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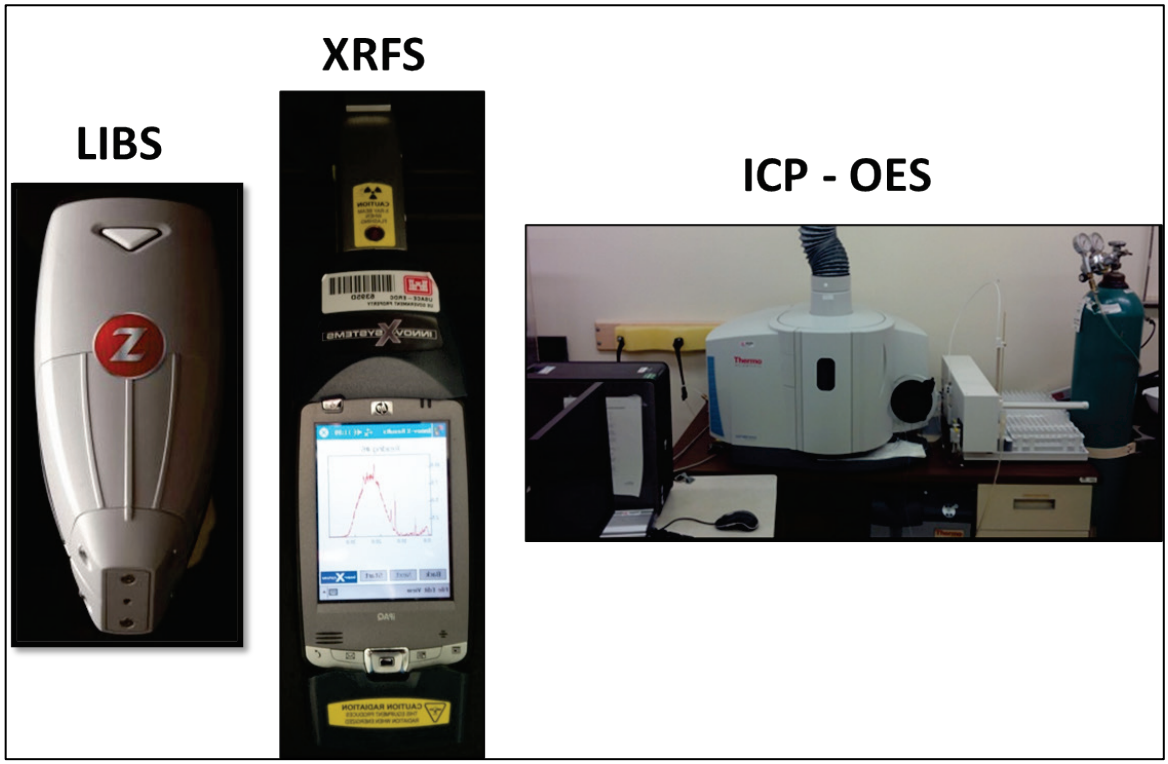




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# Comparison of the Quantitation of Heavy Metals in Soil Using Handheld LIBS, XRFS, and ICP-OES

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# Abstract

Handheld laser-induced breakdown spectroscopy (LIBS) is an emerging analytical technique that shows the potential to replace X-ray fluorescence spectroscopy (XRFS) in the field characterization of soils containing heavy metals. This study explored the accuracy and precision of handheld LIBS for analyzing soils containing copper and zinc to support LIBS as a replacement for XRFS technology in situ. Success was defined by handheld LIBS results that could be replicated across field analyzers and verified by inductively coupled plasma–optical emission spectrometry (ICP-OES). A total of 108 soil samples from eight military installations were pressed into 13 mm pellets and then analyzed by XRFS and LIBS. Handheld LIBS has a spot-size area 100-fold smaller than that of XRFS, and though it provided accurate measurements for NIST-certified reference materials, it was not able to measure unknown soils of varying soil texture with high particle size variability, regardless of sample size. Thus, soil sample particle size heterogeneity hindered the ability to provide accurate results and replicate quantitation results across LIBS and XRFS. Increasing the number of particles encountered by each shot through particle size reduction improved both field-analyzer correlation and the correlation between handheld LIBS and ICP-OES from weak (<15%) to strong (>80%).

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# Preface

This study was conducted for the Naval Information Warfare Center Pacific under "NESKI LIBS Sustainability Development," MIPR N6600121MP00641.

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# 1 Introduction

## 1.1 Background

Military training has introduced heavy metals into natural soil at military firing ranges across the United States. Heavy metal accumulation in the soil can harm ecosystem populations that are exposed to toxic levels and can lead to groundwater contamination when mobilized (Heath et al. 1991; Harmon et al. 2020; Warren et al. 2007; Grigalaviciene et al. 2005). Soil restoration efforts begin with the detection and identification of metal in soil—a process that is made possible by taking advantage of electron transitions. Each element emits various wavelengths of light in a unique way upon excitement from an external energy source, which can be captured through their emission spectra (Chirinos et al. 2014; Ararat-Ibarguen et al. 2014; Radbound University 2022). It is in the intensity of this light that concentration can be determined (Radbound University 2022; SciAps, pers. comm., 2021). Three techniques were designed to capture this phenomenon in a soil sample and to lead to the identification and quantification of an unknown metal: inductively coupled plasma–optical emission spectroscopy (ICP-OES), X-ray fluorescence spectroscopy (XRFS), and laser-induced breakdown spectroscopy (LIBS; Russo 1995; Chirinos et al. 2014).

ICP-OES is a conventional chemical analysis technique that has been used in laboratories since 1974 (Radbound University 2022). This technique uses energy in the form of argon plasma to measure the concentration of elements in a sample (Fichet et al. 2006; Wheal et al. 2011). ICP-OES detects light energy that ranges from 160 to 800 nm* and is emitted from elements and then quantifies the sample's chemical composition in two to six minutes (Tyler and Yvon 1995). ICP-OES and ICP-mass spectrometry (ICP-MS) are often the preferred analytical methods because they provide accurate, reliable results with low detection limits (i.e., in parts per trillion; Merson and Evans 2003; Tyler and Yvon 1995). Though these apparatuses provide effective sample analyses, they are not field-portable. Ex situ sampling and analysis typically require increased time and costs for

* For a full list of the spelled-out forms of the units of measure used in this document and their conversions, please refer to *US Government Publishing Office Style Manual*, 31st ed. (Washington, DC: US Government Publishing Office, 2016), 245–252, https://www.govinfo.gov/content/pkg/GPO-STYLEMANUAL-2016/pdf/GPO-STYLEMANUAL-2016.pdf.

sample collection, shipping, processing, and analysis. In addition, ex situ approaches do not allow for timely generation of data, limiting the flexibility of adjusting the sampling plan based on field observations.

Handheld XRFS became commercially available in 1982 but did not breakthrough until 2001, when X-ray tubes replaced radioisotope excitation (Brand 2015). X-rays are only generated when analyzing the sample; thus, the new generation of XRFS instruments pose a lesser radiation hazard than prior models. The X-250 handheld XRF (X-ray fluorescence) analyzer (SciAps, Woburn, Massachusetts) uses X-rays as an external energy source to generate fluorescence spectra from the elements present in a given sample. It is possible to determine an element's concentration from these spectra by focusing on the peak intensity of secondary X-rays (Billets 2006). The X-250 also provides users with a convenient chemical analysis; the concentration is directly displayed in parts per million in a matter of minutes (Harmon et al. 2020; Walsh 2004). It is most effective when analyzing heavy metals from Mg* to U (Harmon et al. 2020).

LIBS is a relatively new field-portable instrument that has only been commercially available for the past 10 years (Sackett 2021). The Z-300 handheld LIBS analyzer (SciAps, Woburn, Massachusetts) uses laser power to measure the relative abundance (RA) of elements that emit light at wavelengths ranging from 190 nm to 950 nm (Harmon et al. 2020). Though the Z-300 can detect a wide range of light, it provides an optimal analysis of elements from H to Na, along with Br, Cl, K, Cs, Ar, and Rb (Harmon et al. 2020; SciAps, pers. comm., 2021)—analytes not conducive to analysis with XRFS. The advantages of handheld LIBS over XRFS include not only the ability to analyze an expanded list of elements but the speed of the analysis. XRFS analysis of soil materials typically takes several minutes, whereas LIBS acquires the data in seconds (Harmon et al. 2020). Thus, the handheld LIBS technology has the capability to make many measurements in the time it takes XRFS to take a single measurement. Handheld LIBS is also unique in its ability to capture spatial depth in a matter of seconds by drilling into the sample, giving rise to the capability to quantify how the RA of a metal changes across the soil gradient (Harmon et al. 2020; SciAps, pers. comm., 2021). Handheld LIBS also has molecular and speciation capabilities. However, the major drawback of the

*For a full list of the spelled-out forms of the chemical elements used in this document, please refer to *US Government Publishing Office Style Manual*, 31st ed. (Washington, DC: US Government Publishing Office, 2016), 265, https://www.govinfo.gov/content/pkg/GPO-STYLEMANUAL-2016/pdf/GPO-STYLEMANUAL-2016.pdf.

handheld LIBS instruments that are currently commercially available is the lack of internal calibration, which is required for immediate concentration determinations. Quantification of LIBS results requires exporting the data, generating a calibration curve, and then fitting the exported RA values to the calibration curve.

A prior US Army Engineer Research and Development Center (ERDC) study (Harmon et al. 2020) and a study by Tavares et al. (2021) used a multimodal sensor fusion approach to show that handheld LIBS working in tandem with XRFS can lead to optimal results because multiple sensors can counteract limitations that arise from a singular instrument. Analytical restraints include, but are not limited to, elemental sensitivity, limit of detection (LOD), and matrix effects (Harmon et al. 2020; Beal et al. 2020). Emerging handheld LIBS technology provides rapid analysis of a wide range of elements and offers the advantageous in situ feature of elemental mapping (Chirinos et al. 2014). LIBS is a promising candidate for replacing XRFS in the field to mitigate the risk of radiation exposure (Brand 2015).

## 1.2 Objectives

The goals of this experiment were to assess the efficacy of replicating quantitation results across X-250 XRF and Z-300 LIBS field analyzers and to evaluate field-analyzer accuracy. The purpose of this research was to demonstrate the feasibility of using LIBS as a reputable replacement for in situ XRFS chemical analysis of heavy-metal contaminants in soil.

## 1.3 Hypothesis

It was expected that, when following the study's quality assurance protocol, there would not be a statistically significant concentration difference when comparing XRFS to the benchtop ICP-OES (Shefsky 1997). However, it was reasonable to infer that there would likely be a statistical difference in concentration between XRFS and handheld LIBS, and between ICP-OES and handheld LIBS, because LIBS is less sensitive than XRFS and ICP-OES (Harmon et al. 2020). Additionally, the operator's direct influence on the laser–sample interaction during handheld system analysis could cause there to be a statistical difference in percent relative standard deviation (RSD) between LIBS, XRFS, and ICP-OES.

## 1.4 Approach

We centered our approach around the quantification of two specific heavy-metal contaminants, Cu and Zn, in soil from six US military installations, a naval base in San Diego, and a Canadian military base. Concentration and variation results gathered from the handheld analyzers were compared to one another and to the ICP-OES benchtop system to gauge instrument accuracy.

# 2 Methodology

## 2.1 Soil Background

NIST-certified Standard Reference Materials (SRMs) were used to calibrate the LIBS instruments for chemical analysis of Cu and Zn. The SRMs list can be found in Appendix B: Soil Suites. Natural soils gathered from each military location were analyzed for heavy metal particulate contamination. Thirty-four combined natural soils were collected from a naval base in San Diego, California, and a Marine Corps base in Oceanside, California, by Dr. Patrick Sims of the Naval Information Warfare Center Pacific and his Navy Environmental Sustainability Development to Integration (NESDI) LIBS project team. Appendix B: Soil Suites lists the specific site locations. Twenty-three soils, hereafter referred to as *Jenkins/PATAWAWA soils*, were sampled as part of a project under the Strategic Environmental Research and Development Program from the Petawawa military base and processed at Cold Regions Research and Engineering Laboratory (CRREL). These sampling efforts were recorded by Pennington et al. (2006). The remaining natural soils used for this experiment were collected by Dr. Jay Clausen of CRREL from small arms ranges at six US military installations across the US. (Collection dates are listed in Appendix B: Soil Suites.) Approximately seven soil samples from each military installation were analyzed to account for a range of common soil types military personnel encounter in the field (Harmon et al. 2020). Details regarding data collection and processing for US military installation soils can be found in Harmon et al. (2020).

## 2.2 Sample Preparation

### 2.2.1 X-Ray Fluorescence Spectroscopy (XRFS), Handheld Laser-Induced Breakdown Spectroscopy (LIBS), and Benchtop LIBS

A total of 102 CRREL and Navy soils were ground into a fine powder using a mortar and pestle so they could be analyzed with handheld LIBS and XRFS. All samples were loaded into 13 mm aluminum pellet cups and transferred into a 13 mm evacuable pellet die. An additional 0.2 g of ground sample was added to the pellet die and leveled off using the flat end of the die plunger. The loaded die was pressed under 3,000–6,000 lb of pressure for 30 seconds. The 13 mm pellets were made using the Model 3450 Benchtop Laboratory Pellet Press (Carver, Wabash, Indiana) and were stored in 24-well plates.

### 2.2.2 Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES)

All CRREL and Navy soils were digested using a 10% $HCl/HNO_3$ solution and were subsequently diluted with Milli-Q water into 50 mL vials. The samples were further diluted 2× into 10 mL centrifuge tubes, using a ratio of 5 mL filtrate:5 mL matrix solution. Samples that fell outside of the linear range were diluted from 1,000 ppm to roughly 2.5 ppm using a 1% $HCl/HNO_3$ solution.

### 2.2.3 Horiba LA-960 Laser Diffraction Particle-Size Analyzer (LD-PSA)

Soil samples were preprocessed by adding 10 mL $H_2O_2$ to roughly 1.5 g soil in 50 mL centrifuge tubes. The reaction was run to completion (in approximately 1–3 days). Here, another 10 mL of $H_2O_2$ was added and further run to completion (in approximately 7–14 days). Soil samples were heated to 40°C for two hours, diluted to 35 mL, and centrifuged. The supernatant was carefully discarded, and 30 mL of Calgon (38 g/L) was added to each sample. Samples were suspended in the solution for three days prior to wet analysis on the laser diffraction particle size analyzer (LD-PSA).

## 2.3 Instrumentation Calibration

### 2.3.1 Handheld LIBS

The calibration curves were generated in Profile Builder (SciAps, Woburn, Massachusetts) using SRMs (Table A-1). Calibration curves were independently generated for Cu and Zn while in empirical mode; SRMs were analyzed for each element under three trials. The software generated the respective spectra from the concentration (i.e., parts per million) of Cu and Zn found in each SRM. Before firing the laser, a wavelength calibration was prompted by the instrument. For each sample, five emission spectra were gathered using an intensity ratio for Cu, where the numerator was the addition of Cu 324.8, Cu 510.6, Cu 521.8, and Cu 327.4, and the denominator was the addition of Si 251.6 and Si 288.2 (P. Sims, pers. comm., 2021). The intensity ratio used for Zn was composed of the addition of Zn 202.5, Zn 213.9, and Zn 481.1 over the addition of Si 251.6 and Si 288.2 (P. Sims, pers. comm., 2021). The intensity ratios of these spectra were for strong emission lines specific to the combination of SRMs used and the elements of interest. Calibration was verified by checking the average analyzed concentration against known SRMs.

### 2.3.2 Benchtop LIBS

A multivariate calibration curve of wavelength versus intensity was generated in Agilent Clarity Software, Version 18.00210 (Applied Spectra Inc., West Sacramento, California) for Zn and Cu using the SRMs found in Table A-1. SRMs were shot at three different locations with a 2 × 10 grid pattern using spot sizes of 55, 125, and 200 μm. The spectra were cropped to ranges of 320–340, 460–485, and 505–525 to encompass strong Zn and Cu emission lines.

### 2.3.3 XRFS

The XRF X-250 is self-calibrated. Energy calibration was completed on the inside of the detector shuttle (prompted at the start of analysis by the X-250; SciAps, pers. comm., 2021).

### 2.3.4 ICP-OES

Standard solutions (S0–S7) were made by first diluting 1,000 ppm Zn and Cu stock solutions to 20 ppm using a diluent solution made up of $HNO_3$ and HCl in the same proportions as the digested samples (i.e., 5% $HNO_3$/HCl for 500 ppm samples). A 100 ppm standard was created for samples that fell outside of the linear range using a 1% $HNO_3$/HCl diluent solution. This intermediate standard was used to create a serial dilution (S0–S7) using the diluent solution.

## 2.4 Sample Analysis

### 2.4.1 Handheld LIBS

A high powered, 1,064 nm pulsed laser was fired at each pellet to ablate 10 μm of the surface in an argon atmosphere (Harmon et al. 2020; Russo 1995). Each sample was shot 10 times at three different locations (i.e., 30 shots per sample). An increase in energy on the surface of the material creates a plasma composed of atoms and ions in an excited state as the atoms/ions absorb the energy (Russo 1995). When the sample cools, the surface energy subsequently decreases, and electrons from the atoms/ions fall back to their ground state (SciAps, pers. comm., 2021). Light is released during the process of emission and is harnessed and separated by the spectrophotometer built into the Z-300 LIBS to generate emission spectra (SciAps, pers. comm., 2021). Flat-line measurements were not included in the analysis.

### 2.4.2 XRFS

A rhodium X-ray tube in the X-250 XRF analyzer (SciAps, Woburn, Massachusetts) generates and emits X-rays onto the sample (Harmon et al. 2020). Each sample was shot 10 times at three different locations using an analysis time of 15 seconds (i.e., 30 shots per sample). The high energy photons emitted from the XRFS excite electrons in the innermost shells (i.e., K and L) of atoms in the sample (Wirth and Barth, n.d.). Here, electrons from outer shells emit X-ray photons as they move into the empty K and L orbitals (Wirth and Barth, n.d.). This fluorescence is detected by the X-250 in energy (kilovolts) and displayed on a fluorescence spectrum (Wirth and Barth, n.d.).

### 2.4.3 ICP-OES

Digested samples were run through an autosampler, where they were transferred to a peristaltic pump and further transformed into aerosol particles via a nebulizer. Exposure to argon plasma led to the chemical reaction described in the Z-300 sample analysis (Radbound University 2022). Before analyzing unknown samples, calibration standards S0–S7 and the initial calibration verification were run through the ICP-OES. Blanks were sampled after the initial calibration verification and at the end of each run. The continuing calibration verification was sampled after every 15 samples and at the end of each run. Concentrations determined via ICP-OES that were outside of the linear range were re-analyzed using a higher standard concentration of 100 ppm Cu and Zn.

### 2.4.4 Benchtop LIBS

A 266 nm laser using a power setting of 100% was fired at each pellet in an argon atmosphere. Each sample was shot 10 times at three different locations using a 2 × 10 grid pattern for a total of 30 shots. SRM 2710a was analyzed before and after the analysis of unknown samples to ensure that the variation in laser intensity did not significantly alter the results.

### 2.4.5 LD-PSA

Subsets of each sample (i.e., ball milling for zero, two, and four hours) were vortexed and sonicated before wet analysis. To prevent particle settling, the autosampler was used to analyze one subset at a time. The LA-960 measures the size of suspended particles in a medium using Mie scattering theory (Siti Nor Qamarina et al. 2017).

## 2.5 Data Processing

The grand mean (i.e., the mean of three means), standard deviation (SD) of the three means, and %RSD were calculated in Microsoft Excel for each sample analyzed using XRFS, handheld LIBS, benchtop LIBS, and ICP-OES. These statistical tools were computed to compare instrument quantitation results via regression analysis.

Handheld LIBS concentration readings of soil sample FL9 were bootstrapped to evaluate the number of handheld LIBS shots needed to resemble the total population with respect to location ($n$) and number of increments ($k$) at each location. Sample FL9 was chosen based on the sample's high measured concentrations of both Cu and Zn relative to other prepared soils. Bootstrapping with replacement was performed in Python 3.8 on the original population ($N$), which contained 500 shots from a 32 mm pellet. Matrices A1–A3 were randomly resampled with replacement from $N$ at $n$ = 3, 4, 5, and 7 and $k$ = 1, 15, 20, 30, 40, 50, 60, and 70 (T. Georgian, pers. comm., 2022). The total number of handheld LIBS laser shots were averaged in each matrix to find the resampled population mean and SD (T. Georgian, pers. comm., 2022).

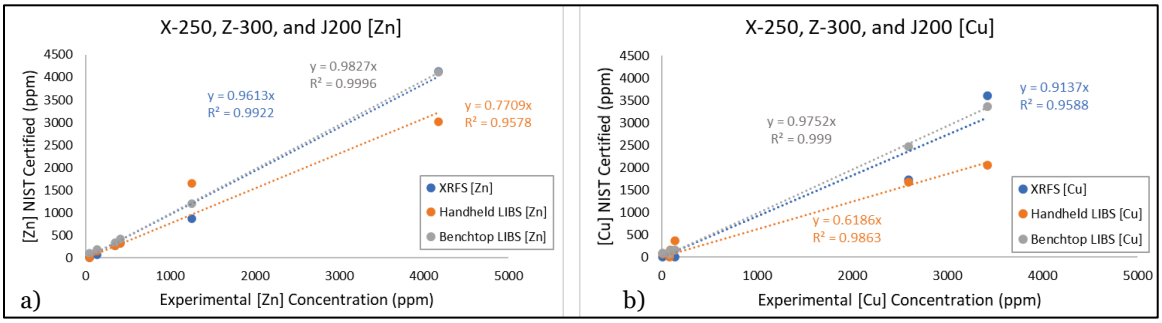
Most combinations of $n$ and $k$ for A1–A3 resulted in right-skewed distributions, mirroring the distribution of $N$. Right-skewed distributions are expected from handheld LIBS because the unit can overestimate at low concentration but can greatly affect a sensitive measure like the confidence interval (CI) of the SD. As a result, matrices A1–A3 were bootstrapped (K) 10,000 times to obtain the population CI of the mean and SD from normal distributions. The mean and SD and the two-sided 95% CI of the mean and SD were computed for each combination of $n$ replicates and $k$ increments of A1–A3, where $K$ = 10,000. Values of $n$ and $k$ that best resembled the total population were identified from plots in Section 3.4.1 . Matrices B1–B3 were then randomly resampled with replacement from $N$ at optimum values of $n$ and $k$, where $K$ = 30. The two-sided 95% CI of the mean was calculated at optimal $n$ and $k$ for CI verification (T. Georgian, pers. comm., 2022). CIs were constructed for the difference in population means at optimal values of $n$ and $k$ for matrix pairs A1–B1, A2–B2, and A3–B3.

# 3 Results and Discussion

## 3.1 Instrument Calibration Verification

A suite of six NIST-certified standards, listed in Appendix B: Soil Suites, were measured to ensure successful instrument calibration. The positive trendlines in Figure 1*a* and *b* indicate a correlation between experimental concentrations and their corresponding NIST-certified values. $R^2$ values close to 1 for XRFS (Figure 1*a* and *b*, Zn $R^2$ = 0.992, Cu $R^2$ = 0.959), handheld LIBS (Figure 1*a* and *b*, Zn $R^2$ = 0.958, Cu $R^2$ = 0.986), and benchtop LIBS (Figure 1*a* and *b*, Zn $R^2$ = 1.0, Cu $R^2$ = 0.999) indicate that the instruments provided accurate readings for Cu and Zn. It is evident that benchtop LIBS was more reliable than the handheld LIBS and XRF field-analyzers when analyzing both Cu and Zn.

Figure 1. X-ray fluorescence spectroscopy (XRFS), handheld laser-induced breakdown spectroscopy (LIBS), and benchtop LIBS calibration curves ($n$ = 3) for Zn (*a*) and Cu (*b*). NIST Standard Reference Materials (SRMs) include 1646a, 2706, 2710a, 2711a, 2586, and 2782.

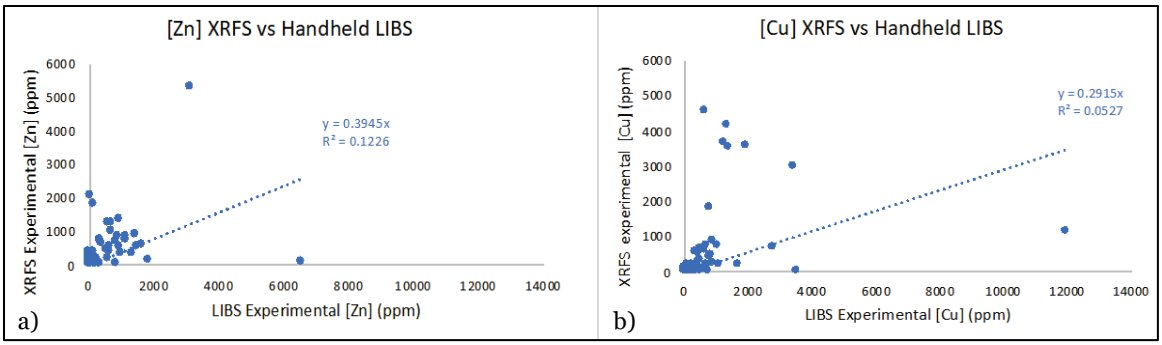



## 3.2 Replication across Different Field Analyzers

A total of 98 soil samples were analyzed using XRFS and handheld LIBS to assess differences in heavy-metal concentration between instruments: 34 soils from the NESDI LIBS Project Soil Suite, 23 Jenkins/PATAWAWA soils, and 41 soils from the US Military Installations Soil Suite. There was no correlation when comparing Cu and Zn quantitation results between XRFS and handheld LIBS (Figure 2*a* and *b*, Zn $R^2$ = 0.123, Cu $R^2$ = 0.053). Handheld LIBS typically reported higher concentrations than XRFS in situations where XRFS indicated that unknown concentrations were below the LOD, which likely influenced the low coefficient of determination. It is not clear why the LIBS indicated a measurable concentration in these situations, but it may be related to sample heterogeneity.

Sample heterogeneity made it impractical to compare quantitation results between handheld LIBS and XRFS because the handheld LIBS unit has a spot size that is two orders of magnitude smaller than that for XRFS (Appendix A; Table A-1). Given the smaller spot size of the handheld LIBS, XRFS can measure a greater sample volume. Particle size analysis revealed that there was a significant difference between the size of particles in the SRMs and the unknown samples; the SRM particles were roughly 10× smaller than those in the unknown samples (Table A-6). Consequently, when using handheld LIBS, a greater number of particles were encountered in SRMs than in the unknown samples in one shot. This explains the difference in performance between the instruments for the analysis of the SRMs versus the unknown samples. Material with larger particle sizes resulted in fewer particles being encountered with the handheld LIBS laser beam and caused its underperformance. Instrument performance can also be impacted by changes in the rate of laser ablation (Krüger et al. 2020; Russo 1995). Handheld LIBS cannot ablate the surface of a soil sample as effectively as XRFS because handheld LIBS operates at a higher wavelength with a lower energetic output than XRFS (Krüger et al. 2020; Russo 1995). Therefore, handheld LIBS results cannot be properly compared to XRFS results.

Figure 2. A comparison of measured concentrations between field analyzers XRFS and handheld LIBS ($n$ = 3) for Zn (*a*) and Cu (*b*).



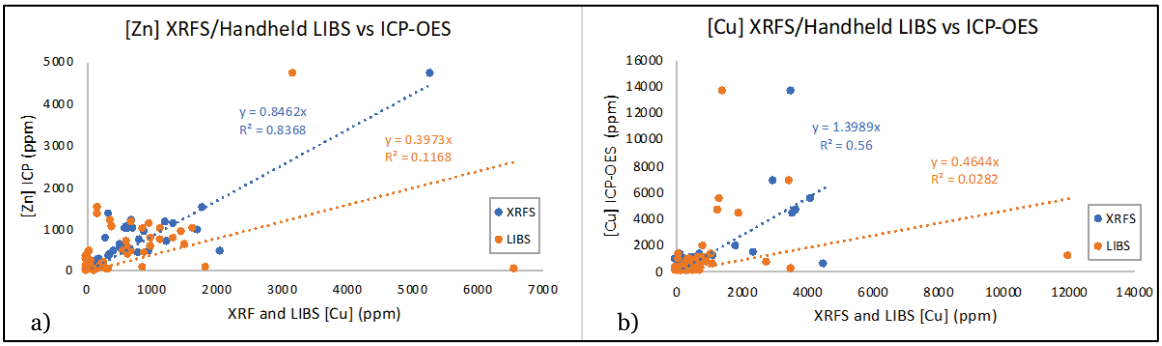

## 3.3 Field-Analyzer Accuracy and Precision

Concentrations gathered from XRFS and handheld LIBS were compared to the benchtop ICP-OES system to assess their accuracy. ICP-OES measures a greater sample volume than the field-portable instruments, enabling the conventional benchtop method to consistently provide accurate results (Appendix A; Table A-1 and Table A-2). XRFS showed moderate accuracy when measuring Zn and Cu, though the instrument provided a more accurate reading for Zn ($R^2$ = 0.837). XRFS also showed evidence

of being precise because the %RSDs were within the acceptable range (Appendix A; Table A-1 and Table A-2).

Figure 3 shows that handheld LIBS did not provide accurate Zn or Cu results for unknown material (i.e., $R^2$ was close to 0 in both instances). Table A-1 and Table A-2 show that handheld LIBS yielded highly variable results, with %RSDs ranging from 30%–100% for Cu and 70%–500% for Zn. Failure to obtain precise handheld LIBS results has previously been observed by researchers; Castle et al. (1998) concluded that heterogenous soil sample analysis lacks reproducibility (see also Michel and Chave 2007). Because of the small laser spot size with handheld LIBS, the instrument can only encounter a few particles for every three replicates in the unknown materials. This shortcoming can be ameliorated by increasing the number of shots and then integrating the results to obtain a mean value (Section 3.4).

Figure 3. A comparison of field analyzer ($n$ = 3) and inductively coupled plasma–optical emission spectrometry (ICP-OES) concentration readings for Zn (*a*) and Cu (*b*).




It is evident that samples with unknown metal concentrations were not as homogenous as the SRMs. The %RSD for handheld LIBS ranged from 30% to 96% for unknown materials; when analyzing a penny, the %RSD for handheld LIBS improved to 29% (Appendix A; Table A-3). Pennies have a uniform outer Cu coating; thus, it was expected that the handheld LIBS instrument would report low %RSDs. Handheld LIBS can provide precise and accurate analytical results; however, this is matrix dependent. In the case of unknown soil material, handheld LIBS intrinsically lacks the ability to replicate results at $n$ = 3 without manipulating the physical characteristics of the soil sample (i.e., homogenization). Even then, homogenizing the unknown soil material and pressing it into pellets was not sufficient to overcome the heterogeneity issue. One possible solution to this dilemma, which will be explored in Section 3.4, is to increase the number of

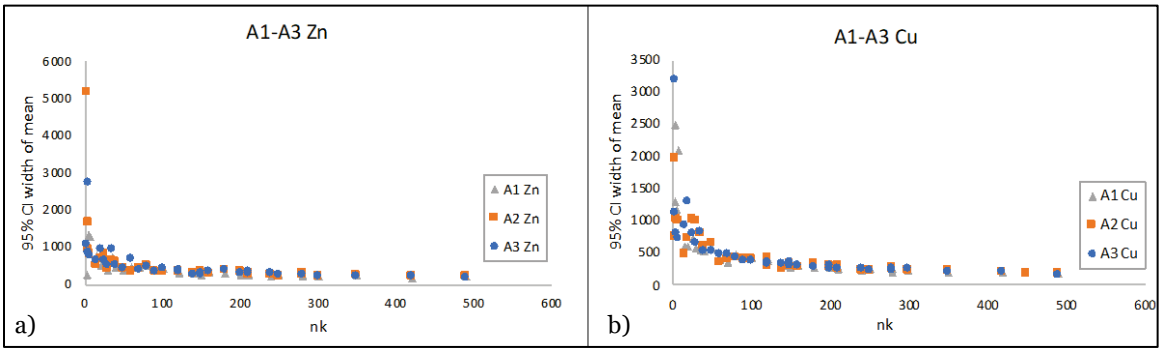
handheld LIBS shots to increase the coverage area so that it approaches that of XRFS.

## 3.4 Efforts to Decrease Handheld LIBS Variability

### 3.4.1 Increase Sample Size

One method used to determine the number of shots necessary to obtain handheld LIBS quantitation results within an acceptable %RSD range was to simulate an increase in sample size (i.e., shots per sample). This was accomplished via bootstrapping by comparing the results of different sample sizes to determine the optimum sample size relative to the concentration uncertainty. Bootstrapping is a statistical application of the law of large numbers that demonstrates that increasing sample size will increase the accuracy of the sample mean, providing a better representation of the true population mean (LibreTexts, n.d.). Figure 4 represents the relationship between sample size and the population estimate of Cu and Zn by bootstrapping $K$ = 10,000. There was a steep decline in the CI width of the mean as the sample size increased, until reaching a plateau at approximately 150 shots for Cu (95% CI for A1: 1328.5, 1604.1) and at approximately 120 shots for Zn (95% CI for A1: 81.23, 372.69). Therefore, we can conclude with 95% confidence that the intervals calculated using a sample size of 150 for Cu and 120 for Zn contain the true population mean (LibreTexts, n.d.). Additional shots did not have a significant effect on the CI width of the population mean, indicating that the sample sizes mentioned yielded the highest degree of precision attainable for sample FL9.

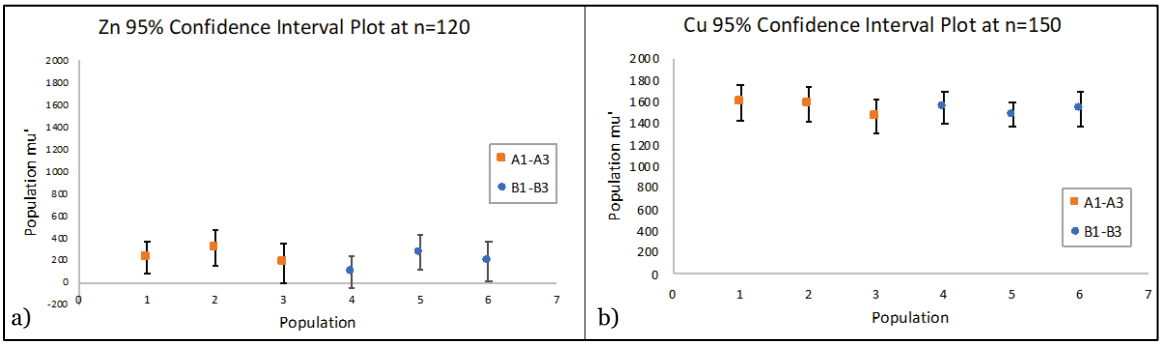
Figure 4. The effect of handheld LIBS sample size on the confidence interval (CI) of the mean concentration for matrices A1–A3 (Sample FL9: particle size 175.37 µm) for Zn (*a*) and Cu (*b*).




In Cu and Zn CI plots generated at optimal sample sizes (Figure 5), it is evident that population means for B1–B3 fall within the CI of the means

calculated for A1–A3. CIs were calculated for the difference in population means between A1–B1, A2–B2, and A3–B3 (Appendix A; and Table A-5) to verify the reproducibility of means at optimal sample sizes. Given that each constructed CI includes zero, it is possible that there is no difference between population means. These findings indicate that using a sample size of 150 for Cu and 120 for Zn will yield results that are reproducible.

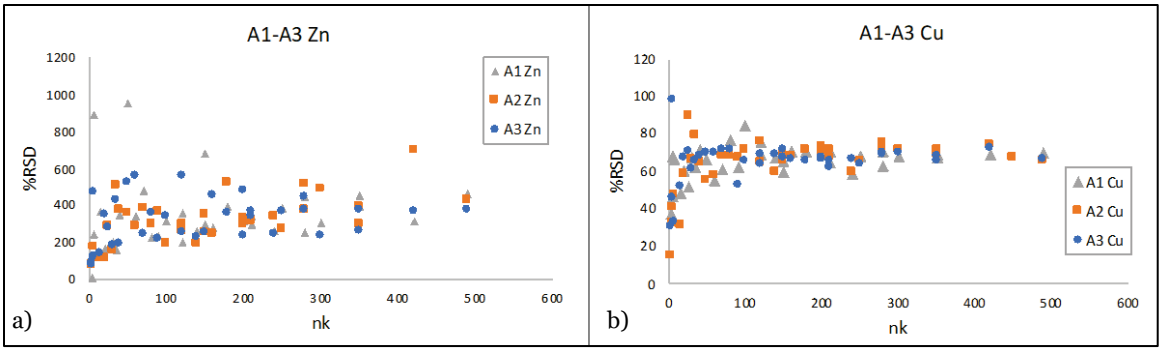
Figure 5. Zn (*a*) and Cu (*b*) interval plots for matrices A1–A3 and B1–B3.




A large sample size led to a narrower CI for Cu and Zn across matrices A1–A3 but did not decrease %RSD (Figure 6*a* and *b*). Sample size does not affect the variation in Zn quantitation results (Figure 6*b*). Note that Zn has a lower mean concentration than Cu in each bootstrapped population (Figure 5). Lower metal concentrations found in a sample can lead to higher variation in handheld LIBS results because the contaminant is more widely dispersed throughout the individual particle population.

For Cu, increasing the number of handheld LIBS shots increased the %RSD of larger sample sizes until showing little change ranging between 60% and 70% RSD. Though it appears that fewer handheld LIBS shots resulted in a low %RSD for Cu, the unit's spot size limits chemical analysis to soil particles within 100 μm per shot. Noting that a singular FL9 soil particle measured, on average, 175.37 μm, analyzing a few particles increases the likelihood that handheld LIBS will analyze particles of similar concentration and can lead to a misrepresentation of the true population uncertainty. Thus, sample heterogeneity is a great challenge to handheld LIBS analysis. Optimum values of *n* and *k* for FL9 can then be reframed to meet the acceptable %RSD for the project and provide greater confidence when drawing conclusions.

Figure 6. The effect of handheld LIBS sample size on percent relative standard deviation (RSD) for A1–A3 for Zn (*a*) and Cu (*b*).




Figures 7 and 8 explain the optimum combination of the number of locations and increments needed to confidently demonstrate the SD of the true population, showing that handheld LIBS yields optimum Cu quantitation results at $n = 5$ and $k = 30$, whereas optimum Zn results can be obtained at $n = 4$ and $k = 30$. Future statistical work is needed to assess the relationship between $nk$ and %RSD as a function of particle size and heterogeneity to better establish a recommended sample size for handheld LIBS analysis. If handheld LIBS analysis is matrix-specific, new challenges arise in situ regarding assessing heterogeneity prior to analysis and reducing sample variability when necessary.

Given the goal of the project, it was crucial to account for the analysis time required for each of the field-portable analyzers. XRFS analysis of three locations per soil sample at 10 shots per location, totaling 30 shots per sample, took an average of 7.5 minutes (i.e., 15 seconds per shot, $n = 3$). XRFS quantitation results that meet the generally accepted %RSD can be collected in less than 30 shots using an analysis time of two minutes at one shot per location.

Handheld LIBS analysis of the project's optimum sample size, between 120 and 150 shots, judgmentally determined from Figures 7 and 8, took an average of 75 to 90 minutes. Though each laser shot takes less than a second, the computer application, Profile Builder, that is needed to convert RA to concentration is a major hindrance that slows down data processing. Persistent, rapid fire of the LIBS unit caused the unit to overheat after 100 shots and Profile Builder to continuously crash after roughly 60 shots. Restarting the application and tethering to the LIBS unit while providing the unit enough time to cool explains the prolonged analysis using handheld LIBS. Manufacturing handheld LIBS with an internal cooling system and

software that allows the unit to internally convert RA to concentration is a possible solution to reduce the amount of time it takes to provide comparable results.

Figure 7. CI of the standard deviation (SD) as a function of *k* at fixed *n* for matrices A1 (*top*) to A3 (*bottom*) for Cu (*left*) and Zn (*right*).

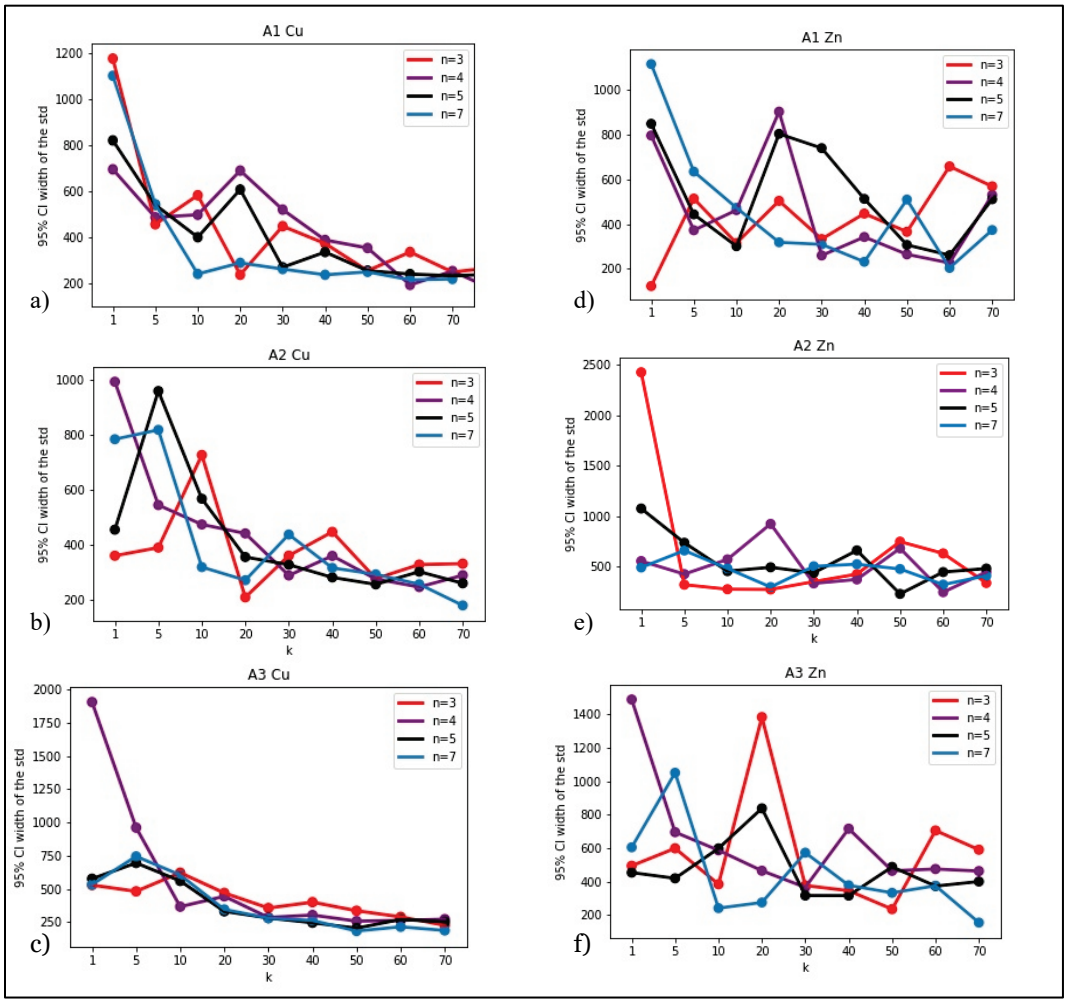
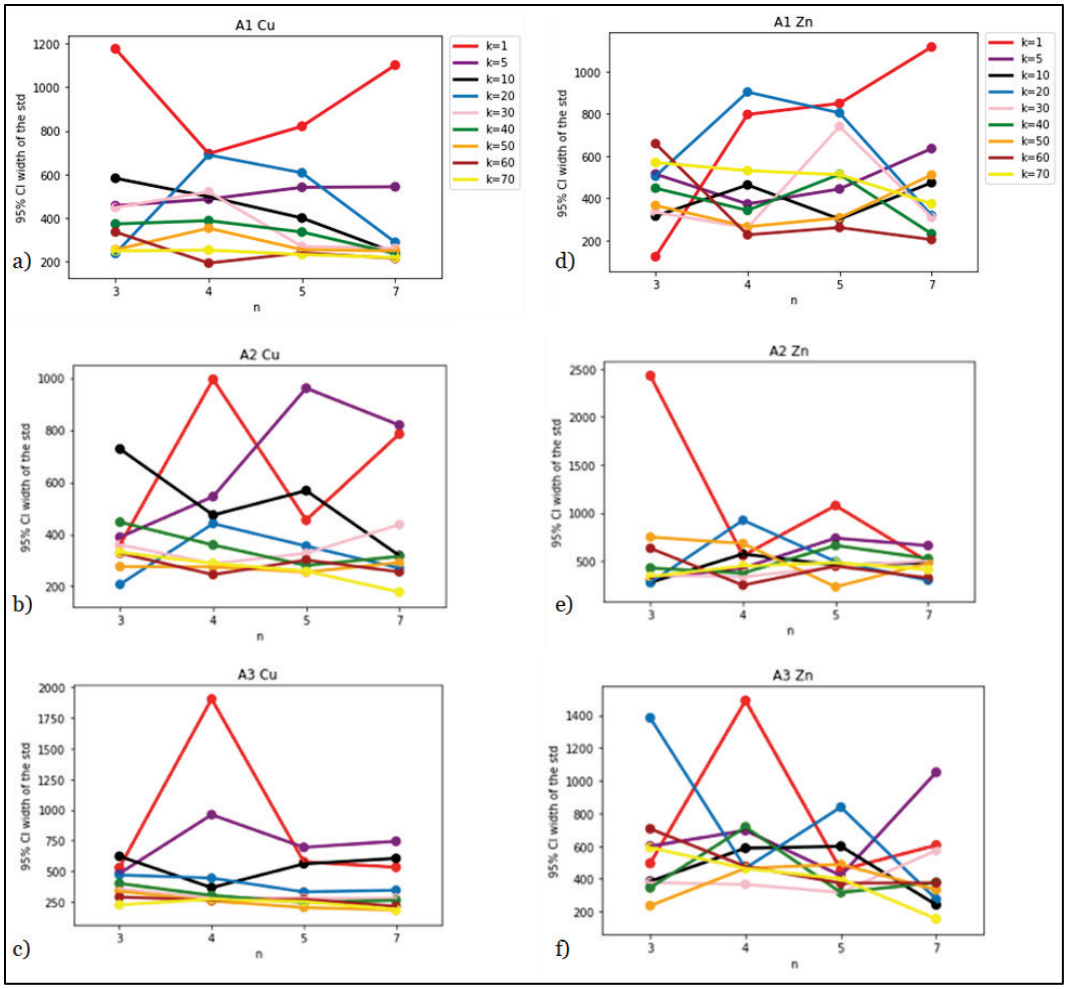


Figure 8. CI of the SD as a function of *n* at fixed *k* for matrices A1 (*top*) to A3 (*bottom*) for Cu (*left*) and Zn (*right*).




### 3.4.2 Decrease Particle Size

Another effort to decrease the variability of handheld LIBS involved milling unknown samples at increments of two and four hours to increase sample homogeneity upon measurement. A prior ERDC study by Beal et al. (2020) observed the effects of particle size on benchtop LIBS analysis and provided evidence to suggest that benchtop LIBS accuracy and precision rely on particle-size reduction to increase sample homogeneity. Particle-size reduction increases the number of particles in the sample and surface area. Figure 9 shows a positive trendline between particle size and %RSD. Ball milling soil samples at both two- and four-hour increments showed decreases in both particle-size distribution and handheld LIBS variability compared to original sampling (Figures 9 and 10). Decreasing particle size decreased %RSD because the collective shots encompassed a

greater sample area, thus increasing the probability of encountering the few contaminant particulates relative to the native material.

Figure 9. A comparison of %RSD between XRFS and handheld LIBS for a milled sample (FL9) at increments of zero, two, and four hours. Samples were shot at three different locations (10× per location).

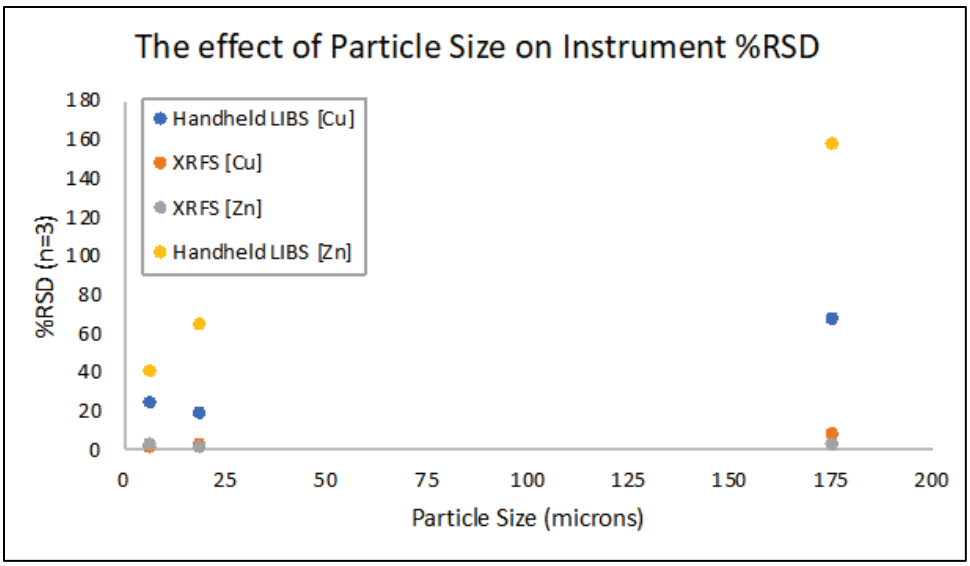



Figure 10. Distribution of B58 at initial size (*red*), two-hour milled (*green*), and four-hour milled (*black*).

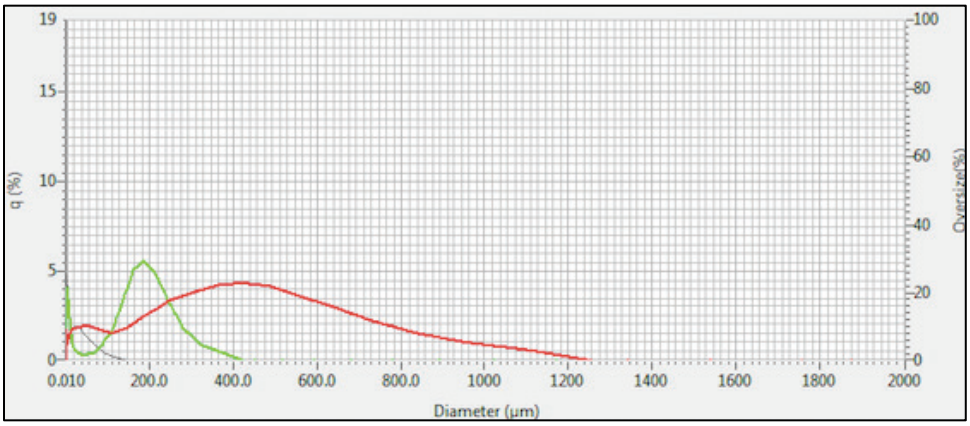
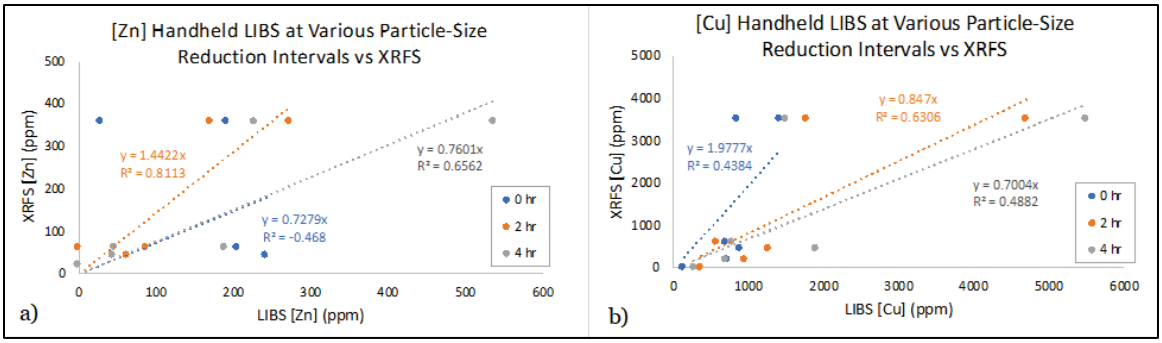



Figure 11 shows that ball milling soil samples for handheld LIBS analysis improves the correlation between handheld LIBS and XRFS results for Cu and Zn. However, there is a stronger correlation between the two field analyzers when ground for two hours (Zn $R^2$ = 0.8113; Cu $R^2$ = 0.6306) than when ground for four hours (Zn $R^2$ = 0.6562; Cu $R^2$ = 0.4882). It is likely that a two-hour particle-size reduction for LIBS analysis allowed handheld LIBS to encounter a number of particles that resembled the number of particles encountered by XRFS, but ball milling these samples even further

caused the particles analyzed per shot by handheld LIBS to exceed the XRFS capabilities.

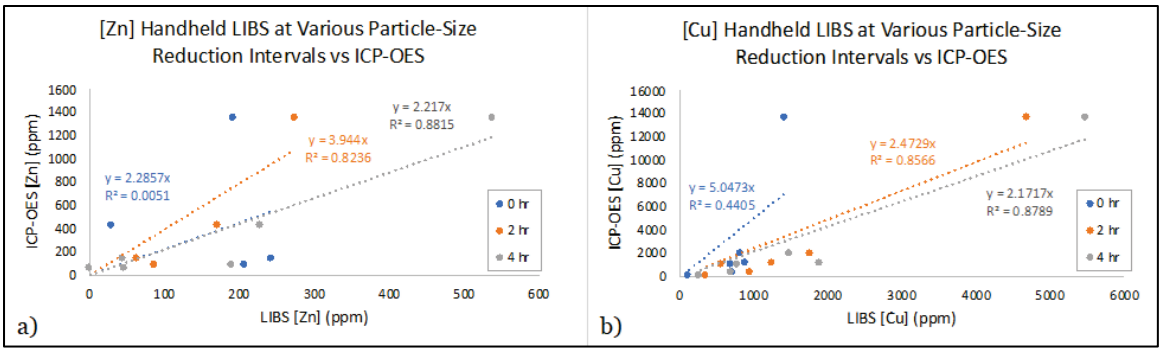
Figure 11. A comparison of field-analyzer quantitation results ($n$ = 3) for Zn ($a$) and Cu ($b$). XRFS soil samples were not further processed. Handheld LIBS soil samples were ball milled at increments of zero, two, and four hours and pressed into new pellets.




As shown in Figure 12, comparing quantitation results between handheld LIBS and ICP-OES reveals that ball milling samples for four hours improved the accuracy of handheld LIBS (Zn $R^2$ = 0.8815; Cu $R^2$ = 0.8789) by 40%–80%. The scatter plots in Figure 12 show that there was an inverse relationship between accuracy and particle size. As particle size decreased, there was a subsequent increase in the accuracy of handheld LIBS. Although reducing soil particle size for four hours yielded optimal handheld LIBS results, recall that XRFS is less accurate and has a smaller sample volume than ICP-OES. Accordingly, Figures 11 and 12 provide evidence to infer that handheld LIBS can serve as a replacement for XRFS using a ball mill time of two hours. Particle-size reduction can be used to overcome the small spot size of handheld LIBS.

Enhanced handheld LIBS performance after particle-size reduction may alternatively be explained by matrix matching. Recall from Section 3.2 that instrument performance can be influenced by the rate of ablation. Table A-6 (Appendix A) shows that reducing the particle size of unknown material yielded particle sizes that were comparable to SRM particle sizes. It is possible that the performance of handheld LIBS was enhanced by minimizing matrix effects. A future study could verify external calibration as the primary source of error by recalibrating handheld LIBS with coarse known material that is comparable to unknown samples to see if $R^2$ improves between handheld LIBS and XRFS or ICP-OES.

Figure 12. A comparison of experimental milled handheld LIBS ($n$ = 3) to original benchtop ICP-OES concentration readings for Zn (*a*) and Cu (*b*). Handheld LIBS soil samples were ball milled at increments of zero, two, and four hours and pressed into new pellets prior to analysis.




## 3.5 Implications

Proper LIBS analysis relies on a matrix-matched calibration such that NIST standard particle sizes are comparable to the unknown soil samples (Beal et al. 2020; Harmon et al. 2020). Current field methodology for military soil samples involves milling samples down to approximately 150 μm. Subsequent particle size analysis using a subset of unknowns revealed that soil samples used in original analyzer comparisons had particle sizes up to 10× larger than supplied NIST standards (Table A-6). Another challenge when analyzing LIBS and XRFS quantitation results was the heavy-metal concentrations of the selected soil samples. The combination of limited samples with high concentrations and abundant samples with very low concentrations can skew the regressions between XRFS and handheld LIBS due to LIBS LOD being approximately 100 ppm (Fu et al. 2020). LIBS outliers are more common and are typically seen on or near zero, which can influence the coefficient of determination if not in proportion to data that surpass the detection threshold for both instruments.

# 4 Conclusions

This research investigated the efficacy of replacing XRFS with handheld LIBS in situ for chemical analysis. Comparing handheld LIBS quantitation results to XRFS and ICP-OES results showed that handheld LIBS did not capture an accurate representation of each sample's chemical composition at any wavelength of interest and that the coefficients of determination were very weak while %RSDs were consistently high. Handheld LIBS successfully measured Cu and Zn concentrations of NIST SRMs that had particle sizes less than 20 μm, indicating that the typical handheld LIBS spot size area of 50–100 μm can create obstacles when measuring coarse unknown material. It is imperative to factor in homogeneity as a function of particle size given that handheld LIBS has a spot size area that is 100-fold smaller than that of XRFS; therefore, direct comparison between field analyzers cannot be carried out practically due to the difference in the number of particles encountered with each analysis.

In an effort to decrease the variation of handheld LIBS results from shot to shot, the effects of sample variation were explored by independently increasing sample size and decreasing particle size. Bootstrapping a soil sample with a high particle size demonstrated that increasing sample size did not decrease handheld LIBS data variation but captured the true variation of the population. Particle-size reduction enabled handheld LIBS to measure additional particles per shot. This effort showed a significant decrease in the %RSD of handheld LIBS. These results reveal limitations in the current military field methodology, which is to mill soil samples down to approximately 150 μm, because further milling of these soils was required to improve results. At the present time, the advantages of handheld XRFS outweigh those of LIBS, principally due to the larger spot size of XRFS allowing for in situ analysis of material with larger soil particles.

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# Appendix A: Data Tables

Table A-1 through Table A-6 contain the data used in this report.

Table A-1. Spot sizes specific to each instrument affect Cu percent relative standard deviation (RSD).

| Sample ID | Instrument | Spot Size Area (µm) | Particles Analyzed per Shot (No.) | Cu Concentration (ppm) | Cu SD | Cu %RSD |
|---|---|---|---|---|---|---|
| GAG12 | LIBS Z-300 | 50–100 | 0.33–0.67 | 833.07 | 375.93 | 45.13 |
| GAG12 | XRF X-250 | 5000–10000 | 33–66 | 1828.46 | 10.82 | 0.59 |
| GAG12 | ICP-OES | | 128.16** | 1919.17 | 21.34 | 1.11 |
| GAG12 | J200 LIBS | 200 | 1.33 | 1136.87 | 161.59 | 14.21 |
| KTS4 | LIBS Z-300 | 50–100 | 0.33–0.67 | 127.17 | 39.07 | 30.72 |
| KTS4 | XRF X-250 | 5000–10000 | 33–66 | 0 | | |
| KTS4 | ICP-OES | | 128.16** | 36.23 | 0.24 | 0.65 |
| KTS4 | J200 LIBS | 200 | 1.33 | 414.57 | 397.53 | 95.89 |
| FL9 | LIBS Z-300 | 50–100 | 0.33–0.67 | 1413.97 | 944.5 | 66.8 |
| FL9 | XRF X-250 | 5000–10000 | 33–66 | 3513.21 | 247.91 | 7.06 |
| FL9 | ICP-OES | | 128.16** | 13654.55 | 119.6 | 0.88 |
| FL9 | J200 LIBS | 200 | 1.33 | 961.89 | 675.09 | 70.18 |
| B58 | LIBS Z-300 | 50–100 | 0.33–0.67 | 833.93 | 308.58 | 34.91 |
| B58 | XRF X-250 | 5000–10000 | 33–66 | 471.78 | 14.21 | 3.01 |
| B58 | ICP-OES | | 128.16** | 1005.97 | 4.18 | 0.41 |
| B58 | J200 LIBS | 200 | 1.33 | 1157.17 | 180.67 | 15.61 |
| RB34S2 | LIBS Z-300 | 50–100 | 0.33–0.67 | 690.14 | 395.05 | 57.24 |
| RB34S2 | XRF X-250 | 5000–10000 | 33–66 | 600.73 | 43.36 | 7.22 |
| RB34S2 | ICP-OES | | 128.16** | 984.21 | 24.32 | 2.47 |
| RB34S2 | J200 LIBS | 200 | 1.33 | 310.45 | 468.70 | 150.98 |
| P07 | LIBS Z-300 | 50–100 | 0.33–0.67 | 719.87 | 689.81 | 95.82 |
| P07 | XRF X-250 | 5000–10000 | 33–66 | 201.13 | 9.24 | 4.59 |
| P07 | ICP-OES | | 128.16** | 221.81 | 2.88 | 1.30 |
| P07 | J200 LIBS | 200 | 1.33 | 279.51 | 313.44 | 112.14 |

**ICP-OES = per sample uptake

Table A-2. Spot sizes specific to each instrument affect Zn %RSD.

| Sample ID | Instrument | Spot Size Area (µm) | Particles Analyzed per Shot (No.) | Zn Concentration (ppm) | Zn SD | Zn %RSD |
|---|---|---|---|---|---|---|
| GAG12 | LIBS Z-300 | 50–100 | 0.33–0.67 | 29.23 | 137.3 | 469.67 |
| GAG12 | XRF X-250 | 5000–10000 | 33–66 | 381.32 | 2.67 | 0.70 |
| GAG12 | ICP-OES | | 128.16** | 415.91 | 0.87 | 0.21 |
| GAG12 | J200 LIBS | 200 | 1.33 | 1061.91 | 173.53 | 16.34 |
| KTS4 | LIBS Z-300 | 50–100 | 0.33–0.67 | 0 | 32.72 | |
| KTS4 | XRF X-250 | 5000–10000 | 33–66 | 20.75 | 1.09 | 5.25 |
| KTS4 | ICP-OES | 6408.24 | 128.16** | 52.98 | 0.81 | 1.53 |
| KTS4 | J200 LIBS | 200 | 1.33 | 683.78 | 203.87 | 29.81 |
| FL9 | LIBS Z-300 | 50–100 | 0.33–0.67 | 191.73 | 300.72 | 146.48 |
| FL9 | XRF X-250 | 5000–10000 | 33–66 | 356.53 | 4.66 | 1.31 |
| FL9 | ICP-OES | 6408.24 | 128.16** | 1348.62 | 14.5 | 1.08 |
| FL9 | J200 LIBS | 200 | 1.33 | 1217.62 | 609.47 | 50.05 |
| B58 | LIBS Z-300 | 50–100 | 0.33–0.67 | 167.99 | 117.95 | 70.21 |
| B58 | XRF X-250 | 5000–10000 | 33–66 | 41.28 | 1.80 | 4.35 |
| B58 | ICP-OES | 6408.240482 | 128.16** | 126.56 | 0.51 | 0.40 |
| B58 | J200 LIBS | 200 | 1.33 | 1049.56 | 154.39 | 14.71 |
| RB34S2 | LIBS Z-300 | 50–100 | 0.33–0.67 | 0 | 379.02 | |
| RB34S2 | XRF X-250 | 5000–10000 | 33–66 | 62.25 | 17.16 | 27.57 |
| RB34S2 | ICP-OES | 6408.24 | 128.16** | 54.71 | 5.95 | 3.27 |
| RB34S2 | J200 LIBS | 200 | 1.33 | 76.10 | 428.77 | 563.46 |
| P07 | LIBS Z-300 | 50–100 | 0.33–0.67 | 149.18 | 679.71 | 455.65 |
| P07 | XRF X-250 | 5000–10000 | 33–66 | 60.21 | 3.86 | 6.41 |
| P07 | ICP-OES | 6408.24 | 128.16** | 79.41 | 1.17 | 1.48 |
| P07 | J200 LIBS | 200 | 1.33 | 214.13 | 235.26 | 109.87 |

**ICP-OES = per sample uptake

Table A-3. LIBS and XRF penny analysis of Cu composition.

| Instrument | Cu Concentration (ppm) | Cu SD | Cu %RSD |
|---|---|---|---|
| LIBS | 6146032.63 | 1811825.17 | 29.48 |
| XRF | 645970.90 | 536.42 | 0.08 |

Table A-4. Confidence intervals (CIs) generated for the difference in Zn population means for sample FL9.

| Zn Population Means for Comparison | CI Lower Limit | CI Upper Limit |
|---|---|---|
| A1–B1 | −101.25 | 350.99 |
| A2–B2 | −164.72 | 262.82 |
| A3–B3 | −267.66 | 227.22 |

Table A-5. CIs generated for the difference in Cu population means for sample FL9.

| Cu Population Means for Comparison | CI Lower Limit | CI Upper Limit |
|---|---|---|
| A1 and B1 | −196.74 | 267.63 |
| A2 and B2 | −340.94 | 149.11 |
| A3 and B3 | −308.80 | 162.42 |

Table A-6. Mean particle size (in micrometers) analysis of a subset of unknowns at ball milled increments of zero, two, and four hours.

| Sample ID | Original (µm) | Milled for 2 Hours (µm) | Milled for 4 Hours (µm) |
|---|---|---|---|
| B58 | 198.51 | 62.11 | 10.49 |
| FL9 | 175.37 | 18.74 | 6.86 |
| GAG12 | 28.41 | 19.56 | 7.60 |
| P07 | 25.38 | 10.96 | 11.25 |
| KTS4 | 164.74 | 58.10 | 26.33 |
| RB34S2 | 99.08 | 15.53 | 10.96 |
| NIST 2710a | 13.45 | — | — |
| NIST 2711a | 18.69 | — | — |

# Appendix B: Soil Suites

Table B-1 through Table B-3 contain information on the soil suites used in this study.

Table B-1. NIST-certified Standard Reference Materials (SRMs).

| Standard | Zn Certified Concentration (ppm) | Cu Certified Concentration (ppm) |
|---|---|---|
| 1646a | 48.90 | 10.01 |
| 2706 | 135.40 | 88.10 |
| 2710a | 4180.00 | 3420.00 |
| 2711a | 414.00 | 140.00 |
| 2586 | 352.00 | 81.00 |
| 2782 | 1254.00 | 2594.00 |

Table B-2. Navy Environmental Sustainability Development to Integration (NESDI) LIBS project soil suite.

| Location | Date Collected |
|---|---|
| Marine Corps Base Camp Pendleton (CPEN), Skeet Range | October 2020 |
| Naval Base San Diego, Dry Side, Parking Lot Behind Commissary | March 2021 |
| Naval Base San Diego, Recycling Center | May 2021 |
| Naval Base San Diego, Building 123 | May 2021 |

Table B-3. US military installations soil suite.

| Location | Date Collected |
|---|---|
| Massachusetts Military Reservation/Joint Base Cape Cod (MMR) | July 2005 |
| Fort Benning, GA | June 2006 |
| Fort Lewis, WA | September 2006 |
| Fort Wainwright, AK | October 2011 |
| Idaho National Guard Camp Kimama | October 2011 |
| Fort Eustis, VA | December 2011 |

# Abbreviations

| | |
|---|---|
| CI | Confidence interval |
| CRREL | Cold Regions Research and Engineering Laboratory |
| ERDC | Engineer Research and Development Center |
| ICP-MS | Inductively coupled plasma–mass spectrometry |
| ICP-OES | Inductively coupled plasma–optical emission spectrometry |
| LD-PSA | Laser diffraction particle size analyzer |
| LIBS | Laser-induced breakdown spectroscopy |
| LOD | Limit of detection |
| NESDI | Navy Environmental Sustainability Development to Integration |
| RA | Relative abundance |
| RSD | Relative standard deviation |
| SD | Standard deviation |
| SRM | Standard Reference Material |
| XRF | X-ray fluorescence |
| XRFS | X-ray fluorescence spectroscopy |

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**14. ABSTRACT**

Handheld laser-induced breakdown spectroscopy (LIBS) is an emerging analytical technique that shows the potential to replace X-ray fluorescence spectroscopy (XRFS) in the field characterization of soils containing heavy metals. This study explored the accuracy and precision of handheld LIBS for analyzing soils containing copper and zinc to support LIBS as a replacement for XRFS technology in situ. Success was defined by handheld LIBS results that could be replicated across field analyzers and verified by inductively coupled plasma–optical emission spectrometry (ICP-OES). A total of 108 soil samples from eight military installations were pressed into 13 mm pellets and then analyzed by XRFS and LIBS. Handheld LIBS has a spot-size area 100-fold smaller than that of XRFS, and though it provided accurate measurements for NIST-certified reference materials, it was not able to measure unknown soils of varying soil texture with high particle size variability, regardless of sample size. Thus, soil sample particle size heterogeneity hindered the ability to provide accurate results and replicate quantitation results across LIBS and XRFS. Increasing the number of particles encountered by each shot through particle size reduction improved both field-analyzer correlation and the correlation between handheld LIBS and ICP-OES from weak (<15%) to strong (>80%).



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Analytical chemistry--Quantitative; Heavy metals; Inductively coupled plasma optical emission spectrometry; Laser-induced breakdown spectroscopy; Soil pollution--Detection; Soils testing; X-ray spectroscopy


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