentration disqualifies OM from the creation of a post-hoc correction equation.

3.5 | Effect of coarse particles on pXRF accuracy

Similar to the OM tests, no clear trend in Pb concentrations changes was observed upon addition of glass beads (Supplementary Materials, Figure S2). However, repeated measures ANOVA with Greenhouse–Geisser correction (Supplementary Materials, Table S4) revealed significant deviation of the measured results from the theoretical dilution expected from the addition of coarse particles

(silicate beads) for Pb ($F_{(1.95, 15.38)} = 8.08, p = 0.002$). Due to the addition of mass in the form of silicate beads to the dry soil, the theoretical response of metal concentrations should be a decrease due to mass-driven dilution. However, we did not observe a decrease in the measured pXRF concentrations in response to the addition of silicate beads. Despite this statistically significant disparity between theoretical and observed analyte concentrations, correction of observed concentrations was not warranted based on these results. The lack of response to increasing particle size heterogeneity suggests that no correction was necessary for this trial.

3.6 | Validation of moisture correction

The correction equation (Equation 4), created for the correction of Pb concentrations measured on moist soils, was assessed for efficacy by applying it to the 80 Hartford surface soil samples. Lead concentrations, as well as the soil moisture content for each sample, were entered into the corresponding empirical correction equation. For comparison, metal concentrations were also corrected using the theoretical dilution correction method described by Shuttleworth et al.³³ This method utilizes Equation (1) to account for dilution of the analytes by soil moisture. Figure 4 displays three datasets as a function of

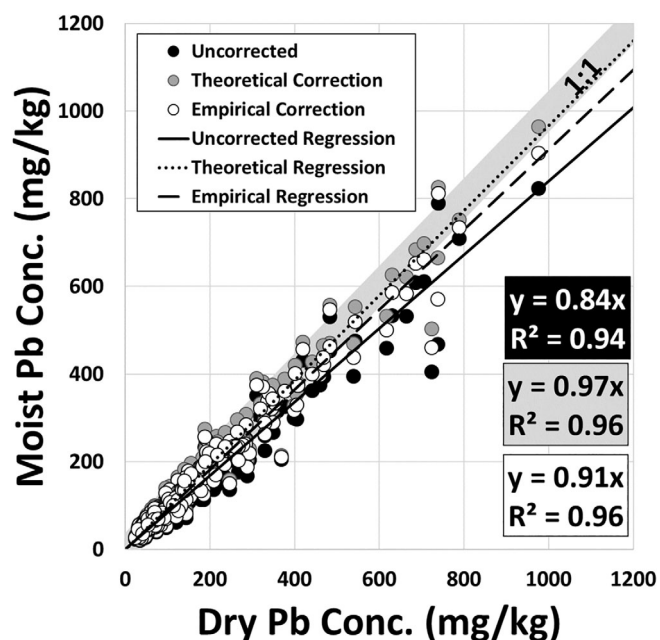


FIGURE 4 Pb concentrations measured via pXRF (Hitachi) on moist soils as a function of concentrations measured after drying soils. Each soil is represented with uncorrected concentrations measured with moisture (black circles), after correction via theoretical dilution equation (Equation 1), and after correction using the empirical correction equations (Equation 4). Conc. stands for concentrations

pXRF concentrations measured on dry soils: (1) the analyte concentrations measured on moist soils before correction (i.e., “Uncorrected”), (2) analyte concentrations after the application of our empirical correction equations (i.e., “Empirical Correction”), and (3) analyte concentrations after the application of a theoretical dilution correction (i.e., “Theoretical Correction”).

The application of theoretical and empirical corrections reduced the discrepancy between moist and dry concentrations as outlined by correlation slope factors closer to 1.

4 | DISCUSSION

4.1 | Instrument comparison

Our assessment of Pb concentrations in a consistent set of natural samples using digestion and two different pXRF instruments showed a good agreement across instruments (Figure 2a). For the Hitachi XMET8000 we used factory calibration while the SciAps X-200 used our developed calibration. The strong correlation across instruments shows that, for Pb, matrix effects known to be the cause for the development of purpose-specific calibration⁴¹ are negligible. As analyzed on the L β emission line, emission energy for Pb (12.61 keV) is strong and it appears that either little absorption from low-Z elements is occurring in soil matrix samples or the fraction of absorption is similar across our concentrations. Therefore, irrespective of the instrument and the calibration, results within our concentration range (0 to 1200 mg/kg) can be used with confidence for glaciated and fluvial soils within the Pb range studied here. Soils with substantially different properties (e.g., high clay, high OM, high carbonates, high Fe oxide content) may need additional calibration methods. While it has been shown that pXRF analysis across instruments can be unreliable,⁴² our results, similar to others,³⁶ suggest that this may not be true for Pb.

4.2 | Correction to digestion values

Our analysis of the seven soils used for correction produced strong linear relationships between pXRF concentrations and pseudo-total digestion ($R^2 = 0.93$, Figure 1). The larger Hartford dataset produced a similar relationship between pXRF and digestion results (Figure 2), irrespective of the instrument used for analysis. By comparing and correcting pXRF-derived total Pb concentration with pseudo-total digestion (>91% recovery), we provided a correction of the Pb value to an

environmentally relevant concentration. The slope of our correction equation was 1.66 which effectively influenced Pb concentrations, particularly at higher values (Figure 2b,c). This has fundamental implications for soil screening as protection agencies set standards based on single values. As an example, application of the correction equation for the Hartford sample set decreased the number of samples above the US. EPA screening level (400 mg/kg) by half (from 4 to 2 samples); using Californian screening values (80 mg/kg), the number of samples above screening value was decreased by nearly 40% (from 58 to 35 samples). Such dramatic changes in the number of sites considered as contaminated have practical implications for local authorities and targeted remediation strategies. While the application of linear corrections using soils collected from four distinct cities—thereby intentionally incorporating site variability—consistently improved the accuracy of the pXRF measurements, it also consistently corrected to values below the digestion values (Figure 2). We perceive this correction as detrimental to an effective remediation of contaminated properties as it tends to artificially decrease the number of contaminated sites. One potential explanation for this overcorrection is the fact that our correction equation was determined using background soils with low Pb values (0 to 150 mg/kg). However, the strong correlation coefficient suggests that addition of soils with higher Pb concentrations would not have dramatically changed the slope of the correction (Figure 1). While previous authors, such as Caporale et al.,²¹ have achieved stronger correlations for Pb, they used site-specific regressions. Here, we show that using multiple sites to establish corrections can lead to a high level of accuracy for other sites, albeit by potentially overcorrecting to lower Pb values.

4.3 | Correction of moisture effects

Moisture, OM, and particle size heterogeneity are commonly cited as major factors impacting in-situ pXRF accuracy and precision. Moisture and OM have been attributed to attenuation of fluorescent signals and subsequent reduction of measured analyte concentrations.^{26,43} Moisture reversibly dilutes soil analytes, but, in order to provide comparable measurements, the desired concentration is that of dry soils.

Repeated measures ANOVA revealed a significant decrease in measured concentration in response to increasing soil moisture (Supplementary Materials, Table S5). This decrease was observed across experimental soils, as well as between pXRF instruments. Our empirically derived correction factor was effective at

correcting Pb pXRF concentrations measured on moist soils to reflect dry analyte concentrations (Figure 4). However, for the purpose of comparison to previously presented correction methods by,³³ the same dataset was also corrected based solely on the theoretical mass dilution of the soil sample with water. Our empirically derived correction and dilution-based theoretical correction performed well in compensating for soil sample moisture and producing values reflective of those measured on dried samples. Therefore, we recommend that a simple dilution-based theoretical correction is more pragmatic for rapid correction of Pb pXRF values measured on moist soils.

The similarity in performance of the empirical correction to the theoretical dilution correction suggests that instrumental deviation as a result of moisture interference does not exert significant control over measurement results. In other words, attenuation as a result of the presence of water molecules had negligible influence on the fluorescence signal aside from dilution. Therefore, the decrease in measured concentrations may be corrected for with a simple theoretical dilution correction, provided that moisture content is known. Previous studies have suggested that scattering and attenuation of the fluorescent signal in the presence of water can have a significant influence on the accuracy of pXRF measurement.^{32,44} While it has been shown that attenuation is a greater factor for fluorescence of low Z elements,³¹ our results provide further evidence that the pXRF measurement of high Z elements, such as Pb, experiences a negligible impact from soil moisture. As previously demonstrated by Shuttleworth et al.,³³ simple dilution correction remains a more rapid and accessible means of improving pXRF accuracy for this metal.

4.4 | Correction of organic matter effects

We found pXRF measurements of Pb decreased proportionally to OM%. Repeated measure ANOVA of pXRF concentrations did not identify any significant deviation of pXRF values from theoretical soil mass dilution. Figures 3b displays the variance of observed pXRF concentrations from theoretical dilution concentrations, as a function of OM concentration and normalized to Pb concentration. The weak correlations, with an R^2 coefficient of 0.06, suggesting that OM concentration explains little of the variation between the decrease of observed and theoretical analyte concentration. Based upon these results, we conclude that pXRF concentrations for Pb do not require correction in the presence of OM up to 20% by mass.

As OM is principally composed of light elements (oxygen, carbon, hydrogen), which produce very low-energy fluorescent signals, OM contributes to the attenuation of the overall sample outgoing fluorescence signal.²⁶ This attenuation by OM is often cited as the cause for the apparent lowering of trace metal concentrations in organic-rich soils.^{26,45} Our results however are not in agreement with this observation as we observed no significant deviation in metal concentrations from the anticipated mass dilution with OM.

4.5 | Correction of grain size heterogeneity

Particle size heterogeneity, modeled with silicate beads, did not initiate any significant deviation in pXRF-measured concentrations relative to sieved soils (Figure 3c). This is contrary to the theoretical mass-driven dilution effect that would be anticipated to result in decreasing analyte concentrations where similar to OM addition, the addition of coarse particles increased the dry mass of a soil. Increasing the dry mass of a sample via coarse particles will theoretically dilute the relative concentration of analytes within the soil.⁴³

Given that a decrease in analyte concentrations would be expected following the addition of silicate beads, the observed lack of change within our pXRF results was found to be significantly different from theoretical dilution values. This observation was consistent across all soils, as well as between both pXRF instruments (Figure 3c). Because trace metal concentrations are typically reported on dry, sieved soils however the lack of deviation between analyte concentrations measured on sieved soils and after the addition of coarse silicate particles did not, therefore, warrant correction.

4.6 | Comparison to existing corrections

The effects of soil moisture, OM content and particle size on the accuracy of pXRF measurements are not new because of a combination of both a matrix effect leading to decreased X-ray absorption and dilution of the signal.^{46,47} As a result, increased soil moisture content tends to exponentially reduce the pXRF-perceived concentrations of trace elements.^{18,32,46,48} Similarly, the presence of OM in soils decreases the average atomic mass in the soil and attenuates X-rays from pXRF beams, and X-rays fluoresced by analytes in a soil.^{26,45} In the case of rock fragments and coarse particles, the general effect on accuracy is an increase in the heterogeneity of the measurement due to the similarity between the coarse particle size and

the critical X-ray penetrating depth of many pXRF, and due to the increase in pore space.

As a result of these complications, a common approach consists in treating soils prior to analysis as for example recommended by the USEPA Method 6200⁴⁹ which advises that pXRF operators perform analysis on dry, ground soils, free of large organic debris. While it lowers artifacts, such practice diminishes the advantage of pXRF which is to provide fast and relatively free of pre-treatment analyses.

For that reason, many studies are attempting to correct these artifacts. Here, we show that OM concentration explains little of the variation between the decrease of observed and theoretical analyte concentration and that particle size heterogeneity did not initiate any significant deviation in pXRF-measured concentrations relative to sieved soils, therefore not warranting correction besides dilution corrections. Regarding moisture effects, however, we empirically derived correction factors effective at correcting Pb pXRF concentrations. Several studies have proposed corrections for soil moisture effects of pXRF analysis of metals. Recently, Nakano et al.⁴⁶ proposed a correction method based on a combination of matrix-based Compton scattering factors and water content factors. In this correction, the Compton correction was performed by normalizing the moist intensity of the element of interest over the RhK α Compton scattered X-ray and the correction for water content consisted of a simple dilution correction. Testing on Cr, the authors showed that the matrix effects contributed to roughly the same amount of signal decrease as dilution. This moisture correction differs from previously proposed corrections which used empirical exponential parametric corrections based on multiple samples.^{32,48} Here, our correction factor is based on an exponential trend too (Equation 4) with a parameter dependent on the moisture level of the soil. Over a 0 to 100% moisture range, our correction was similar to that of Schneider et al.⁴⁸ for Pb, never deviating for more than 10% (Supplemental Material, Figure S3). This close correspondence suggests that our correction can be used irrespective of soil type and, unlike the correction proposed by Nakano, does not require sample-dependent investigation of the X-ray intensity attenuation.

5 | CONCLUSIONS

Our study showed that for the in-situ determination of Pb concentrations in urban soils, pXRF deviated from digestion values in predictable ways. We provided an empirically defined pathway for the correction of Pb concentrations measured by pXRF-measured by pXRF to

better reflect pseudo-total digestion values. For soil moisture, where dilution does not contribute to the dry mass of the sample, we show that dilution correction is both rapid and effective at compensating for decreases in measured analyte concentrations.

We suggest that mass addition of non-contaminated material can effectively explain concentration decreases observed within our experiments, and that attenuation outside of dilution is negligible. This interpretation is supported by the lack of a significant difference between the theoretical dilution and the measured concentration of the given analytes in the presence of OM. In addition, the similar performance of our empirically derived correction factor and a theoretical dilution correction for minimizing the effect of moisture indicates that dilution is the dominant influence on pXRF measurement of Pb on moist soils. Our results add to the growing body of work suggesting that pXRF provides accurate and precise analysis for Pb in soils at a fraction of the time and currency costs associated with traditional digestion methods.

AUTHOR CONTRIBUTIONS

Sandra Walser: Investigation, Formal Analysis, Writing-Original Draft. Eric Sirkovich: Investigation, Formal Analysis, Writing-Review & Editing. Justin Richardson: Conceptualization, Supervision, Writing-Review & Editing. Ainsley McStay: Investigation, Formal Analysis, Writing-Review & Editing. Nicolas Perdrial: Conceptualization, Supervision, Writing-Review & Editing.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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