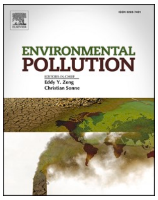
Environmental Pollution 336 (2023) 122441

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol



Evaluating trace elements in urban forest soils across three contrasting New England USA towns and cities by pXRF and mass spectrometry☆

Eric C. Sirkovich[a], Sandra L. Walser[b], Nicolas Perdrial[b], Justin B. Richardson[a,*]

[a] Department of Geosciences, University of Massachusetts Amherst, 611 North Pleasant Street, Amherst, MA, 01003, USA
[b] Department of Geography & Geosciences, University of Vermont, Burlington, VT, 05405, USA

ARTICLE INFO

Keywords:
Urban soils
Toxic metals
X-ray fluorescence
pXRF methodology

ABSTRACT

Urban forest soils perform important ecosystem services, such as the sequestration of potentially toxic elements, but some can serve as a source for human exposure if ingested or eroded by wind. Assessment of trace elements in urban soils through traditional methods is costly but portable X-ray fluorescence (pXRF) can allow for rapid screening for hazardous concentrations. Our objectives were (1) evaluate trace elements (As, Cd, Cr, Cu, Pb, and Zn) at 460 locations in and around urban forests across three town and cities in New England and across multiple land-uses, (2) evaluate accuracy and precision of pXRF compared with traditional digestion-inductively coupled plasma analyses, (3) determine if pXRF measurements are improved by processing the soil (oven drying, rock fragment removal, and organic matter (OM) removal). Our findings show that urban forest soils have extensive Pb accumulations (42 out of 460 with >200 mg/kg), while As and Zn exceeded regulatory limits in limited outlier samples. Urban forest soils adjacent to multi-family residences have higher Pb and Zn concentrations than recreational and open lots. Fortunately, Cd, Cr, and Cu were far below hazardous concentrations. Our comparisons suggest pXRF measurements of Cu, Pb, and Zn can be considered accurate while Cd and Cr may be screened by pXRF. However, As should not be considered qualitative nor quantitative due to 70% type 1 (false positive) error on samples. While the accuracy and precision were nominally improved through soil drying, removal of rock fragments, and removal of OM (<5% decrease in relative error), our results show processing soil samples is likely not needed.

1. Introduction

Urban forest soils are an important subgroup of soils that provide ecosystem services with respect to energy, water, and elemental cycling that support terrestrial organisms and protect aquatic ecosystems (Escobedo et al., 2011; Wang et al., 2018). Urban forest soils are typically characterized by the presence of woody plants, leaf litter layers, less human disturbance and management than lawns and landscaped areas, and typically have grass-limited understory (Airola and Buchholz, 1984). Urban forest soils provide the ecosystem service of trace element immobilization. Trace elements, such as As, Cd, Cr, Cu, Pb, and Zn, are an important group of elements that may serve as essential nutrients but may also pose a hazard to ecosystem and human health. Urban forest soils are important accumulators for trace elements (e.g. Richardson, 2020, Pecina et al., 2021; Wade et al., 2021), which has several implications for movement to surface and groundwater and sequestration within soil (e.g. Richardson, 2021). Urban forest soils in New England often contain highly elevated concentrations of trace elements (e.g. Bower et al., 2017; Richardson, 2020), the sources of which include industrial waste, vehicle emissions, coal burning, and use of leaded paint, among others (Argyraki et al., 1997; Wang et al., 2005; Wu et al., 2012; Kubier et al., 2019). Routes of exposure of trace elements in urban forest soils include inhalation of trace element-laced dust blown up from exposed soils, ingestion of soils, which is a particular concern for young children, and ingestion of trace elements in produce grown in contaminated soil (Wang et al., 2005; Clark and Knudsen, 2013; Paulette et al., 2015; Bower et al., 2017; Ravansari and Lemke, 2018). Urban forest soils need further characterization in urban areas to assess risks to human health and patterns of ecosystem services of trace element sequestration.

Traditional analytical methods of soil digestion and analysis by inductively coupled plasma-mass spectrometry (ICP-MS), inductively

---

☆ This paper has been recommended for acceptance by Dr Hefa Cheng.

* Corresponding author.
E-mail address: Jbrichardson@umass.edu (J.B. Richardson).

https://doi.org/10.1016/j.envpol.2023.122441
Received 22 June 2023; Received in revised form 11 August 2023; Accepted 22 August 2023
Available online 29 August 2023

coupled plasma-optical emission spectrometry (ICP-OES), and atomic absorption spectroscopy (AAS) for determining the concentration and distribution of trace elements in soils are limited due to their prohibitive cost and long wait time for sample processing and instrumental analyses (Caporale et al., 2018; de Lima et al., 2019; Wang et al., 2005; Wu et al., 2012). This challenge presents a need for new, more accessible analytical methods. One such technology that has received much attention over the past few decades is portable X-ray fluorescence (pXRF). Compared to traditional methods, pXRF analyses produce rapid results in the field within minutes and are less expensive than traditional laboratory equipment. According to the USEPA Method 6200 (2007), the most effective way to measure elemental concentrations with pXRF is to process the soils before analysis, which adds time and labor costs to the analytical process, thus detracting from the primary advantages of pXRF over traditional methods. Several studies have compared traditional digestion methods with pXRF for metals (Radu and Diamond, 2009; Al Maliki et al., 2017; Caporale et al., 2018; Borges et al., 2020; Walser et al., 2023). From these, it appears that soil processing can improve the accuracy and precision of pXRF measurements of trace elements by reducing interferences created by soil moisture, rock fragments, and organic matter (OM) content, which have been widely observed to reduce the accuracy and precision pXRF measurements of trace elements (Potts and West, 2008; Parsons et al., 2013; Mejía-Piña et al., 2016; Ravansari et al., 2020; Walser et al., 2023). Increased soil moisture content tends to exponentially reduce the pXRF-perceived concentrations of trace elements (Kalnicky and Singhvi, 2001; Ge et al., 2005; Schneider et al., 2016). Weindorf and Chakraborty (2016) suggest that pXRF operators identify and avoid measuring areas of a soil that clearly contain rock fragments or other obvious sources of heterogeneity (e.g., concretions, nodules, large roots, etc.) before conducting in-situ measurements as larger rock fragments exacerbate issues regarding shallow critical X-ray penetrating depth. Testing the accuracy and precision of pXRF in urban trace element pollution needs diverse regional examples to capture unknown limitations.

Our objectives were the following: (1) evaluate trace elements (As, Cd, Cr, Cu, Pb, and Zn) among three towns and cities in New England and across land-uses (evaluated using 2021 zoning ordinances) or governed by soil properties (%OM, pH, nonsilicate Fe), (2) evaluate accuracy and precision of pXRF measurements of trace elements in urban forest soils versus traditional digestion and ICP-MS analyses, (3) determine if pXRF trace element measurements are improved by levels of processing (field moist, oven dried, sieved of rock fragments >2 mm, and OM content removed by loss on ignition (LOI)). We hypothesized that urban forest soils in industrial and commercial areas would have significantly higher trace element concentrations than residential, recreational, and open space land-uses due to the greater potential for point sources of trace elements. We also expected pXRF measurements to be significantly affected by moisture, rock fragments, and OM as described in previous studies. Examining trace elements in urban forest soils is important for quantifying their ecosystem services and the potential impacts for human and terrestrial ecology.

2. Materials and methods

2.1. Location descriptions and sampling

Urban forest soils (N = 460 in total) were collected from three locations across southern New England: Hartford CT (N = 140), Lexington MA (N = 152), and Springfield MA (N = 168). The three town and cities are chosen because of their historical pollution legacy and varying levels of urbanization typical of the northeastern US. According to the Web Soil Survey, the soils of all 3 cities are predominantly classified as "Udorthents" and "Urban land". However many of these are unmapped and cannot be used with confidence as often the case in urban soil studies (Shuster et al., 2011). The town and cities are borderline humid continental (Dfa) to humid subtropical (Cfa) according to the Köppen climate types, with mean annual precipitation of approximately 1050 mm/yr and mean annual temperature of 10 °C. Summers are warm to hot (30 °C) with humidity while winters are cold (−7 °C) and can be bitter (−15 °C) with no dry season. Native forests are dominated by northern hardwoods of American beech (*Fagus grandifolia*), maple (*Acer* spp.), oak (*Quercus* spp.), birch (*Betula* spp.), pine (*Pinus* spp.), hickorys (*Carya* spp.), ash (*Fraxinus* spp.), poplar (*Populus* spp.), northern Catalpa (*Catalpa speciosa*), spruce (*Picea* spp.), and Eastern Hemlock (*Tsuga canadensis*), but are impacted by exotic and invasive trees such as tree of heaven (*Ailanthus altissima*), Norway maple (*Acer platanoides*) and black locust (*Robinia*).

European settlement of all three sites traces back to the mid seventeenth century. Springfield and Hartford are major urban centers in the region, with 2021 populations of 154,789 and 120,576, respectively and land areas of 45.01 km^2 and 82.54 km^2, respectively (US Census Bureau, 2019, US Census Bureau QuickFacts, 2019). Located in the suburbs of Boston and with a 2019 population of 34,071, Lexington provides a contrast to the two other locations, but with a land area of 42.55 km^2, it is similar in size to Hartford (US Census Bureau, 2019). Economic differences between the three locations are highlighted by the median household income between 2017 and 2021, which increase from Hartford CT at $37,477 per year to Springfield MA at $43,308 per year to the wealthy suburb of Lexington MA at $202,852 per year. Based on the US Forest Service data (Housman et al., 2023), we determined that the tree cover is 21.8% for Hartford, 33.0% Springfield, and 54.5% for Lexington.

Land-use denomination were acquired from the assessor database of each of the cities for the current year. For each sampling location, the Land-use code was extracted using the QGis 3.28 "extract attribute by location" algorithm. However, because land use codes are complex and often state- or city-specific, we simplified the codes into 7 main categories: i) single-family residential, ii) multi-family residential, iii) Commercial, iv) industrial, v) education, vi) land and parks (including vacant lots) and vii) all other or unknown land-uses. The attribution of these land-use denomination was subsequently ground-truthed visually using satellite imagery.

2.2. Soil sample processing

Following collection of the top 10 cm of soil by auger (described in the supplemental material), the mass of each soil sample at field moisture was determined using a digital scale. Immediately following this mass determination, the samples were placed in aluminum containers and were allowed to dry to a constant mass in a convection oven at a temperature between 40 °C and 50 °C. The polypropylene bags used to store the samples were also dried to prevent the samples from encountering residual moisture when transferred back into these bags. Next, the soil samples were sieved to 2 mm particle size. A mortar and pestle were used to break up soil aggregates as needed. Rock fragments, large (>2 mm diameter) organic materials such as roots, leaves, etc., and anthropogenic materials such as glass, plastic, etc. were all massed individually. Finally, a determination of the OM content of the soil samples was completed via loss on ignition (LOI) analyses. For the LOI procedure, aliquots of samples weighing between 8 g and 10 g were placed in ceramic crucibles, and were fired in a muffle furnace at 550 °C for at least 4 h. Once cool, the samples were massed again to determine the %OM that had been oxidized from samples.

2.3. pXRF analyses

The pXRF unit used in this study was a SciAps X-200 portable XRF analyzer (SciAps, Woburn, MA). This energy-dispersive pXRF uses a 6–40 kV, 200 μA Rh anode and a 6–50 kV, 200 μA Au anode excitation source and a solid state 20 mm^2 silicon drift detector with a resolution of 135 eV full width at half maximum height of the Mn Kα peak at 5.89 keV. Calibration curve is described in Supplemental Table 1.

All pXRF analyses were performed ex-situ. To isolate the effects that soil moisture, rock fragments, and OM have on pXRF analyses of trace elements in soil, the soil samples were measured in between each step of sample processing. For all measurements, the pXRF unit was held in its stand, and samples were placed directly on the detector window. For analyses of soils at field moisture, after drying, and after sieving, samples were measured four times each through polypropylene bags. To account for the heterogeneity of these soil samples, the position of the polypropylene bags on the detector window was adjusted between each measurement.

2.4. Soil digest and ICP-MS analysis

USEPA method 3050B was used to perform strong acid digestions to quantify pseudo-total concentrations of As, Cd, Cr, Cu, Pb and Zn (USEPA, 1996). While pXRF analysis determines total elemental concentrations, pseudo-total digestions have been used in a number of related studies for the purpose of comparing pXRF-perceived trace element concentrations to ICP-MS- or ICP-OES-perceived trace element concentrations (Al Maliki et al., 2017; Caporale et al., 2018; Killbride et al., 2006). Following the drying and sieving processes, 5 mL of aqua regia (AR) composed of a9:1 ratio of HNO_3 to HCl was added to each sample, sample containers were sealed and samples were heated on a hot plate at 70 °C for 1 h, after which they were diluted with deionized water to 50 mL. Between every twenty-five soil samples, a blank sample, a 0.100 ± 0.001 g sample of SRM 2709a, and a duplicated soil sample were included to identify any inconsistencies in ICP-MS performance. Before ICP-MS analysis, 2 mL aliquots of these diluted solutions were again diluted to a final volume of 15 mL. For quality assurance and quality control, the average values of the procedural blanks included in ICP-MS analyses of AR digests were as follows: 1.14 ng/g As, 0.02 ng/g Cd, 0.056 ng/g Cr, 0.28 ng/g Cu, 0.78 ng/g Pb, and 0.84 ng/g Zn. Also, the percent recoveries of SRM 2709a from AR digests were 114% for As, 110% for Cd, 80% for Cr, 103% for Cu, 73% for Pb, and 101% for Zn.

2.5. Data analyses and statistical tests

MATLAB ver. R2019b (Mathworks, Natick, MA, USA) was used to generate simple linear regressions between pXRF-perceived trace element concentrations of the soil samples and ICP-MS scans of the soil AR digests. MATLAB R2019b was also used to generate simple linear regressions between pXRF relative percent error (RPE) values and percent soil moisture, percent rock fragment, and percent OM. RPE values for pXRF measurements as calculated according to (2).

$$RPE = \frac{replicate\ standard\ deviation\ \left(\frac{mg}{kg}\right)}{average\ concentration\ \left(\frac{mg}{kg}\right)}\ x\ 100\% \tag{2}$$

Raw data from quadruplicate scans of soil samples with the SciAps X200 analyzer consisted of four concentrations for each of the six trace elements, as well an error value associated with each concentration and reported as 2 standard deviations. To identify outliers, the mean trace element concentration and the standard deviation for three of the four quadruplicate scans were calculated. Once all outliers were identified and eliminated, the remaining concentration values for each trace element from each set of scans were averaged. To calculate the error, the average of the error values produced by the pXRF (i.e. ±2 standard deviations for each individual measurement) was calculated.

To examine relationships among trace elements and soil properties, data were tested for normality, logarithmically transformed when necessary, and compared with Pearson linear regressions. Furthermore, relationships between trace element concentrations and soil properties were explored using a normalized principal component analysis. In the principal component analysis, data were normalized with their respective standard deviations to remove the weighted effect of data with larger numerical values.

Distribution maps of the metals concentrations determined by soil digests were generated using QGis 3.28. For each element, the gradient scale was set to reflect the Massachusetts CMR 310 regulatory limit for soils so that the deepest red colored points were above the limit (20 mg/kg for As, 10 mg/kg for Cd, 130 mg/kg for Cr, 300 mg/kg for Cu, 200 mg/kg for Pb and 500 mg/kg for Zn).

3. Results

3.1. Soil physicochemical and trace elements properties

3.1.1. Soil trace elements and physicochemical properties overall and among the town and cities

Under field conditions, the soils ranged from 1.4% to 186% gravimetric moisture content, with a median value of 16.3%. Soils were dried and sieved to <2 mm. The dried soils ranged from 0.0% rock fragments to 67% rock fragments by mass, with a median value of 5.5%. Mean rock fragments were not significantly different among the three locations. LOI was used to estimate %OM content of each sample. The soils ranged from 1.3% to 56.3% OM, with a median value of 9.1%. Lexington had significantly higher mean OM than Hartford and Springfield ($p < 0.05$; Table 1). The median soil pH across the cities was 4.3 and ranged from 6.5 to 2.0. Lexington had significantly lower mean soil pH than Springfield soil pH, which was significantly lower than Hartford soil pH ($p < 0.05$; Table 1). Lastly, mean strong acid extractable Fe concentrations were significantly higher for Hartford compared to Lexington and Springfield ($p < 0.05$; Table 1).

ICP-MS analyses of the urban forest soils for As, Cd, Cr, Cu, Pb, and Zn were conducted using USEPA Method 3050B for a pseudo-total digestion using reverse aqua regia, and yielded the following range and median concentrations: 0.5–58.5 mg/kg As with a median of 3.7 mg/kg, 0.04–3.7 mg/kg Cd with a median of 0.27 mg/kg, 3.55–117 mg/kg Cr with a median of 25.8 mg/kg, 4.13–271 mg/kg Cu with a median of 19.5 mg/kg, 5.8–1087 mg/kg Pb with a median of 59 mg/kg, and 8.6–1362 mg/kg Zn with a median of 60 mg/kg.

Using ICP-MS data, we observed that trace element concentrations in the urban forest soils exhibited some significant differences among the town and cities (Supplemental Fig. 2). Soil As concentrations were significantly higher for Springfield than Hartford and Lexington ($p < 0.05$; Table 1). Soil Cd, Cr, Cu, Pb, and Zn were significantly higher for Hartford than Springfield and Lexington ($p < 0.05$; Table 1).

3.1.2. Differences in soil trace elements and physicochemical properties among land use

Across the different land-uses, there were some significant differences in soil physicochemical properties. There were no significant differences in the rock fragments or %OM among the land-uses (Supplemental Table 2). Soil pH was significantly higher for urban forest soils in Multi-family residential areas (4.95 ± 0.13) than Park/Open lot (4.37 ± 0.15) and Other land-uses (4.28 ± 0.06) ($p < 0.05$). Moreover, urban forest soils in Commercial land-uses (4.95 ± 0.13) also had significantly higher soil pH than Park/Open lot soils (4.37 ± 0.15) ($p < 0.05$). There were no significant differences in soil Fe concentrations among the land-uses.

ICP-MS analyses of urban forest soils for As, Cd, Cr, Cu, Pb, and Zn revealed some significant differences among land-uses. Multi-family residences had significantly higher Pb and Zn than Education and Parks/Open lots land-uses ($p < 0.05$; Fig. 1). Soil Pb exceeded Massachusetts limitations for soils in samples collected from all land-uses except Education land-use. Commercial land-uses had significantly higher Cr than Education and Parks/Open lots land-uses ($p < 0.05$; Fig. 1). Soil Cr concentrations were well-below Massachusetts limitations for soil concentrations. Lastly, Multi-family residences and Commercial land-uses had significantly higher Cd than Education and Parks/Open lots land-uses ($p < 0.05$; Fig. 1). Fortunately, soil Cd concentrations were well

Table 1
Descriptive statistics for soils across the town and cities. Elemental concentrations were measured using ICP-MS.

		Rocks	OM	pH	Fe	As	Cd	Cr	Cu	Pb	Zn
		%	%		g/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Hartford	Mean	9.9	9.3	5.1	16.2	4.1	0.59	36.5	35	129	147
N = 140	Std Dev	11.0	4.2	0.8	5.7	5.8	0.56	16.5	31	142	178
	Min	0.0	3.3	3.2	2.5	0.8	0.06	10.7	5	14	12
	Q1	1.5	6.4	4.5	12.5	2.0	0.24	27.3	20	51	67
	Median	6.4	8.1	5.2	15.3	2.9	0.40	33.1	27	84	95
	Q3	14.2	10.8	5.8	18.9	4.1	0.70	40.2	36	143	156
	Max	64.1	30.8	6.5	41.0	58.5	3.70	117.2	271	1087	1362
Lexington	Mean	9.2	17.4	4.02	11.0	3.7	0.31	24.3	17	82	57
N = 152	Std Dev	10.6	13.2	0.70	4.8	5.4	0.24	13.7	12	89	39
	Min	0.0	1.4	2.90	1.7	0.5	0.06	3.6	4	6	9
	Q1	1.6	9.5	3.43	7.6	1.8	0.17	16.9	10	34	31
	Median	6.0	13.0	3.94	10.5	2.5	0.25	21.1	14	57	47
	Q3	13.7	20.8	4.46	13.5	4.0	0.35	28.1	21	96	72
	Max	67.0	75.3	6.10	26.8	51.1	1.47	106.8	127	630	234
Springfield	Mean	8.9	9.2	4.31	9.5	7.8	0.31	27.4	23	86	67
N = 168	Std Dev	10.5	7.2	0.78	3.4	6.6	0.31	15.7	29	121	70
	Min	0.0	1.3	1.97	3.0	1.8	0.04	8.5	4	6	16
	Q1	1.4	5.4	3.71	7.3	4.2	0.13	17.5	10	30	30
	Median	5.0	7.5	4.13	8.9	5.9	0.21	23.2	17	49	46
	Q3	13.5	10.1	4.86	11.0	9.0	0.35	32.2	25	94	72
	Max	56.4	54.4	6.41	23.1	49.1	1.77	110.4	261	861	504

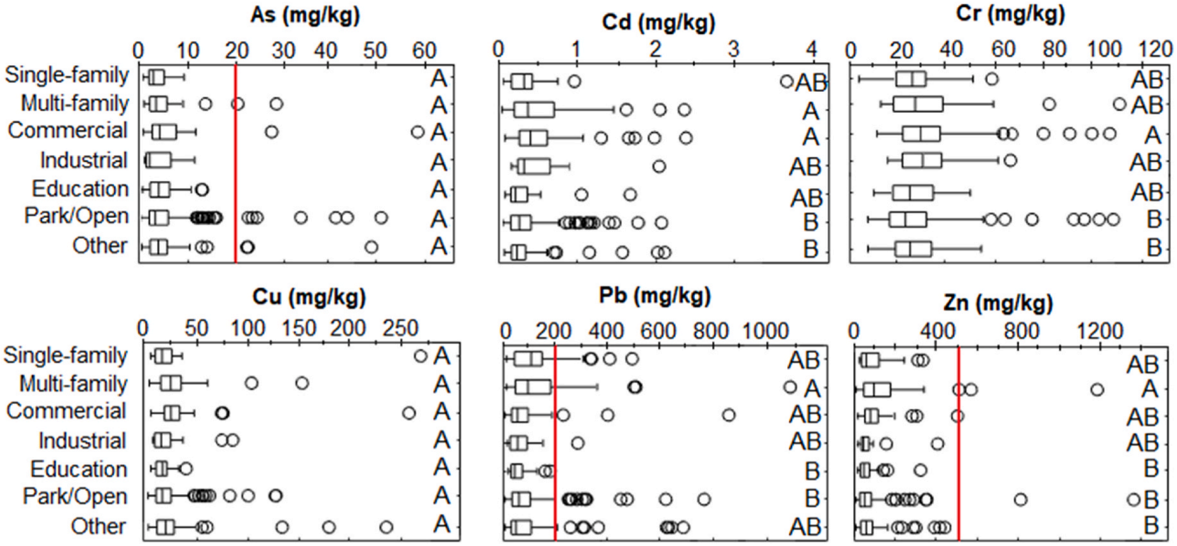


Fig. 1. Boxplot of trace element concentrations measured by ICP-MS among the seven land-uses studied pooled across the town and cities. Red lines indicate Massachusetts state upper concentration limits in soils. Letters indicate significant differences (p < 0.05) determined by one-way ANOVA.

below concentrations considered to pose a hazard to human health by Massachusetts. There were no significant differences for As and Cu among land-uses, but As exceeded concentrations considered to pose a hazard to human health by Massachusetts at two sites in Multi-family areas, two sites in Commercial areas, seven Park/Open lot areas, and three other land-uses. Soils Cu concentrations were well-below concentrations considered to pose a hazard to human health by Massachusetts.

Table 2
Matrix of Pearson's (R^2) correlation coefficient of soil ICP-MS trace elements and soil properties across all three cities together. (–) indicates positive or negative direction and bold indicates significant correlations at $p < 0.05$.

	As	Cd	Cr	Cu	Pb	Zn	SOM	pH	Fe
As	1.00	0.00	0.12	0.01	0.02	0.00	−0.00	−0.00	0.00
Cd		1.00	0.02	**0.35**	**0.21**	**0.32**	0.03	0.12	0.10
Cr			1.00	0.10	0.03	0.08	−0.01	0.06	0.18
Cu				1.00	0.18	0.19	0.00	0.07	0.12
Pb					1.00	**0.30**	0.00	0.02	0.04
Zn						1.00	0.00	0.17	0.12
SOM							1.00	−0.08	−0.01
pH								1.00	0.12
Fe									1.00

3.1.3. Relationship between soil digestible trace elements and physicochemical properties

We utilized Pearson's correlations to evaluate if soil physicochemical properties were enhancing the accumulation of ICP-MS measured trace elements in soils across the three locations (Table 2). We expected higher OM or higher soil pH to promote adsorption and retention of trace elements. Further, we utilized the nonsilicate Fe concentration as a proxy for Fe oxyhydroxides that can promote retention of trace elements. However, we did not observe any significant positive or negative correlations with OM, soil pH, or nonsilicate Fe. The only significant correlations we observed were among Cu, Cd, Pb, and Zn, suggesting a similar process driving their enrichment in soil.

We followed up our investigation of relationships among potentially toxic element concentrations and soil properties using principal component analysis (Supplemental Fig. 3). When combined, the PCA largely shows the same findings as the correlations: Cu, Cd, Pb, and Zn are clustered in the positive axis and As and Cr are in the negative axis for Principal Component 1, suggesting associations amongst those metals. OM, soil pH, and Fe were largely associated with variations in Principal Component 2 and only weakly associated with any trace element studied. PCA analysis for the individual cities show a slightly different pattern, with As, Cr, Fe, and soil pH being associated. Explanatory power among PC1 ranged from 24% up to 34% while PC2 ranged from 15% up to 20%, suggesting that much of the variability in the data cannot be explained by the variables considered in these analyses.

3.2. Trace element concentrations by pXRF

3.2.1. pXRF trace element concentrations across soil processing treatments

Soil processing was used to explore impacts of field moisture content, rock heterogeneity, and OM on pXRF-measured trace element concentrations. Soil processing increased median pXRF As concentrations to 39.4 mg/kg following drying, to 42.5 mg/kg following sieving, and 48.2 mg/kg following LOI (Table 3). Soil processing did not affect perceived pXRF Cd concentrations as median 9.8 mg/kg following drying, median 9.9 mg/kg following sieving and 10.0 mg/kg following LOI. Soil processing had an impact on Cr measurements as drying increased the median to 46.3 mg/kg, sieved soils had a median of 46.2 mg/kg, and LOI had a median of 59 mg/kg. Soil processing did not have a significant effect on pXRF Cu measurements. Soil processing had an impact on pXRF Pb measurements: dried soils had a median of 107 mg/kg, sieved soils had a median of 111 mg/kg, LOI had a median of 116 mg/kg. Soil processing affected perceived pXRF Zn concentrations: dried soils had a median of 122 mg/kg, sieved soils had a median of 126 mg/kg, LOI had a median of 127 mg/kg.

3.2.2. pXRF trace element relative percent error across soil processing treatments

Relative percent error (RPE) values for pXRF measurements were calculated via Eq (2). Overall, soil processing (drying, sieving, LOI) correlated with improvements in the pXRF measurements of As and Pb but small to no improvements the pXRF measurements of Cd, Cu, Cr, and Zn (Table 3). Soil processing decreased the mean instrument error (6–7 mg/kg to 3–4 mg/kg) and RPE (11–18% to 7–8%) of pXRF As measurements. Both Lexington and Springfield had RPE values decrease by half. Similarly, for Pb, soil processing also improved instrument error (13–17 mg/kg to 12–13 mg/kg) and RPE (9–15% to 6–9%) of pXRF Pb measurements. Lexington had pXRF Pb RPE values decrease by >50% and Springfield had pXRF Pb RPE decrease by a 30%. The pXRF measurements of Zn decreased the RPE from 7 to 8% to 5–6%, which are small but consistent improvements in RPE. Soil processing did not improve pXRF measurements of Cd, Cu, and Cr as instrument error and RPE values were similar before and after treatment.

3.2.3. Comparing pXRF and ICP-MS trace element analysis of urban forest soils

Results of pXRF analyses of As, Cd, Cr, Cu, Pb, and Zn in the soil samples at four different processing stages – field moist, dried, sieved, after LOI – were compared against ICP-MS values, and linear regressions were performed to assess pXRF measurement accuracy. Concentrations of As and Cd as perceived by pXRF showed minimal accuracy compared to ICP-MS results at all four soil processing stages, with R^2 values ranging from 0.03 to 0.04 for As, and from $0 < 0.01$ for Cd (Table 4). Slightly greater levels of accuracy were observed for Cr, with R^2 values ranging from 0.29 to 0.44 (Table 4). Much greater levels of accuracy were observed for Cu, Pb, and Zn at all processing stages where the R^2 values ranged from 0.78 to 0.87 for Cu, from 0.88 to 0.95 for Pb, and from 0.83 to 0.93 from Zn (Table 4).

To evaluate the efficacy of field-moist pXRF measurements of trace elements with respect to the standard ICP-MS based analysis, we utilized a focus on type 1 (false positive) and type 2 (false negative) errors as

Table 3

Summary of pXRF mean concentrations and instrument error and relative percent error (RPE) among the four replicate measurements for each soil under four conditions: field moist, after oven drying, after sieving to remove rock fragments, and after LOI to remove OM.

City		Mean values and mean instrument standard deviation				Relative percent error (RPE)			
		Field Moist	Oven drying	Sieved <2 mm	After LOI	Field Moist	Oven drying	Sieved <2 mm	After LOI
		mg/kg	mg/kg	mg/kg	mg/kg	%	%	%	%
As	Hartford	51 ± 6	52 ± 5	55 ± 5	53 ± 4	11	9	9	7
	Lexington	45 ± 7	58 ± 6	60 ± 6	54 ± 4	15	10	10	8
	Springfield	38 ± 7	40 ± 5	45 ± 5	42 ± 3	18	12	12	8
Cd	Hartford	10 ± 3	10 ± 4	10 ± 4	11 ± 4	34	36	36	35
	Lexington	10 ± 4	11 ± 4	11 ± 4	11 ± 4	39	37	35	35
	Springfield	10 ± 3	10 ± 3	10 ± 3	10 ± 3	36	33	32	35
Cr	Hartford	50 ± 4	55 ± 5	56 ± 5	70 ± 5	8	8	8	8
	Lexington	35 ± 3	41 ± 4	42 ± 4	53 ± 5	8	9	9	9
	Springfield	42 ± 4	48 ± 4	48 ± 4	61 ± 5	9	9	9	9
Cu	Hartford	68 ± 10	72 ± 9	75 ± 9	74 ± 9	15	12	13	12
	Lexington	49 ± 8	64 ± 9	64 ± 9	63 ± 9	16	15	14	15
	Springfield	56 ± 9	59 ± 9	64 ± 9	61 ± 9	15	15	15	14
Pb	Hartford	163 ± 14	190 ± 16	197 ± 16	201 ± 12	9	8	8	6
	Lexington	93 ± 13	148 ± 14	151 ± 13	164 ± 12	14	10	9	7
	Springfield	115 ± 17	128 ± 14	141 ± 14	140 ± 13	15	11	10	9
Zn	Hartford	180 ± 12	195 ± 12	193 ± 11	190 ± 9	7	6	6	5
	Lexington	102 ± 7	138 ± 11	141 ± 10	141 ± 9	7	8	7	6
	Springfield	118 ± 9	128 ± 10	133 ± 10	133 ± 8	8	8	7	6

Table 4
Summary of the R^2 values associated with the linear regressions between ICP-MS measurements and pXRF measurements performed on soils at field moisture, after drying, after sieving, and after LOI analysis.

	Field Moist		Oven Dry		Sieved <2 mm		After LOI	
	R^2	m	R^2	m	R^2	m	R^2	m
As	0.02	0.85	0.03	0.92	0.04	1.12	0.03	0.85
Cd	0.00	0.36	0.01	0.87	0.01	0.52	0.00	0.32
Cr	0.29	0.34	0.35	0.41	0.37	0.42	0.44	0.61
Cu	0.87	1.06	0.83	1.16	0.84	1.25	0.78	1.17
Pb	0.88	0.98	0.95	1.35	0.94	1.37	0.94	1.49
Zn	0.93	0.74	0.87	0.84	0.83	0.84	0.86	0.99

opposed to a simple regression-based analysis. Here, we examined the propensity of field moist pXRF measurements to generate type 1 and type 2 errors to show if the limitations in accuracy and precision leaned toward conservative overestimates or hazard-generating underestimates (Fig. 2). Arsenic field moist pXRF measurements had very low correlation with ICP-MS of R^2 of only <0.02 (Table 4). Despite the low correlation, pXRF As measurements generated 0% type 2 errors of false negatives but unfortunately generated 70% type 1 errors of false positives. Cadmium field moist pXRF measurements had very low correlation with ICP-MS of R^2 of only <0.02 (Table 4). Accordingly, pXRF Cd measurements had 0% type 2 errors of false negatives but unfortunately generated 30% type 1 errors of false positives due to the overestimation. Chromium field moist pXRF measurements had a weak correlation with ICP-MS of R^2 of only 0.29 and a slope of 0.34 (Table 4). However, pXRF Cr measurements were as effective as ICP-MS analyses as they generated 0% type 1 and 2 errors. Copper field moist pXRF measurements had a very strong correlation with ICP-MS of R^2 of 0.87 and a slope of 1.06 (Table 4) and generated 0% type 1 error and type 2 errors. Next, Pb field moist pXRF measurements had a very strong correlation with ICP-MS of R^2 of 0.88 and a slope of 0.98 (Table 4) and generated 5.8% type 1 error and only 0.4% type 2 errors of false negatives. Lastly, Zn field moist pXRF measurements had a very strong correlation with ICP-MS of R^2 of 0.93 and a slope of 0.74 (Table 4) and only generated 0.4% type 1 error and 0.4% type 2 errors of false negatives.

4. Discussion

4.1. Urban forest soil trace elements

Our first objective was to evaluate trace elements in urban forest soils across Hartford CT, Lexington MA, and Springfield MA as well as across land-uses. Urban forest soils in all three cities had outliers in soil As and Zn concentrations that exceeded Massachusetts 310 CMR 40.00 Reporting Category for Soil (RCS)-1 as well as WHO/FAO (2001) regulatory values, but mean and median concentrations were below the regulatory values. Soil As pollution is typically limited to point source releases such as pesticides, wood preservatives, or historical industries like leather tanning, but diffuse emissions from burning fuels may also occur (Patel et al., 2023). Although there were no spatial patterns in hazardous As concentrations in urban forest soils for Hartford and Lexington, there were more outliers and centralized distribution in Springfield MA (Fig. 3). Springfield MA has been home to many industrial activities from weapons manufacturing (e.g. Smith and Wesson Brands, Inc. an American firearm manufacturer), vehicle production (e.g. Indian Motorcycle Manufacturing Company), cement production, and other industries. Urban forest soil As was not associated with any particular land-use due to three potential scenarios. First, diffuse

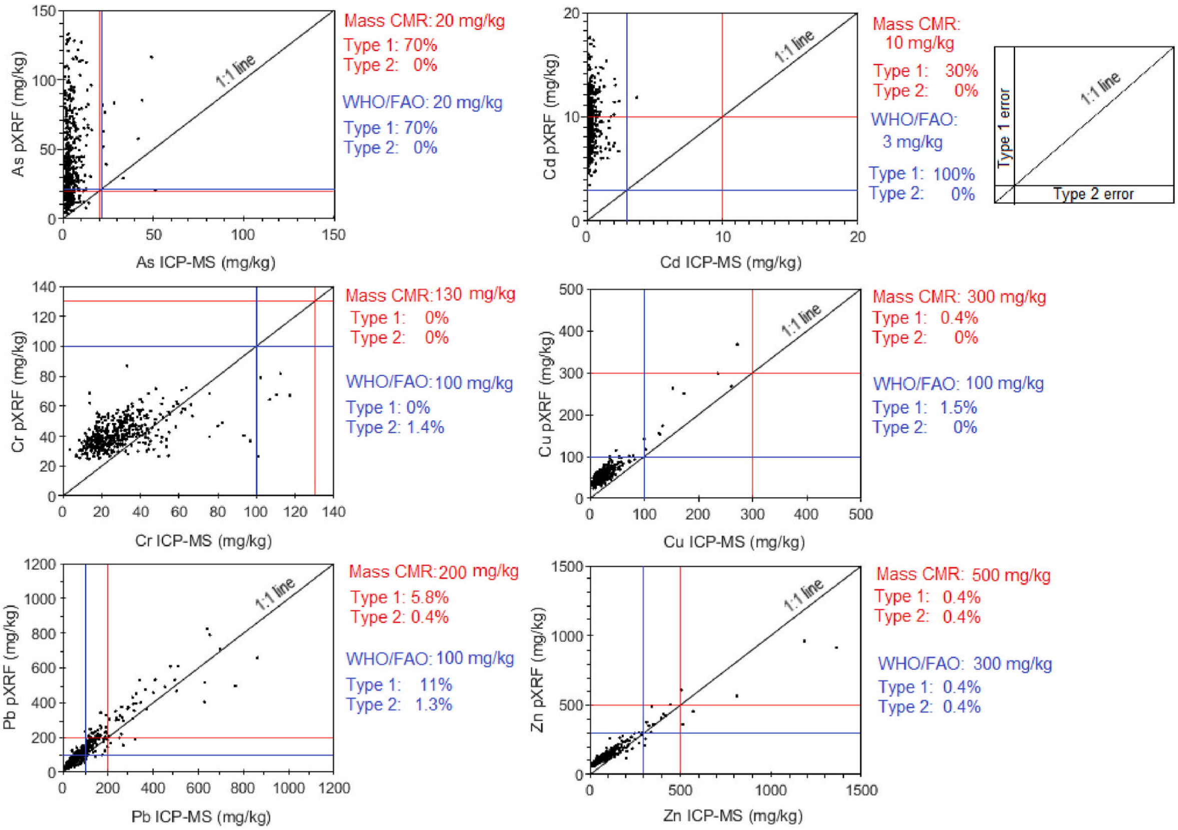


Fig. 2. Concentrations of As, Cd, Cr, Cu, Pb, and Zn in soil samples as measured by ICP-MS and by pXRF. Percentages of Type 1 and Type 2 errors are shown, in addition to results of linear regressions, and a 1:1 line as a reference. Red lines (Mass CMR) correspond to the Massachusetts regulation 310 CMR 40.00 Reporting Category for Soil (RCS)-1 and blue lines correspond with WHO/FAO permissible soil limits and the percent value the fraction of samples providing a false positive (type 1) or false negative (type 2) error.

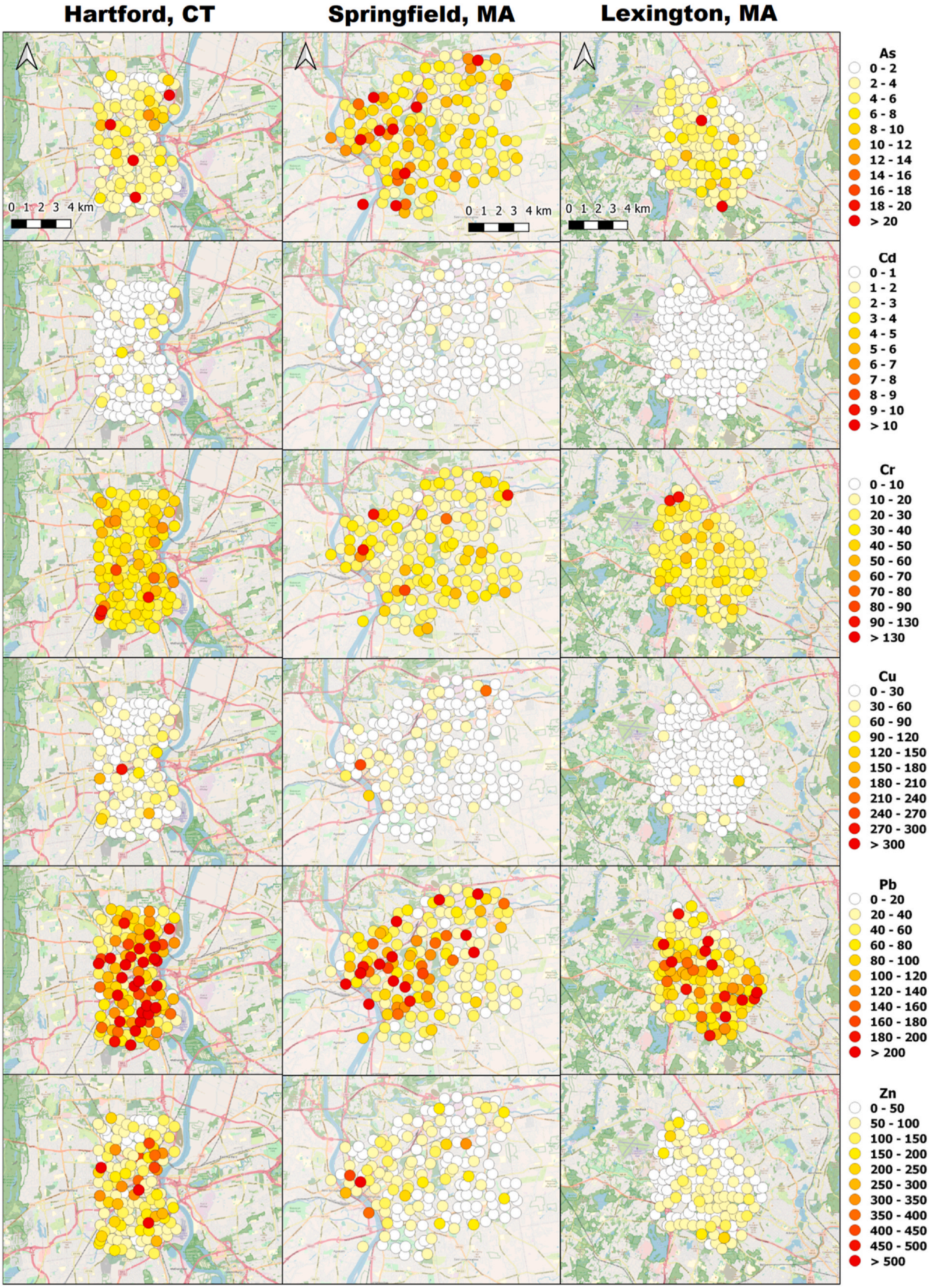


Fig. 3. Distribution map of As, Cd, Cr, Cu, Pb, and Zn concentrations measured by ICP-MS across the three cities. The upper category (indicated by deep red) corresponds with the Massachusetts 310 CMR 40.00 RCS-1 regulatory limit for soil.

enrichment in soils is not linked to specific urban land use patterns. Second, current As distribution is masked by shifts in historical land-uses. Lastly, the elevated As concentrations of rocks across New England have been documented (Ayotte et al., 2003; Richardson et al., 2023) and glaciofluvial movement of the material may have enhanced As in soil regionally. Urban forest soils Zn was significantly higher for multi-family housing than areas with low human population density, such as school areas (Education) and Parks/Open Lots. This implies that Zn-enrichment of soils may be linked to domestic human activities, such as building materials, cars, and other non-point sources, which agrees with excessive Zn in stormwater runoff from buildings and automobiles (Davis et al., 2001; Richardson et al., 2015).

One of the most important findings from this study is how widely distributed Pb pollution is across the three cities. Urban forest soils Pb had 42 of the 460 sites exceeding Massachusetts 310 CMR 40.00 RCS-1 regulatory value of 200 mg/kg and WHO/FAO (2001) permissible limits for soil of 100 mg/kg. Urban forest soil Pb pollution can be due to industrial activities, paint, building materials, and leaded-gasoline combustion (Markus and McBratney, 2001; Richardson et al., 2014), which is supported by the significant correlations of Pb with Cd and Zn but lack of correlation of Pb with soil properties. Similar to Zn, urban forest soils Pb was significantly higher for multi-family housing than areas with low human population density, such as school areas (Education) and Parks/Open Lots, implying domestic human activities can enrich Pb, such as degradation of building materials particularly leaded paint and other domestic non-point sources (e.g. Mielke and Reagan, 1998; Dignam et al., 2019; Wade et al., 2021).

Spatially, urban forest soil Pb was centered in the most developed areas of Springfield, implying historical land-use legacy effects (Fig. 3). Surprisingly, the non-metropolitan area of Lexington also had several exceedances of soil Pb (Fig. 3), potentially due to historical leaded-gasoline emissions or point-source industrial activities despite its current status as an affluent Boston suburb. There are some important notes about higher urban forest soil Pb in multi-family but not single-family residential areas. This may imply that higher number of people, including children, may be exposed to Pb, particularly those in lower socio-economic positions (Mielke and Reagan, 1998). Unfortunately, the association of higher soil Pb with higher urban density, lower socio-economic individuals, and children of color has been well-documented (e.g. Brown and Longoria, 2010; Aelion et al., 2013).

Urban forest soil mean, median, and Q3 quartile Cu, and Cr concentrations were well-below Massachusetts 310 CMR 40.00 RCS-1 regulations and WHO/FAO permissible levels. Urban forest soil Cd concentrations exceed both state and international regulations. The location of urban forest soils with higher Cd, Cu, and Cr concentrations did not appear to be driven by soil pedogenesis. Soil physicochemical properties commonly associated with Cd, Cu, and Cr retention (SOM, pH, nonsilicate Fe) were poorly associated with their concentrations. This suggests that geogenic and pedogenic processes are unlikely driving trace element accumulation in these urban forest soils. Instead, Cu and Cr sources appear driven by point-source industrial pollution and non-point source vehicle pollution (Richardson et al., 2015; Chrysochoou et al., 2016; Ballabio et al., 2018). Although Ballabio et al. (2018) show that spatial variation of Cu is largely tied to agricultural practices, the soils studied are forested and unlikely to be receiving agriculturally sourced Cu. Urban forest soil Cd and Cr were both significantly higher in Commercial land-uses than Park/Open lots and other land-uses. Since Commercial land-uses are largely retail spaces as opposed to manufacturing, the elevated soil Cd and Cr may reflect high vehicle traffic compared with low vehicles traveling in recreational parks and open undeveloped lots. Urban forest soil Cu was not significantly different among land-uses, which suggests a diffuse source of Cu such as vehicles (Gunawardena et al., 2015) or potential parent material and geologic effects influence Cu as opposed to human sources (Ballabio et al., 2018).

4.2. Accuracy of pXRF analyses compared to ICP-MS

Our second objective was to investigate if pXRF and traditional digestion and ICP-MS analysis yielded comparable assessments of trace elements in urban forest soils. PXRF measurements of Cu, Pb, and Zn were comparable to ICP-MS measurements performed on AR digests (Fig. 3), which is evidenced by the consistently high R^2 values (R^2 ranged from 0.88 to 0.95) and slopes close to 1.0 (Table 4). Moreover, there were low rates of type 1 errors (<8%) and type 2 errors (<1%). These findings support that pXRF may be an effective tool for rapid Cu, Pb, and Zn assessment. However, our results also demonstrated that pXRF measurements of As, Cd, and Cr concentrations were not comparable to ICP-MS measurements performed on AR digests of the same soil samples. This is evidenced by the low R^2 values associated with the linear regressions of As, Cd, and Cr concentrations as perceived by pXRF and by ICP-MS, indicating a low level of agreement between measurements of these trace elements from the two instruments (Fig. 3). pXRF As measurements had unacceptable high rates of type 1 errors (70%). pXRF Cd and Cr measurements had 0% type 1 and type 2 errors, implying their potential ability to be screened by pXRF. However, we did not have any soils with Cd or Cr concentrations that approached or exceeded levels considered to be hazardous to human health and thus did not have the opportunity for type 2 errors. These findings support that pXRF may be an effective tool for rapid Cu, Pb, and Zn assessment as reported by many previous studies such as Wu et al. (2012), Paulette et al. (2015), and Caporale et al. (2018). pXRF may potentially serve as a screening tool for Cd and Cr particularly with additional sample process (e.g. Mejía-Piña et al., 2016) or post-measurement corrections (as done by Ravansari et al. 2018). However, pXRF should not be used for qualitative or quantitative As measurements as the chances for Type 1 error of false positives at 70% rate is too inaccurate. In general, the pXRF-perceived concentrations of these six trace elements were overestimating concentrations reported by ICP-MS analyses, as shown by the linear regression lines above the 1:1 lines (Table 4) and has been reported by previous studies (Caporale et al., 2018; Killbride et al., 2006; Borges et al., 2020).

4.3. Influences of moisture, OM, and rocks fragments, on pXRF accuracy

For our last objective, the influence of soil moisture, %OM, and rock fragments content on the accuracy of pXRF measurements was seen in the change of R^2 values from measurements performed on samples at field moisture compared to measurements performed on dried samples (Table 4). Measurement accuracies increased for Cr and Pb, decreased for Cu and Zn, and were essentially unchanged for As and Cd (Table 4). There was no apparent trend relating varying levels of gravimetric moisture content and %OM to RPE for any of the six trace elements, as evidenced by the exceptionally low R^2 values associated with the linear regressions between gravimetric moisture content and percent relative error (Table 4). Increased soil moisture content tends to exponentially reduce the pXRF-perceived concentrations of trace elements (Kalnicky and Singhvi, 2001; Ge et al., 2005; Schneider et al., 2016). Moreover, we had expected increases in OM would decrease pXRF trace element concentrations from interferences by lighter elements (Kalnicky and Singhvi, 2001; Ravansari et al. 2018). Therefore, our third hypothesis of measurement improvement was supported for measurements of Cr and Pb, which displayed increased measurement accuracies with the removal of soil moisture and %OM, although R^2 values for Cr were low for measurements on field moist and dried samples. Our third hypothesis was not supported for the accuracy of measurements of As, Cd, Cu, and Zn, which did not display significant increases in measurement accuracy with the removal of soil moisture.

5. Conclusions and recommendations for pXRF trace element analyses

Our findings show that urban forest soils have extensive Pb accumulations while As and Zn had reached hazardous concentrations only occur in isolated hot spots. Urban soils have sequestered Cd, Cr, and Cu but not to hazardous concentrations. Geogenic and pedogenic processes do not appear to be driving the variability of trace elements within the three locations due to limited correlations with OM, pH, and nonsilicate Fe. Instead, the individual site history and modern land-uses likely hold the key to predicting urban forest soil As, Pb, and Zn concentrations. We did not observe strong spatial relationships between land-use and As, Pb, and Zn concentrations. The elevated soil Pb concentrations in multi-family land-uses is of concern due to the higher density of people and historically higher minority and lower socioeconomic populations that are underserved by U.S. and state policies.

Based on the results of this study, it is recommended that in-situ pXRF measurements of Cu, Pb, and Zn can be considered accurate when measurements are performed on soils with gravimetric moisture contents of up to 187%, rock fragment contents of up to 67% by mass, and OM contents of up to 45% by mass. Urban forest soil pXRF measurements of As should not be considered quantitative but Cr and Cd may be screened by pXRF but will require secondary verification.

CRediT author statement

Eric C. Sirkovich: Conceptualization, Methodology, Investigation, Writing – Original Draft, Writing – Review and Editing, Data Visualization. Nicolas Perdrial: Methodology, Conceptualization, Writing – Original Draft, Writing – Review and Editing. Sandra Walser: Methodology, Conceptualization, Writing – Review and Editing. Justin B. Richardson: Conceptualization, Methodology, Supervision, Project Administration, Investigation, Writing – Original Draft, Data Visualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

Data availability

Data uploaded to urban soil pollution mapping institute website.

Acknowledgements

We are thankful for those who granted permission to study and collect soil samples in their urban forests. This research was supported by the USDA-NRCS Grant # NR193A750023C007 with funding to Dr. Justin Richardson at the University of Massachusetts Amherst and Dr. Nicolas Perdrial at the University of Vermont.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2023.122441.

References

Aelion, C.M., Davis, H.T., Lawson, A.B., Cai, B., McDermott, S., 2013. Associations between soil lead concentrations and populations by race/ethnicity and income-to-poverty ratio in urban and rural areas. Environ. Geochem. Health 35, 1–12.

Airola, T.M., Buchholz, K., 1984. Species structure and soil characteristics of five urban forest sites along the New Jersey Palisades. Urban Ecol. 8 (1–2), 149–164.

Al Maliki, A., Al-lami, A.K., Hussain, H.M., Al-Ansari, N., 2017. Comparison between inductively coupled plasma and X-ray fluorescence performance for Pb analysis in environmental soils. Environ. Earth Sci. 76, 433.

Argyraki, A., Ramsey, M.H., Potts, P.J., 1997. Evaluation of portable X-ray fluorescence instrumentation for in situ measurements of lead on contaminated land. Analyst 122, 743–749.

Ayotte, J.D., Montgomery, D.L., Flanagan, S.M., Robinson, K.W., 2003. Arsenic in groundwater in eastern New England: occurrence, controls, and human health implications. Environ. Sci. Technol. 37 (10), 2075–2083.

Ballabio, C., Panagos, P., Lugato, E., Huang, J.H., Orgiazzi, A., Jones, A., Fernández-Ugalde, O., Borrelli, P., Montanarella, L., 2018. Copper distribution in European topsoils: an assessment based on LUCAS soil survey. Sci. Total Environ. 636, 282–298.

Borges, C.S., Weindorf, D.C., Nascimento, D.C., Curi, N., Guilherme, L.R.G., Carvalho, G. S., Ribeiro, B.T., 2020. Comparison of portable X-ray fluorescence spectrometry and laboratory-based methods to assess the soil elemental composition: applications for wetland soils. Environ. Technol. Innovat. 19, 100826.

Bower, J.A., Lister, S., Hazebrouck, G., Perdrial, N., 2017. Geospatial evaluation of lead bioaccessibility and distribution for site-specific prediction of threshold limit. Environ. Pollut. 229, 290–299.

Brown, R.W., Longoria, T., 2010. Multiple risk factors for lead poisoning in Hispanic sub-populations: a review. J. Immigr. Minority Health 12, 715–725.

Caporale, A.G., Adamo, P., Capozzi, F., Langella, G., Terribile, F., Vingiani, S., 2018. Monitoring metal pollution in soils using portable-XRF and conventional laboratory-based techniques: evaluation of the performance and limitations according to metal properties and sources. Sci. Total Environ. 643, 516–526.

Chrysochoou, M., Theologou, E., Bompoti, N., Dermatas, D., Panagiotakis, I., 2016. Occurrence, origin and transformation processes of geogenic chromium in soils and sediments. Curr. Pollut. Rep. 2, 224–235.

Clark, J.J., Knudsen, A.C., 2013. Extent, characterization, and sources of soil lead contamination in small-urban residential neighborhoods. J. Environ. Qual. 42 (5), 1498–1506.

Davis, A.P., Shokouhian, M., Ni, S., 2001. Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. Chemosphere 44 (5), 997–1009.

de Lima, T.M., Weindorf, D.C., Curi, N., Guilherme, L.R.G., Lana, R.M.Q., Ribeiro, B.T., 2019. Elemental analysis of Cerrado agricultural soils via portable X-ray fluorescence spectrometry: inferences for soil fertility assessment. Geoderma 353, 264–272.

Dignam, T., Kaufmann, R.B., LeStourgeon, L., Brown, M.J., 2019. Control of lead sources in the United States, 1970-2017: public health progress and current challenges to eliminating lead exposure. J. Publ. Health Manag. Pract. 25 (Suppl. 1 LEAD POISONING PREVENTION), S13.

Escobedo, F.J., Kroeger, T., Wagner, J.E., 2011. Urban forests and pollution mitigation: analyzing ecosystem services and disservices. Environ. Pollut. 159 (8–9), 2078–2087.

FAO/WHO, 2001. Food Additives and Contaminants. Joint Codex Alimentarius Commission, vol. 34. FAO/WHO Food standards Program, pp. 745–750.

Ge, L., Lai, W., Lin, Y., 2005. Influence of and correction for moisture in rocks, soils, and sediments on in situ XRF analysis. X Ray Spectrom. 34, 28–34.

Gunawardena, J., Ziyath, A.M., Egodawatta, P., Ayoko, G.A., Goonetilleke, A., 2015. Sources and transport pathways of common heavy metals to urban road surfaces. Ecol. Eng. 77, 98–102.

Housman, I., Heyer, J., Ruefenacht, B., Schleeweis, K., Bogle, M., Megown, K., 2023. National Land Cover Database Tree Canopy Cover Methods V2021-4. U.S. Department of Agriculture, Forest Service, Geospatial Technology and Applications Center, Salt Lake City, UT.

Kalnicky, D.J., Singhvi, R., 2001. Field portable XRF analysis of environmental samples. J. Hazard Mater. 83, 93–122.

Killbride, C., Poole, J., Hutchings, T.R., 2006. A comparison of Cu, Pb, As, Cd, Zn, Fe, Ni and Mn determined by acid extraction/ICP-OES and ex situ field portable X-ray fluorescence analyses. Environ. Pollut. 143, 16–23.

Kubier, A., Wilkin, R.T., Pichler, T., 2019. Cadmium in soils and groundwater: a review. Appl. Geochem. 108, 104388.

Markus, J., McBratney, A.B., 2001. A review of the contamination of soil with lead: II. Spatial distribution and risk assessment of soil lead. Environ. Int. 27 (5), 399–411.

Mejía-Piña, K.G., Huerta-Diaz, M.A., González-Yajimovich, O., 2016. Calibration of handheld X-ray fluorescence (XRF) equipment for optimum determination of elemental concentrations in sediment samples. Talanta 161, 359–367.

Mielke, H.W., Reagan, P.L., 1998. Soil is an important pathway of human lead exposure. Environ. Health Perspect. 106 (Suppl. 1), 217–229.

Parsons, C., Grabulosa, E.M., Pili, E., Floor, G.H., Roman-Ross, G., Charlet, L., 2013. Quantification of trace arsenic in soils by field-portable X-ray fluorescence spectrometry: considerations for sample preparation and measurement conditions. J. Hazard Mater. 262, 1213–1222.

Patel, K.S., Pandey, P.K., Martín-Ramos, P., Corns, W.T., Varol, S., Bhattacharya, P., Zhu, Y., 2023. A review on arsenic in the environment: contamination, mobility, sources, and exposure. RSC Adv. 13 (13), 8803–8821.

Paulette, L., Man, T., Weindorf, D.C., Person, T., 2015. Rapid assessment of soil and contaminant variability via portable x-ray fluorescence spectroscopy: Copşa Mică, Romania. Geoderma 243–244, 130–140.

Pecina, V., Brtnický, M., Baltazár, T., Juřička, D., Kynický, J., Galiová, M.V., 2021. Human health and ecological risk assessment of trace elements in urban soils of 101 cities in China: a meta-analysis. Chemosphere 267, 129215.

Potts, P.J., West, M., 2008. Portable X-Ray Fluorescence Spectrometry. Capabilities in In-Situ Analysis. RSC Publishing, Cambridge.

Radu, T., Diamond, D., 2009. Comparison of soil pollution concentrations determined using AAS and portable XRF techniques. J. Hazard Mater. 171, 1168–1171.

Ravansari, R., Lemke, L.D., 2018. Portable X-ray fluorescence trace metal measurement in organic rich soils: pXRF response as a function of organic matter fraction. Geoderma 319, 175–184.

Ravansari, R., Wilson, S.C., Tighe, M., 2020. Portable X-ray fluorescence for environmental assessment of soils: Not just a point and shoot method. Environ. Int. 134, 105250.

Richardson, J.B., 2020. Urban forests near municipal solid waste incinerators do not show elevated trace metal or rare earth element concentrations across three cities in the northeast USA. Environ. Sci. Pollut. Control Ser. 27, 21790–21803.

Richardson, J.B., 2021. Comparing trace elements (As, Cu, Ni, Pb, and Zn) in soils and surface waters among Montane, Upland Watersheds and Lowland, urban Watersheds in new England, USA. Water 13 (1), 59.

Richardson, J.B., Donaldson, E.C., Kaste, J.M., Friedland, A.J., 2015. Forest floor lead, copper and zinc concentrations across the northeastern United States: Synthesizing spatial and temporal responses. Sci. Total Environ. 505, 851–859.

Richardson, J.B., Friedland, A.J., Kaste, J.M., Jackson, B.P., 2014. Forest floor lead changes from 1980 to 2011 and subsequent accumulation in the mineral soil across the northeastern United States. J. Environ. Qual. 43 (3), 926–935.

Richardson, J.B., Thrasher, S.A., Saccardi, B., Clark, E.V., 2023. Sulfidic schist release of As, Cu, and Pb in laboratory experiments and across eleven watersheds in central Massachusetts, USA. Environ. Geochem. Health 1–19.

Schneider, A.R., Cancès, B., Breton, C., Ponthieu, M., Morvan, X., Conreux, A., Martin, B., 2016. Comparison of field portable XRF and aqua regia/ICPAES soil analysis and evaluation of soil moisture influence on FPXRF results. J. Soils Sediments 16, 438–448.

Shuster, W.D., Barkasi, A., Clark, P., Dadio, S., Drohan, P., Furio, B., Gerber, T., Houser, T., Kelty, A., Losco, R., Reinbold, K., 2011. Moving beyond the Udorthent—a proposed protocol for assessing urban soils to service data needs for contemporary urban ecosystem management. Soil Surv. Horiz. 52 (1), 1–8.

US Census Bureau, 2019. QuickFacts: Lexington town, Middlesex County, Massachusetts; Massachusetts. Census Bureau Quickfacts. Available at: https://www.census.gov/quickfacts/fact/table/lexingtontownmiddlesexcountymassachusetts,MA/PST045219. Accessed 30 April 2021.

US Census Bureau QuickFacts, 2019. Springfield city, Massachusetts; Hartford city, Connecticut. Census Bureau Quickfacts. Available at: https://www.census.gov/quickfacts/fact/table/springfieldcitymassachusetts,hartfordcityconnecticut/PST045219. Accessed 30 April 2021.

USEPA (United States Environmental Protection Agency), 1996. Method 3050B. Acid Digestion of Sediments, Sludges, and Soils. Revision 2. December 1996, Washington D.C.

USEPA (United States Environmental Protection Agency), 2007. Method 6200. Field Portable X-ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soils and Sediment. Revision 0. February 2007, Washington D.C.

Wade, A.M., Richter, D.D., Craft, C.B., Bao, N.Y., Heine, P.R., Osteen, M.C., Tan, K.G., 2021. Urban-soil pedogenesis drives contrasting legacies of lead from paint and gasoline in city soil. Environ. Sci. Technol. 55 (12), 7981–7989.

Walser, S.L., Sirkovich, E.C., Richardson, J.B., McStay, A.E., Perdrial, N., 2023. X Ray Spectrom. 52 (2), 72. https://doi.org/10.1002/xrs.3321.

Wang, X.S., Qin, Y., Sang, S.X., 2005. Accumulation and sources of heavy metals in urban topsoils: a case study from the city of Xuzhou, China. Environ. Geol. 48 (1), 101–107.

Wang, P., Zheng, H., Ren, Z., Zhang, D., Zhai, C., Mao, Z., Tang, Z., He, X., 2018. Effects of urbanization, soil property and vegetation configuration on soil infiltration of urban forest in Changchun, Northeast China. Chin. Geogr. Sci. 28, 482–494.

Weindorf, D.C., Chakraborty, S., 2016. Portable X-Ray Fluorescence Spectrometry Analysis of Soils, vol. 84. Soil Science Society of America, pp. 1384–1392.

Wu, C.M., Tsai, H.T., Yang, K.H., Wen, J.C., 2012. How reliable is X-ray fluorescence (XRF) measurement for different metals in soil contamination? Environ. Forensics 13 (2), 110–121.