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Article

Sample Preparation Influences pXRF Results: A Case Study on a Tailings Pond

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Abstract

The concentrations of PTEs and Fe_2O_3 increase from the sand fraction to the silt fraction, although the magnitude of this increase is not uniform ($\text{Zn} > \text{Cu} > \text{As} > \text{Pb}$), while SiO_2 content is not affected by particle size. In general, PTE concentrations are lower in wet samples than in dry samples. The ratio of the element concentration in the wet sample to that in the air-dried sample, together with the gravimetric moisture content (%), were plotted in central scatter plots, which allowed the identification of outliers. The inverse relationship observed between the concentration of certain elements and moisture content may be explained by the geochemical characteristics of the sample. Moisture in both manually and mechanically ground samples influences analytical accuracy, even when the processing time is identical. Triplicate samples indicate small-scale heterogeneity driven by post-depositional alteration of the tailings, as well as element associations (e.g., Fe_2O_3 –As) dictated by the mineralogical composition of the source material (e.g., arsenopyrite).

Keywords: sample preparation; sediments; tailing pond; potentially toxic elements; X-ray fluorescence

1. Introduction

An inventory of scientific articles based on the keywords "X-ray fluorescence (pXRF)–methods" in the Web of Science database for the period 2003–2025 indicates a slight increase in the number of publications, from 42 to 58. When applying subject area filters such as Environment, Geology, Chemistry, and Archaeology, the number of articles addressing sample preparation methods decreases to fewer than five, while studies specifically referring to samples from mine waste dumps are even fewer [1–3]. Furthermore, the keyword combination "pXRF sample preparation" yielded an even smaller number of scientific publications (6–14) over the same time interval [4,5].

Field-portable X-ray fluorescence (pXRF) analyzers have advanced rapidly in recent years, allowing for increasingly sensitive and rapid measurements. As a result, they are widely applied in environmental monitoring and geological research [6], with implications for the rapid monitoring of abandoned mine sites.

The performance of pXRF technology ranges from very good for certain trace elements (Cu, Pb, As) to good for others [7], and the elements analyzed in this study fall within these categories. Many studies have focused on the variability of XRF measurements, which results from both the heterogeneity of soils and sediments and sample preparation methods. Moisture content reduces the apparent concentration due to dilution effects and increased scattering; however, pXRF measurements are generally considered acceptable when moisture levels remain below 20% [8,9].

Texture is a key factor controlling the retention and release of trace elements, with coarse-textured materials exhibiting lower sorption capacity compared to fine fractions [10]. Studies conducted in sulfide deposits have reported a positive correlation between trace element concentrations and the proportion of particles $< 63 \mu\text{m}$ [11], whereas in soil samples with particle sizes $< 2 \text{ mm}$, sample heterogeneity and matrix effects may be considered negligible [12]. When higher

analytical precision is required, pulverization of the samples is recommended in order to minimize grain-size effects [13].

The post-mining evolution of waste material (hydration–dehydration, oxidation, etc.) and the deposition of materials with distinct geochemical characteristics at the edges of the waste pile, as observed at Horse Creek, can accentuate geochemical variability over very small spatial scales. The formation of surface crusts on tailing ponds results from the precipitation of secondary minerals [14] which leads to increased concentrations of certain potentially toxic elements (PTEs), such as As, Cu, Pb, and Zn, within the uppermost centimeters of the deposit [15].

Crystals or localized enrichments of oxides and trace elements frequently occur in unhomogenized samples, whether of natural or anthropogenic origin, thereby increasing analytical uncertainty due to the nugget effect [16,17]. If sieving is not possible, the uncertainty in the measurements of these elements can be reduced by performing multiple measurements of a single sample [16]. Nugget effects can also be mitigated and uncertainty reduced by averaging multiple measurements [8].

This study aims to assess the variability in concentrations of selected PTEs and oxides within the surface layer of the Horse Creek tailing pond (Romania) as a function of sample preparation method.

2. Materials and Methods

2.1. Study Area and Physiography

The Horse Creek tailing pond is situated in the northeastern sector of the Eastern Carpathians at 47°32'37" N latitude and 25°26'37" E longitude (Figure 1a). It was constructed within the riverbed of the stream of the same name, although the watercourse is protected by a system of pipes. The tailing pond covers an area of 7.5 hectares and comprises of nine terraces on its southern side, which are affected by deep erosion, whereas the lower terraces have been stabilized with planted vegetation (Figure 1b). The nearest settlement, Fundu Moldovei, lies 1.4 km to the southwest, and the closest urban center, Câmpulung Moldovenesc, is located 4 km to the west.

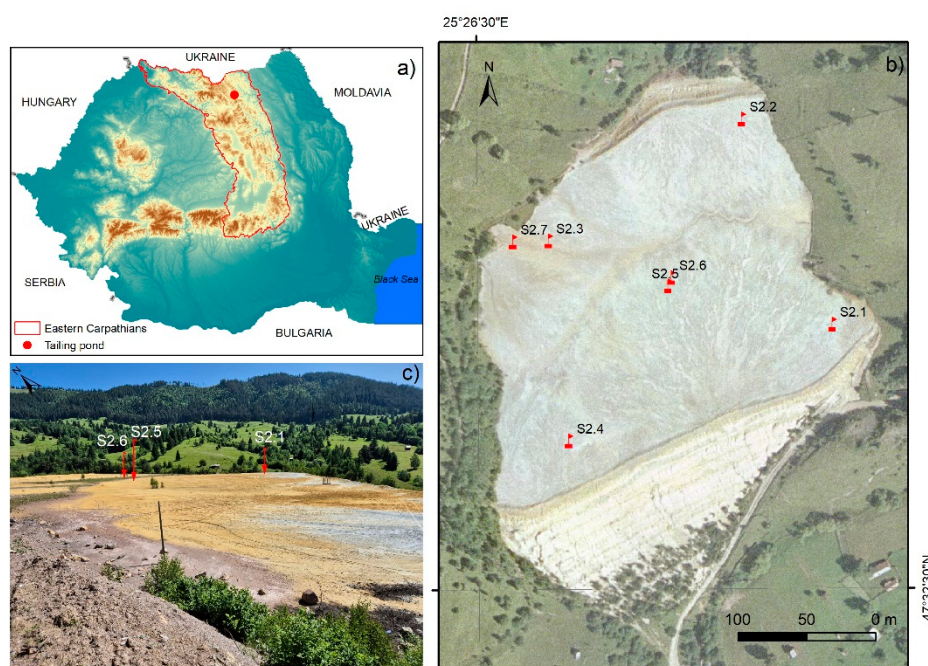


Figure 1. The location of the Horse Creek tailings pond (a), the positioning of the samples on the dump (b), and new deposit (c).

The south-east mountain slope promotes the accumulation of precipitation-derived runoff in the western sector of the tailing pond, where a small gully has formed and drains water in the opposite direction. At the contact between the slope and the pond, excavated material (metamorphic rocks, limestone, and dolomite) from a nearby quarry was deposited in 2023 and 2024 (Figure 1c). Subsequently, precipitation mobilized the fine fraction of this material, which was redeposited on the tailings surface as a band, 2-5 m wide and millimeter thick, extended along the thalweg.

This sulfide-rich tailing pond contains elevated concentrations of harmful metals, and the oxidation of sulfides has led to the formation of acid mine drainage [18], preventing natural revegetation of the pond surface. However, the allochthonous material, combined with increased moisture availability, created locally favorable conditions for herbaceous vegetation along the thalweg (Figure 1c). Pine and birch trees have been planted on the lower terraces of the tailings pond, but deep erosion has led to the development of rills along which the material is transported downstream, contributing to the expansion of the tailings pond surface.

2.2. Geochemical Characteristics

The tailing pond is located in an area dominated by sedimentary rocks (conglomerates, dolomites, sands, and clays); however, the waste stored in the Horse Creek tailing pond originates from the Crystalline–Mesozoic Zone of the Eastern Carpathians, specifically from the district characterized by polymetallic and manganese mineralization associated with epimetamorphic rocks of the Tulgheș Lithogroup [19]. The metamorphic formations of the Tulgheș unit host massive polymetallic sulfide mineralizations in the Fundu Moldovei area. Within this complex, the Tulgheș 3 (Tg3) lithostratigraphic unit represents a metasedimentary rhyolitic formation associated with polymetallic ore deposits [20].

The ore deposits consist of sulfide minerals dominated by Cu-rich pyrite and chalcopyrite, associated with sphalerite and galena, and subordinately with arsenopyrite, pyrrhotite, tetrahedrite, bournonite, and ilmenite [21]. Consequently, the relatively high concentrations of Al, Fe, Mg, and K in the tailings are primarily linked to the presence of chlorite, sericite, biotite, and pyrite [22]. The Horse Creek tailing pond was constructed using waste generated by the Fundu Moldovei processing plant, which extracted Cu from polymetallic ores until 2004 [23,24]. After processing, the material was transported through a pipeline and deposited in the Horse Creek riverbed as a tailing pond with a decantation basin. Following the closure of mining operations in 2004, the tailing pond was abandoned and placed under passive conservation without subsequent remediation measures.

2.3. Soil Sampling and Preparation

Six samples were collected from the surface of the spoil heap: four from its peripheral zones (S2.1–S2.4) and two from the central area (S2.5 and S2.6) (Figure 1b). The seventh sample (S2.7) was collected from the area covered by allochthonous material, where the layer reached its maximum thickness (5–7 cm) near the contact with the slope. The dominant grain-size fractions within the spoil heap, sample moisture content, the degree of comminution, and analytical variability were identified as key parameters influencing the observed fluctuations in major oxide and trace element concentrations. Fieldwork was conducted over a single day (24 June 2025). Approximately 500 g of sediment was collected from each sampling location and stored in high-density polyethylene zip-seal bags [25]. After each sampling, the knife blade was rinsed with distilled water.

The first set of sample capsules was prepared using unprocessed (unmilled) sediments at their in situ moisture content, and pXRF scanning was performed the following day. After homogenization, the sediment samples were packed into plastic cups with a diameter of 32 mm, sealed with a 6 µm Mylar film, and subsequently analyzed using the pXRF instrument [26]. This procedure was designed to minimize the influence of temperature and moisture variability at the spoil heap surface, which could otherwise affect measurement accuracy. Following the initial analysis, the protective film was carefully removed, and the samples were left to air-dry at room temperature for ten days (23–27 °C). After this period, pXRF measurements were repeated.

The mass of each cup was recorded before and after drying with a precision of 0.01 g, and moisture content (%) was calculated based solely on the sediment mass, excluding the container [27].

The samples stored in bags were transferred into Petri dishes and allowed to dry for ten days at room temperature, under environmental conditions comparable to those used for the capsules. After drying, visually identifiable organic debris (e.g., leaf fragments) was manually removed with tweezers.

Five samples (S2.1–S2.4 and S2.6) were selected to assess the variation in PTEs as a function of particle size. The mineral material was sieved into the following grain-size fractions: 200–125 μm , 125–63 μm and $\leq 63 \mu\text{m}$, using the AS200 vibratory sieve shaker (Retch GmbH, Germany) for 3 min at an amplitude of 1.5 [28]. Previous studies have indicated that the waste pile is predominantly composed of medium and fine sand (>61%)[22], followed by silt (35.3%)[24], without significant contribution from particles larger than 2 mm. Therefore, the fine sand, very fine sand, and silt fractions represent the most relevant components for determining the concentration of PTEs. Samples S2.5 and S2.6 were collected from a proximity to each other (approximately 5 m apart); therefore, grain-size fractionation was performed only for the latter. Sample S2.7 was excluded from granulometric analysis, as it does not fully represent the waste heap material due to the presence of allochthonous deposits.

Reducing the sample size by grinding increases sample homogeneity and considerably improves the quality of the pXRF analysis results. Two aliquots of each composite sample were prepared under different conditions. The first aliquot was oven-dried at 105 °C for 8 h over two consecutive days and subsequently ground manually using an agate mortar and pestle [29]. The second aliquot was air-dried at room temperature and then ground using a Pulverisette 6 planetary ball mill (Fritsch GmbH, Germany).

To minimize atmospheric exposure after removal from the oven, the capsules were immediately sealed with a glass lid and ground only after reaching room temperature. The agate mortar and pestle, the 250 mL milling bowl, and the grinding balls were thoroughly rinsed with deionized water between samples to prevent cross-contamination [30]. Sample preparation followed the “one-third rule” recommended for dry milling in planetary ball mills [31].

Mechanical grinding was carried out in a stainless-steel grinding jar using nine new tempered steel balls with a diameter of 20 mm [32]. An amount of sediment equivalent to twice the volume of a capsule (approximately 20 g) was milled at a rotational speed of 300 rpm for 3 minutes. After milling, each capsule was gently tapped on the laboratory bench to resettle the particles and obtain a leveled surface.

2.4. pXRF Measurements and Quality Control

Major element oxides and potentially toxic elements (PTEs) were determined using a portable S1 Titan 800 X-ray fluorescence (pXRF) analyzer equipped with a 50 kV X-ray tube (Bruker, Kennewick, WA, USA). Measurements were performed for 90 s using the GeoExploration application and the Oxide3phase method. The resulting spectra and analytical data were processed and visualized using Bruker Data Stream software [33].

Based on the mineralization characteristics of the Tg3 lithostratigraphic unit, copper (Cu), zinc (Zn), lead (Pb), and arsenic (As) were selected as target PTEs, together with two major oxides (SiO_2 and Fe_2O_3), to evaluate concentration variability as a function of sample preparation method. The pXRF data were converted to oxide values using standard conversion factors for SiO_2 and Fe_2O_3 and reported as percentages [34]. Comparability between datasets was ensured by accounting for variability within paired analyses (e.g., hand-ground versus ball-milled samples).

Hand-ground samples were scanned in triplicate by rotating each cup between measurements [12]. The mean value and standard deviation were used for comparative analysis with the results obtained using other preparation methods.

Quality control was performed by comparing the concentrations of selected elements in the seven samples with those previously determined by energy-dispersive X-ray fluorescence (EDXRF) using an Epsilon 5 XRF instrument for 30 samples from the same site [35]. In that study, samples

were dried at 50 °C for 24 h and subsequently sieved through meshes of varying sizes. Therefore, the results can be directly compared with the present data obtained from samples dried at room temperature. The mean values measured by pXRF, with the exception of Cu, closely correspond to the previous research for Pb (1204 mg kg⁻¹), Zn (222 mg kg⁻¹), and As (155 mg kg⁻¹) [35](see Section 3.1). These discrepancies are interpreted as reflecting post-depositional changes in the material rather than analytical uncertainty.

In the present study, relative standard deviation was employed to assess the reproducibility of results obtained from triplicate samples, which were dried at 105 °C and manually ground, for both analyte groups: oxides and PTEs [36].

2.5. Data Analysis

Descriptive statistics for the pXRF measurements were generated using SPSS 27 (International Business Machines Corporation, IBM) and OriginPro 2025 (OriginLab Corporation, Northampton, MA, USA), including measures such as the mean, minimum, maximum, standard deviation, and skewness. Nonparametric statistical approaches are well-suited for small datasets, with the Wilcoxon signed-rank test effectively mitigating the influence of extreme outliers in skewed distributions [37]. Mine waste materials, including tailing ponds, typically produce datasets that deviate from normal distribution patterns, particularly for PTEs and specific oxides. In cases where continuous variables exhibit non-normal distributions, the median is regarded as a more reliable measure of central tendency compared to the mean [38]. However, some authors suggest that normality constraints may be relaxed for small sample sizes [39]. The Shapiro–Wilk test remains the most statistically robust method for assessing normality under such conditions [40].

In this study, the gravimetric moisture content (%) and the ratio between the elemental concentration in the wet sample and that in the air-dried sample (C_w/C_d), visualized using a central scatter plot, were used as diagnostic indicators to identify potential anomalies, which were characterized by higher concentrations in the wet sample relative to those in the dry sample.

The null hypothesis (H_0) of the Wilcoxon signed-rank test asserts that the median difference between sample pairs ground manually (in triplicate) and those processed using a mechanical mill is zero. Under the assumption that the material in the tailing was relatively homogeneous after flotation, additional grinding does not provide new information regarding concentration. In contrast, the alternative hypothesis (H_1) posits that the median difference between the two datasets deviates significantly from zero.

In the second analytical framework, the null hypothesis (H_0) assumes significant differences between mechanically milled and unmilled samples dried at room temperature. Because both datasets present comparable moisture contents, the alternative hypothesis (H_1) reduces the role of textural variability as a factor influencing concentration differences.

3. Results

3.1. Statistical Approach

The SiO₂ content remained relatively constant across the three selected grain-size fractions. This behavior may be attributed to the high hardness of SiO₂, ranked 7 out of 10 on the Mohs scale, which preserves this oxide at higher concentrations within the coarse fractions. Conversely, this high hardness may also limit the mechanical breakdown of quartz, resulting in a lower SiO₂ abundance within the finer fractions. In contrast, the Fe₂O₃ content increased as the particle size decreased. The Fe₂O₃ value recorded in the very fine sand fraction was comparable to those observed in both grinded and ungrinded samples, indicating a distribution closer to normal (Table 1).

The mean concentrations of PTEs showed notably higher values for Pb (1391 mg kg⁻¹), Cu (505.1 mg kg⁻¹), and As (149.4 mg kg⁻¹) in the three analyzed grain-size fractions (not shown) compared with the mean concentrations in both the ground and unground samples (Table 1). Without exception, PTE concentrations progressively increase from medium sand (200–125 µm) to silt (≤63

µm). In the grounded and ungrounded samples, no consistent trend can be identified, except for Zn, which shows higher mean concentration in the ground samples.

Both major oxides and PTEs displayed a symmetrical distribution in the 200–125 µm fraction, with the exception of Fe₂O₃ and As. However, in the remaining two granulometric fractions, the skewness values indicate asymmetric data distributions (Table 1). The datasets for Cu and Zn in both grinded and ungrinded samples are characterized by pronounced skewness, while Fe₂O₃ shows a distribution around the mean, contrasting with the pattern observed for the other elements.

Table 1. Statistical indicators for major oxides and PTEs for three sample preparation methods.

		Texture ^a (µm)			Grinded samples ^b		Ungrinded samples	
		200-125	125-63	≤63	Ball mill	Mortar & Pestle ^c	Wet	Dry
Mean	SiO ₂	62.5	62	60.4	56	62.5	40.2	51.5
	Fe ₂ O ₃	4.4	5.7	8.2	6.8	7	5.4	5.9
	Cu	284.6	658	927.6	354.8	333.1	220	332.2
	Pb	740	1102.2	2331.2	943.1	844.6	930.8	1070.4
	Zn	58	141.8	462.4	125.4	126.2	211.7	289.7
	As	94	131.2	223.2	127	127.7	117.2	128.5
Min.	SiO ₂	48.4	57	55.5	39.1	46	27.6	37.3
	Fe ₂ O ₃	2.1	3.6	6.1	3.3	3.4	2.2	2.3
	Cu	42	56	92	55	59	50	56
	Pb	74	122	261	65	72.6	52	54
	Zn	27	60	88	48	49	53	64
	As	34	40	95	23	17.3	28	22
Max.	SiO ₂	75.1	75.5	68.2	77	77.3	52.8	63.7
	Fe ₂ O ₃	9.4	7.3	11.9	10	10.4	8.9	8.9
	Cu	621	2278	3103	1496	1521.3	696	1179
	Pb	1499	3492	7983	2465	2430	1931	2398
	Zn	92	427	1686	278	314.6	960	1263
	As	224	286	408.5	238	236	218	251
StDev	SiO ₂	10.2	7.6	4.91	11.2	10.1	8.8	10.3
	Fe ₂ O ₃	2.9	1.3	2.24	2.7	2.1	2.3	2.2
	Cu	287	947.4	1276.2	512.3	527.6	223.2	395.8
	Pb	552	1356.9	3184.5	795.9	773.3	634.7	794.2
	Zn	29.3	159.8	685.8	72.1	85.8	330.5	435.8
	As	74.4	92.8	120.2	78.4	66.9	68.2	82.9
Skewness	SiO ₂	-0.2	2.1	1.1	0.7	-0.1	-0.1	-1.6
	Fe ₂ O ₃	1.6	-0.8	1.4	0.4	0.4	0	-0.4
	Cu	0.6	1.8	1.7	2.4	2.5	2	2.1
	Pb	0.3	2	2.1	1.1	1.6	0.4	0.8
	Zn	0	2	2.2	1.8	2.2	2.6	2.4
	As	1.9	1.5	0.9	-0.3	0.4	-0.6	0.4

Note: ^aResults for 5 samples^a, ^bresults for 7 samples^b, ^caverage for triplicate samples^c.

3.2. The Effect of Sample Heterogeneity on pXRF Measurements

The concentration of PTEs across the three granulometric fractions showed a general increasing trend from medium and fine sand toward silt (Table 1). A detailed examination of the dataset for each sample indicates a decrease in PTE concentration in sample S2.3 between the medium- and fine-sand fractions, followed by an increase toward the finer fraction (Figure 2).

The increase in concentration from medium to fine sand was moderate for Pb (×1.4), As (×1.7), and Cu (×1.8), but more pronounced for Zn (×2.3). A similar trend was observed between the fine

sand and silt fractions. When comparing the largest and smallest particle-size classes, concentrations increased by approximately five- to sixfold for the first three PTEs, whereas Zn exhibited a particularly substantial increase ($\times 20$) (Figure 2).

The results further show that SiO_2 represents the highest compositional proportion of the waste material, with an average value of 61.6% and a variation range between 48.4% and 75.5% across the analyzed samples. The average Fe_2O_3 concentration is 6.15% and increased progressively from coarse to fine particles by a factor of approximately 1.3–1.4 (Table 1).

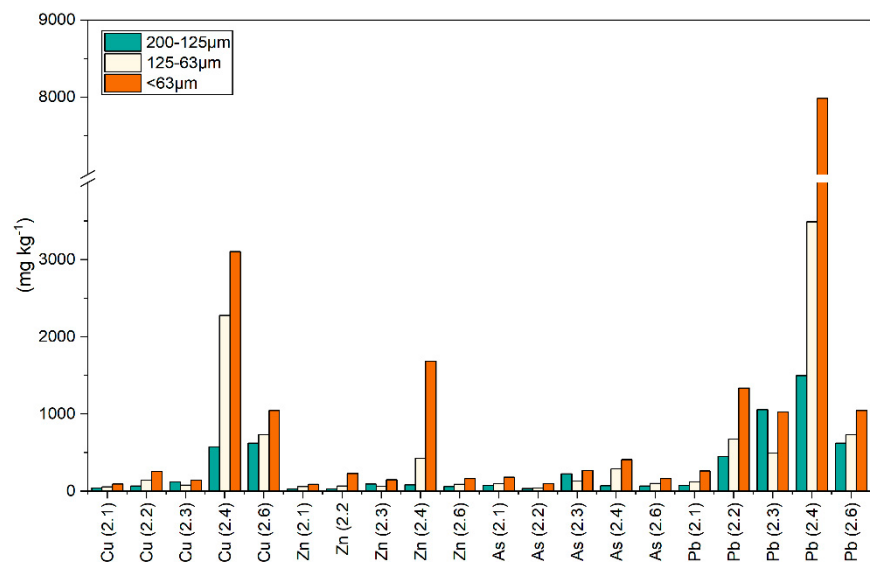


Figure 2. Concentration of PTEs in three particle size fractions.

Surface micromorphology and the presence of allochthonous sediments are key factors influencing moisture variability in certain areas of the tailings dump. After drying at room temperature, the sediment level in several containers dropped below the rim, which may have led to measurement inaccuracies. To remedy this problem, after sealing the container with the film, it was gently tapped on the work surface to ensure full contact between the sediment and the foil.

Unmoistened samples generally exhibited gravimetric moisture contents below 20% (ranging from 7.3% to 18.6%), with the exception of sample S2.6. This sample, collected from the temporary stream channel, show a substantially higher moisture content of 66.3%. Of the 72 pXRF measurements performed on unmoistened samples, most wet samples displayed lower concentrations than their corresponding air-dried samples at room temperature, for both oxides and potentially toxic elements (PTEs). However, five measurements did not follow this overall trend.

To further assess these discrepancies, the ratio between the element concentration in the wet sample and that in the air-dried sample (C_w/C_d), plotted against gravimetric moisture (%) in a central scatter representation, was employed. A ratio of $C_w/C_d = 1$ indicates no difference between wet and dry sample concentrations, while a ratio greater than one may reflect analytical bias or specific physical-chemical properties of the sample.

The highest supra-unitary C_w/C_d ratios were observed for Fe_2O_3 (1.36) and As (2.27) in sample S2.2, which had a gravimetric moisture content of 15.4%. The red-brown coloration of the material reflects geochemical heterogeneity associated with Fe_2O_3 enrichment. Notably, several samples with relatively low moisture contents ($<10\%$), including S2.7 (8.7%) and S2.3 (7.3%), also displayed supra-unitary C_w/C_d ratios for Cu, As, and Pb (1.08, 1.14, and 1.19, respectively). In contrast, the sample with the highest moisture content (S2.6) showed C_w/C_d values below unity (Figure 3).

These findings suggest that, at low moisture levels ($<20\%$), geochemical heterogeneity can lead to artificially elevated concentrations of certain elements in wet measurements relative to air-dried

samples, most likely as a result of the nugget effect. In addition, physical changes during drying—such as sample contraction, crust formation, and the development of microfractures (e.g., in samples S2.4 and S2.6)—may introduce further analytical uncertainties (Figure 3).

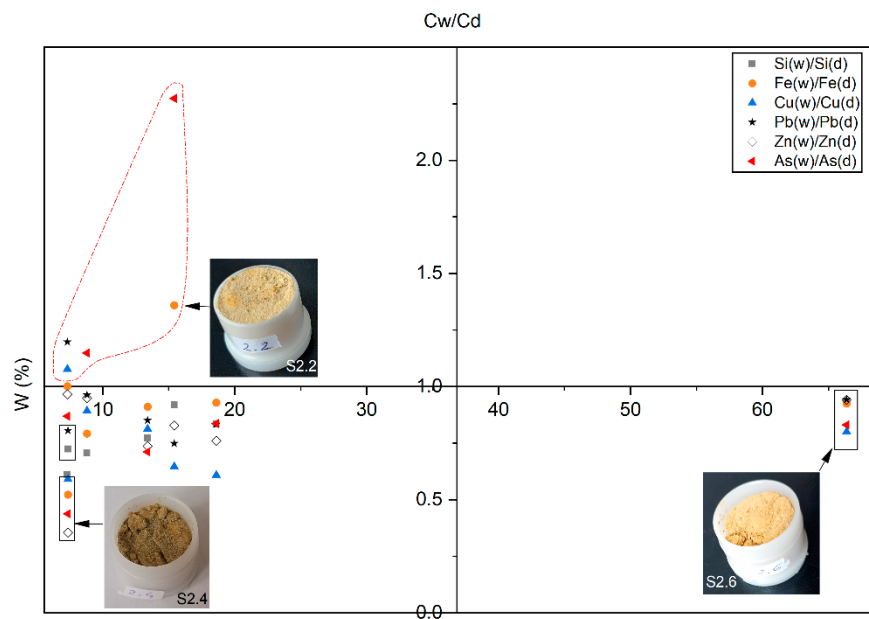


Figure 3. Relationship between Cw/Cd and gravimetric moisture (%).

The results of the Wilcoxon signed-rank test for paired samples indicate no statistically significant differences in the concentrations of PTEs and Fe₂O₃ between mechanical and manual grinding methods, with one exception. The null hypothesis—assuming no concentration differences between the two sample preparation techniques—was rejected only for SiO₂ (Table 2).

Both mechanically ground and unground samples share the characteristic of having been dried at room temperature, implying that residual moisture was not completely removed—unlike the samples dried at 105 °C and subsequently manually ground. Accordingly, the alternative hypothesis is supported. The Wilcoxon signed-rank test applied to these two sample sets confirms that the median difference between ball-milled and unground air-dried samples is not statistically different from zero (Table 2).

Table 2. Wilcoxon signed-rank values for paired samples.

	Ball mill vs. Mortar & Pestle	Ball mill vs. Ungrided dry samples
	Significance level	vs. decision
SiO ₂	0.01*	0.49
Fe ₂ O ₃	0.49	0.17
Cu	0.23	0.23
Pb	0.06	0.23
Zn	1	0.49
As	0.17	1

Note: The significance level was set at 0.05, *reject null hypothesis.

In the manually ground triplicate samples, the median values and the upper and lower whiskers show greater variability for oxides, while the variability of certain PTEs is markedly lower. This pattern reflects the intrinsic heterogeneity of the tailings pond material. The narrow whisker range observed for Cu—except in sample S2.4—further indicates low variability among triplicate measurements and relatively stable concentration levels associated with ore processing (Figure 4).

The box plot reveals a clear pattern in elemental concentrations across the triplicate samples, allowing two compositional clusters to be distinguished: one comprising Cu, Pb, and Zn, and a second characterized by Fe₂O₃ and As (Figure 4). The strong Spearman correlation coefficients between Cu and Pb (0.83) and between Fe₂O₃ and As (0.81) indicate common mineralogical sources, such as bournonite and arsenopyrite. In contrast, although the correlation between Pb and Zn is relatively high (0.68), it is noticeably weaker by comparison.

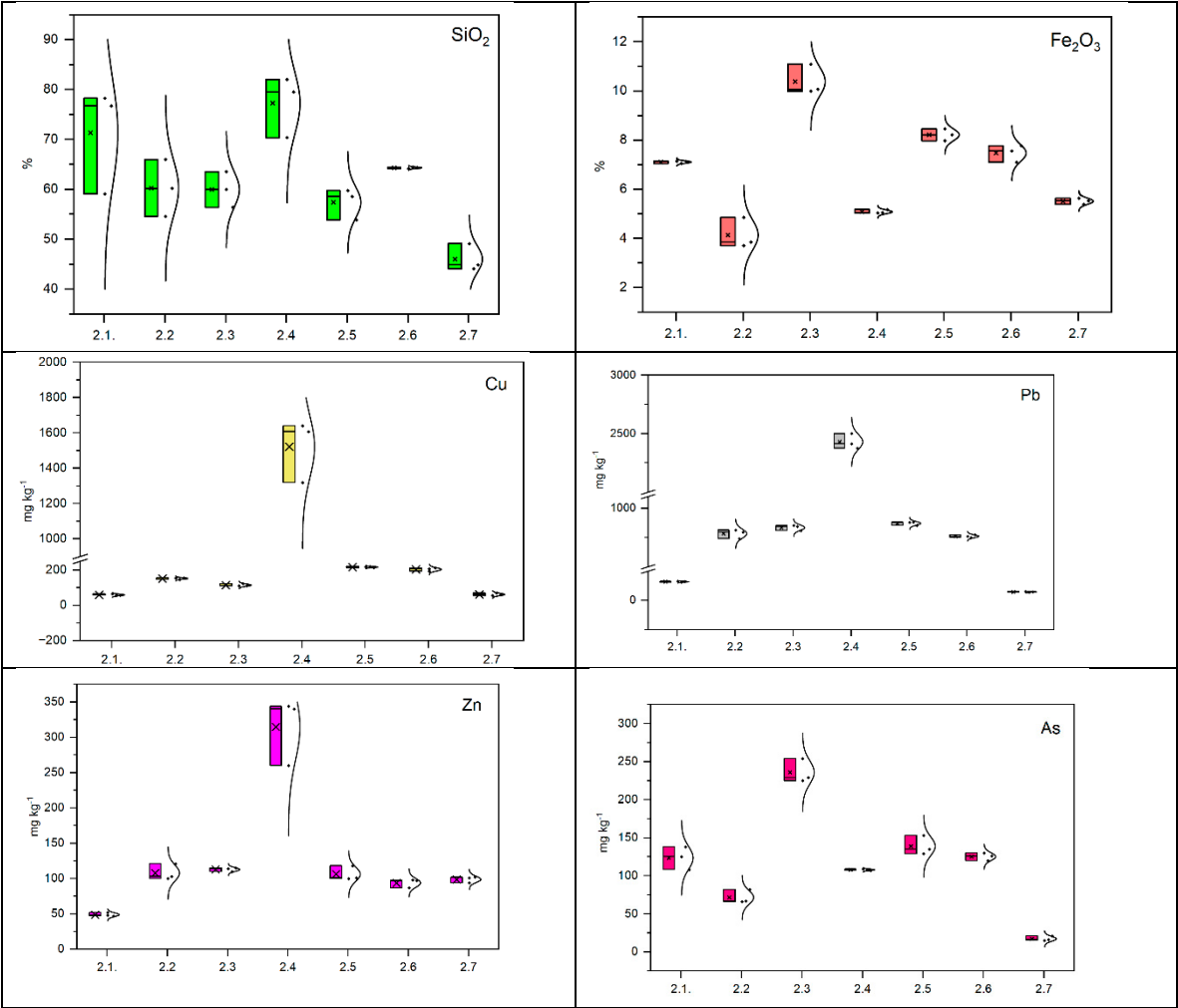


Figure 4. Boxplot representation of triplicate samples for oxides and PTEs.

4. Discussion

Particle-size distribution controls the retention and mobilization of various elements in sediments. Numerous studies on PTE-contaminated sediments indicate that decreasing particle size is commonly associated with increasing trace-element concentrations (grain-size effect) [41](Figure 2). In contrast, coarse-grained materials typically exhibit a lower sorption capacity for PTEs compared to fine-grained fractions [10]. This relationship is also observed in the Horse Creek tailings pond sediments.

The similarity between mean and median values reflects the central tendency of trace-element concentrations in soils originating from different geographical regions and exhibiting variable textural characteristics along the soil profile [42]. In the present study, mean and median values are comparable only for major oxides (SiO₂ and Fe₂O₃), whereas pronounced differences are observed for PTEs, with the exception of Zn in the 125–200 μm fraction (58 and 59 mg kg⁻¹, respectively). These results indicate that, unlike soils, PTE concentrations in the tailings pond show substantial variability both within each of the three particle-size fractions and among individual samples. Consequently, evaluating PTE concentrations solely on the basis of particle-size distribution is not appropriate for

this type of environment. Nevertheless, when contamination in adjacent soils is also considered, this approach may represent the most appropriate methodological option.

Fine sand exhibits intermediate PTE concentrations relative to medium sand and silt, a pattern that is consistent with other environments, such as fluvial sediments [43]. In none of the three fractions are the PTE concentrations identical to those obtained from samples prepared using the other methods; however, the mean concentrations of Pb and As in the very fine sand fraction are very similar to those measured in unground samples dried at room temperature (Table 1).

Dedicated pXRF analytical protocols, supported by numerous published studies, indicate that increasing sample moisture generally results in lower measured concentrations of certain PTEs and associated compounds [9,30]. Dedicated pXRF analytical protocols, supported by numerous published studies, indicate that increasing sample moisture generally results in lower measured concentrations of certain PTEs and associated compounds (Table 1).

Although no formal minimum moisture threshold is required for reliable PTE analysis, a moisture range of 5–20% is generally considered optimal for minimizing analytical uncertainty. Air-drying samples can increase pXRF-measured concentrations; however, the magnitude of this effect depends on soil texture and mineralogical composition [26,44].

Previous studies have reported no significant differences between air-dried soil samples and those with moisture contents of approximately 10% [45]. In the present dataset, one sample (S2.4) with a moisture content below 10% (7.35%) exhibits greater variability in PTE concentrations compared with other samples below the same threshold, as well as those within the 10–20% moisture interval (Figure 3). This sample was not homogenized by grinding, and the observed deviation may therefore reflect a nugget effect. Nevertheless, the particle size of the waste material (<2 mm), originating from primary ore processing, provides a degree of homogeneity that is generally adequate for pXRF analysis.

The ratio between the concentration of an element measured at maximum water content and its concentration in the dry certified reference material was employed to estimate the attenuation coefficient [46,47]. The simple C_w/C_d ratio, together with gravimetric moisture content (%), enables the visualization and identification of elements exhibiting supra-unitary values. Arsenic exhibits supra-unitary ratios in two samples (S2.2 and S2.7), occurring at distinct moisture contents of 15.4% and 8.7%, respectively (Figure 3).

Several authors have reported that, at a moisture content of 20%, As concentrations decrease by approximately 37% relative to dry samples [48]. When the C_w/C_d ratio for As obtained for sample S2.7 is compared with those of samples exhibiting similar moisture contents (e.g., S2.3 = 7.31% and S2.4 = 7.35%), the latter display sub-unitary ratios. Although pXRF measurements may be affected by Pb–As interference [26], this effect cannot explain the present observations, as the supra-unitary C_w/C_d values for As (S2.2 and S2.7) do not correspond to the sample characterized by elevated Pb concentrations (S2.3). Since pXRF measurements cannot be conducted at the exact same location within the sample cup under both moisture conditions, it is plausible that an additional factor contributed to the result obtained for sample S2.4.

Silicon oxide is more strongly affected by moisture, a trend also reported for other environmental matrices, including marine sediments and tropical soils [49,50]. In contrast, the C_w/C_d values for Fe_2O_3 are closer to unity than those observed for SiO_2 , indicating a lower variability between the two moisture conditions. Reliability reflects the proportion of “true” information in measurements, with higher values indicating greater consistency [51]. A two-way random-effects intraclass correlation analysis yielded a lower mean reliability for SiO_2 (0.83) than for Fe_2O_3 (0.96), consistent with the patterns indicated by the C_w/C_d ratios. The performance of pXRF analysis on wet samples is generally reduced for light elements such as Si [49], whereas it is improved for heavier elements including Fe, Cu, Pb, Zn, and As [9,46,47]. Nevertheless, these effects are highly dependent on the type of sample.

The quantification error in powder samples is primarily attributable to grain-size effects, while the impact of heterogeneity can be mitigated through grinding [13]. Allocating the same preparation

time (3 minutes) for both manual and mechanical grinding does not result in significantly different pXRF measurements. A Wilcoxon signed-rank test performed on paired samples subjected to manual and mechanical grinding revealed no significant concentration differences for PTEs; however, for oxides, the null hypothesis was rejected in the case of SiO_2 (Table 1, 2).

Geochemical and environmental datasets are often spatially dependent, and their processing commonly involves transformations, such as the natural logarithm [52]. After applying an $\ln$ -transformation to SiO_2 , the data for mechanically ground samples remain non-normally distributed ($p = 0.019$). In sample S2.7, the SiO_2 content decreases from 49% in the manually ground sample to 39.1% in the mechanically ground sample, both values being lower than the mean of the other samples (S2.1–S2.6), which are 69.1% and 55.9%, respectively. Examination of other oxide concentrations in S2.7 revealed a two- to threefold increase in CaCO_3 (7.9% and 8.9% in the mechanically and manually ground samples, respectively) compared with the remaining samples. A slight spatial variation is observed for MgCO_3 (2.9% and 2.3%), with values comparable only to those of samples S2.5 and S2.6, likely reflecting material transport from the recently deposited waste toward the central part of the dump (Figure 1c).

The deposition of new materials along the margins of the waste dump, originating from the overburden of the nearby limestone quarry, has resulted in an unintended form of ecological rehabilitation. The newly deposited material exhibits distinct geochemical properties and a finer texture compared to that of the Horse Creek waste dump, which promotes water retention and facilitates the establishment of vegetation along the temporary watercourse.

5. Conclusions

The analysis of sediments using pXRF provides a significant advantage for assessing the geochemical characteristics of tailing ponds; however, sample preparation methods may yield divergent results. The concentration of potentially toxic elements (PTEs) increases inversely with particle size, although in the case of oxides this trend persisted only for Fe_2O_3 , while the SiO_2 content was not affected by particle-size variation. The magnitude of concentration increases among different particle-size fractions is not uniform across all PTEs.

After samples were air-dried at room temperature, pXRF measurements for both PTEs and oxides yielded higher values compared to those obtained under field-moist conditions. Central scatter analysis indicates that some PTEs and oxides exhibited higher values in the moist samples than in the dried ones, a phenomenon likely attributable to geochemical heterogeneity within the sample. Moreover, SiO_2 content is more strongly influenced by moisture compared to Fe_2O_3 .

For an equivalent working time, pXRF measurements on samples ground in a ball mill and subsequently homogenized in an agate mortar showed comparable results, with the exception of SiO_2 . Pre-treatment—specifically, the drying method and spatial variability resulting from the post-depositional evolution of the tailing deposit induces small-scale variations in oxide content and PTE concentrations.

pXRF results obtained from manually ground triplicate samples demonstrate both the spatial variability of the dominant compound (SiO_2) and the co-occurrence of certain PTEs (e.g., Cu–Pb), which reflect the source minerals within the deposit.

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