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Portable X-ray Fluorescence (pXRF) as a Tool for Environmental Characterisation and Management of Mining Wastes: Benefits and Limits

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Abstract: Portable X-ray fluorescence (pXRF) is one of the main geochemical techniques employed in multi-elemental analysis screening for contaminated sites management. As the confidence of pXRF analyses are matrix-specific, efforts are made to provide studies of pXRF quality on different geochemical datasets, focusing on less investigated elements such as mercury (Hg) and antimony (Sb), to help both new and experienced users. The analysis of environmental solid samples from two decommissioned mining sites in NE Italy, characterised by Pb-Zn and (Hg-rich) Cu-Sb ore deposits, were prepared with two different protocols and compared with traditional destructive analyses. Sample composition was found strictly dependent to the occurrence of false positives and overestimation at low concentrations. In contrast, milling the sample did not produce major variations in the overall quality. Lead (Pb), Sb, and Zn reached the definitive data quality in at least one of the two datasets. Consequently, as far as a thorough QA/QC protocol is followed, pXRF can rapidly produce chemical data that is as accurate as that produced by destructive standard laboratory techniques, thus allowing to identify potential sources of contamination that could be reprocessed for the extraction of valuable elements and mitigating the dispersion of contaminants and ecological or health risks.

Keywords: portable X-ray fluorescence (pXRF); validation; mining wastes; contamination; sample preparation

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1. Introduction

Portable X-ray fluorescence (pXRF) is widely accepted as geochemical in situ or laboratory instrumentation in several scientific and industrial fields such as mining exploration, environmental characterisation of contaminated sites for remediation, waste management, or archaeometry. It is a non-destructive, rapid, simultaneous multi-element analytical technique for solid sample analysis. Since it can be used in situ or in the laboratory for the analysis of unprepared or lab-prepared samples, it provides a cost- and time-saving alternative solution compared to the more accurate and expensive standard laboratory analytical procedures (e.g., Inductively Coupled Plasma Atomic Emission and Mass Spectrometry—ICP-AES and ICP-MS; [1–4]). Moreover, pXRF allows for the rapid collection of a considerable amount of data, facilitating geostatistical approaches and decision making. Even showing a relatively elevated analytical uncertainty, as long as a quality assurance/quality control (QA/QC) for pXRF measurement is followed, the confidence level of the decisions made onsite will actually be higher than with a small number of laboratory-prepared samples and fewer geochemical data [5]. Thanks to its compact size and weight, pXRF can also be used in remote regions, providing cost-effective technology for real-time data, especially when immediate action is needed as a result of environmental disasters [6].

The description of the technique and its applications have been reported in several studies and reviews [5,7,8]. Portable XRF offers many advantages and few disadvantages compared to conventional laboratory analysis of environmental samples. Sensitivity to trace element variations is one of the strong points of pXRF. However, there are possible pitfalls when a new pXRF instrument is employed, and it is worth focusing on the possible errors that occur during pXRF analyses since these instruments can be easily used by any operator.

The limit of detection (LOD) varies with different analysers and measurement time. Overall, the best instruments are capable of a LOD in the 5 to 100 mg/kg range for elements with an atomic number (Z) between 19 (K) and 68 (Pb). Hence, pXRF is not suitable for analysing very low concentrations although the sensitivity can vary among different analytes. For most of the elements of environmental concern, pXRF may not be capable of discriminating values above or below national regulatory threshold levels (e.g., in soils, for public, private, and residential use, the limit for Hg is fixed at 1 mg/kg according to Italian Legislative Decree 152/2006 [9]). However, this technique is particularly useful in the detection of samples with “anomalous” high concentrations with respect to background levels or weakly impacted environmental areas. Based on pXRF analysis on large datasets, a subset of samples can be selected for further analyses such as, for instance, mineralogical, compositional, or related to the speciation of potentially toxic elements (PTEs). Otherwise, old mining wastes with exceptional high metal concentrations can be identified for potential reprocessing. Thus, the extraction of valuable elements would be followed by the mitigation of dispersion of the contaminant and ecological or health risks. However, to achieve the best overall results, pXRF data should be validated using conventional laboratory-based spectrometric techniques, and geochemical expertise is required for the reliable interpretation of pXRF data. This is especially important since pXRF can over- or underestimate concentrations as well as detect false positives, with varying levels of accuracy for different elements.

The handling of the sample prior to pXRF analysis greatly affects the accuracy of the technique. Variations in soil moisture, particle size, heterogeneity, and density directly affect the accuracy of the results. For instance, Laiho and Perämäki [10] found that sample preparation could lead to more significant errors than the use of different pXRF instruments. When the sample preparation procedure is the same as the laboratory standard procedures, and the sample is sieved, dried, milled, and homogenised (“lab-prepared samples”), pXRF can provide accurate results comparable to destructive standard laboratory analyses (e.g., ICP-OES, ICP-MS), hereafter referred to as “laboratory analyses” [5,6,11]. However, the standard procedure can be so time-consuming that pXRF analysis on lab-prepared samples may not be cost-effective, as the gain in accuracy is followed by a reduction in the geochemical dataset.

The last issue affecting pXRF analyses is related to interferences and matrix effects. Interferences among elements can be produced by overlaps of the characteristic X-ray emission lines. Matrix effects appear as either X-ray absorption or enhancement phenomena, which can affect the determination of a single analyte. In the absence of a clear bias with any possibility to correct the output (e.g., adjusting the calibration slope of the linear regression), those errors may not be corrected. However, those effects can occur particularly in sites characterised by a uncommon geochemical composition, such as metal-bearing mineralised rocks or geological materials affected by mining, where trace elements that normally occur in the environment in the ppm or ppb range can reach notably higher concentrations, up to wt.%, with a variability of several orders of magnitude [12].

Mining exploration and industrial use of common and uncommon elements (e.g., precious metals, rare-earth elements—REEs) have increased in recent years due to an exponentially growing demand. As a result, there is still substantial concern regarding the subsequent risk of dispersion into the environment of those elements known for their high toxicity, such as mercury (Hg) or antimony (Sb). In the last decades, many studies [7,11,13–17] have reported the performance of pXRF instruments based on QA/QC validation procedures using certified reference materials (CRMs), blank samples, and/or traditional laboratory analyses on site-specific samples, studying different groups of elements in various matrices. Moreover, pXRF analyses of soil, lato sensu, samples are usually performed on common elements such as base metal(loid)s (e.g., As, Cu, Fe, Mn, Pb, Zn), whereas, curiously, highly toxic elements such as Hg and Sb have not been considered or have not been found in concentrations high enough and were detected in a small number of studies, e.g., [18,19]. Thus, the main purpose of this research was to evaluate the advantages and disadvantages of the use of pXRF on samples collected from two different decommissioned mining areas in Italy characterised by Pb-Zn and (Hg-rich) Cu-Sb ore deposits found to have very low to very high concentrations of As, Cu, Hg, Pb, Sb, and Zn. In order to reach this objective, a validation with traditional laboratory analyses considering various metal(loid)s was performed on a large geochemical dataset, including samples of soils, stream sediments, and mining wastes. Moreover, this research may provide insights as to how analytical determinations using pXRF can be influenced by (1) different spectral interferences and matrix effects at Pb-Zn and Cu-Sb mining sites, (2) low concentrations, and (3) heterogeneity and sample preparation.

2. Materials and Methods

2.1. Sampling Strategy and Sample Preparation

A total of 95 discrete samples of soils, stream sediments, mine wastes, and flotation tailings from two decommissioned mining sites in the Friuli Venezia Giulia Region (north-eastern Italy) were collected and analysed by means of pXRF, ICP-MS, and DMA-80 for As, Cr, Cu, Fe, Hg, Mn, Pb, Sb, and Zn determination. The two mining sites are the carbonate-hosted "Alpine-type"/"Mississippi-Valley-type" (MVT) Pb-Zn Raibl mine [20–23] and the Mt. Avanza "fahlore-type" Cu-Sb(-Ag) tetrahedrite mine [24,25]. The Pb-Zn Raibl site (46.442772° N, 13.568707° E) is a base metal hydrothermal ore deposit hosted in a Triassic massive dolomitic reef, characterised by a mineralogical assemblage where sphalerite (ZnS), galena (PbS), and pyrite/marcasite (FeS_2) are the dominant constituents. The host rocks generally show a dominant carbonate composition. The main lithology is Triassic dolostone with a limited presence of shales, sandstones, tuffs, and ignimbrites [26]. At the Cu-Sb(-Ag) Mt. Avanza site (46.618780° N, 12.755281° E), the ore is composed of a (Zn-Hg)-rich variety of tetrahedrite, a complex Cu-Sb sulfosalt hosted in Palaeozoic rocks with a more pronounced silicate composition. The ore veins are located at the tectonic interface between the metamorphic Devonian limestones and Carboniferous, siliciclastic metapelites [24].

From each original sample, two aliquots of 0.5–1 kg were collected. Rock and plant fragments were removed, and the aliquots were manually pre-homogenised in situ. Once in the laboratory, the samples were dried in the open air to prevent Hg volatilisation and sieved using a 2.0 mm sieve. The first aliquot was heterogeneous and prepared via a "fast lab-preparation" mode similar to the "intrusive-unprepared" mode reported by the U.S. EPA [11], with a very similar approach to the GTK procedure described by Laiho and Perämäki [10] for sampling preparation. This "fast lab-preparation" mode simply consists of drying and sieving the sample using a 2.0 mm sieve and placing it into a pXRF sample cup. This procedure is a good compromise in terms of time if compared to the in situ mode ("point-and-shoot"), during which the analyser probe is placed in direct contact with the soil surface for a real-time measurement. The only differences between the procedure followed in this study and the GTK are represented by the use of 5 g of the sample placed in sample cups with a window X-ray film (Kapton) instead of plastic bags and a counting time of 60 s (three beams with different keV of 20 s each) instead of 120 s. The second aliquot of each sample was treated following a "lab-type preparation" [5], which is the "intrusive mode" described by the U.S. EPA [11], consisting of a time-consuming procedure in which 5 g of the sample were dried, milled in a tungsten carbide (WC) mill or an agate mortar, and homogenised into a fine powder.

2.2. Analytical Determinations by Means of Portable X-ray Fluorescence (pXRF)

In this research, an Olympus Vanta C Series with a 4 W Ag anode X-ray tube (VCA) and a silicon drift detector was used. The VCA has an excitation source ranging from 8 to 50 keV and is capable of detecting elements from magnesium (Mg) to uranium (U). As is the case with many pXRF instruments, there are various factory methods available, each with different calibrations. The “soil” method is more suited for trace concentrations, whereas the “geochem” method is more accurate at higher concentrations. Both methods were used to determine as many elements as possible with the best data quality [27] without moving the analyser between two measurements [5]. In this study, pXRF data > 1 wt.% were selected from the geochem method, whereas values < 1 wt.% were determined using the soil method. Both methods used three beams set to 20 s each, with a total of 1 min for analysis, replicated three times. Although the payback for longer analyses would be lower LODs, a reasonable measurement time was selected to maintain the analysis fast enough to characterise a large number of samples. The accuracy was evaluated by means of certified reference materials (CRMs; “PACS-3” and “MESS-4”, Marine Sediment, NRCC, Whitehorse, YT, Canada), which were analysed in the same batch of samples using both methods.

2.3. Confirmatory Analyses: Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Direct Mercury Analyser (DMA-80)

As a confirmatory analysis for the determination of metals (Cu, Fe, Mn, Pb, Zn) and metalloids (As, Sb) except for Hg, 250 mg of “lab-prepared” samples were acid-digested in PTFE vessels through a total acid dissolution in a closed microwave system (Multiwave PRO, Anton Paar) using two heating steps. In the first mineralisation step, inverse aqua regia (3:1, HNO_3 67–69% and hydrochloric acid HCl 34–37%; hydrofluoric acid (HF, 47–51%, VWR Normatom), suprapure H_2O_2 (30%, Merck, only in the case of soil samples), and U.S. EPA method 3052 [28] were used. In the second step, boric acid (suprapure H_3BO_3 6%, Merck) was added to buffer the excess HF. Blank samples and CRMs were also digested for each microwave batch to evaluate the quality of the analysis. After mineralisation, the solutions were diluted up to a volume of 25 mL by adding Milli-Q water and stored at 4 °C until analysis. Total digestion with HF was chosen for its capability to dissolve refractory minerals such as silicate minerals.

Major and trace elements were determined by means of ICP-MS (NexION 350x equipped with an ESI SC autosampler, Perkin Elmer). In order to avoid and minimise cell-formed polyatomic ion interference, the analysis was performed using Kinetic Energy Discrimination (KED) mode. The instrument was calibrated via an analysis of standard solutions ranging between 0.5 and 500 μg/L prepared by dilution from multistandard solutions for ICP analyses (Periodic Table MIX1 and MIX2, TraceCERT Sigma-Aldrich). Several aliquots of CRMs were analysed to check for accuracy, and allowable recoveries ranging between 70–119% (PACS-3) and 83–107% (MESS-4) were obtained. Except for Cu in PACS-3 CRM, ICP-MS produced 106 of 112 results (94.6%) within the 80–120% recovery acceptance range for all analytes and replicates in the two CRMs. Moreover, potential matrix effects were evaluated by means of laboratory-fortified samples prepared by spiking a standard solution different from that employed for instrument calibration (Multielement quality control standard for ICP, VWR Chemicals) into actual samples. The repeatability of the ICP-MS analysis expressed as RSD% was <3%.

Total Hg in powders was determined using a Direct Mercury Analyzer (DMA-80, Milestone, Sorisole, Italy) atomic absorption spectrophotometer, according to EPA method 7473 [29]. The LOD was calculated as 3 times the standard deviation of 10 blanks and divided by the slope of the calibration curve was 0.004 mg/kg. Regarding accuracy, acceptable recoveries were obtained using certified reference material (PACS-3), ranging between 100 and 105%.

All ICP-MS and DMA-80 analytical results were at least 10 times over the LODs. Data below such threshold were not considered in the statistical analysis. A summary of the accuracy of both methods is reported in Table S1.

2.4. Statistical Analysis

Data were processed in Python, with SciPy as the main package used for statistical analysis. Accuracy was determined by "recovery" calculated with ((pXRF value/CRM value) × 100), while repeatability, which is indicated as precision in the U.S. EPA report [11], was determined by RSD% as ((standard deviation/mean) × 100) on replicates for each analyte and technique. For further statistical analysis and data quality levels for pXRF results, the U.S. EPA [11] procedure was followed according to the majority of recent studies, e.g., [13,24,25,30]. Comparability of pXRF with confirmatory data (ICP-MS and DMA-80) was assessed using linear regression statistics, where optimal correlations were found with a coefficient of determination $r^2 = 1$, slope equal to 1, and intercept with the y-axis equal to 0. Since a wide range in concentrations can be associated with a wide range in variance, to provide a correlation that was equally influenced by both high and low values, all data were $\log_{10}$ transformed according to the U.S. EPA method [11], providing equal weight in the square regression analysis to both small and large values. A Z-test was used to test the statistical similarity between the slope regression and an ideal slope = 1 and between the y-intercept of the regression function and an ideal y-intercept = 0. Furthermore, the *t*-test was also carried out on $\log_{10}$-transformed data to evaluate if the two datasets, respectively, obtained by means of pXRF and the confirmatory data for each element and sample treatment procedure belong to the same population, implying that any significant difference between the two analytical techniques occurred. *t*-Test, slope and y-intercept z-tests are successful for p-value > 0.05. Lower values of p-value imply significant differences between sample populations or from the ideal slope and y-intercept and vice versa. According to criteria established by the U.S. EPA [11], 3 levels of pXRF data quality can be defined: the definitive level is considered the highest level of quality, quantitative screening level data provide the quantification although it may be relatively imprecise, whereas qualitative screening level data indicate the presence or absence of elements of interest but do not provide reliable concentration estimates (Table 1).

Table 1. US EPA Criteria for establishing data quality [11].

Data Quality Level	Statistical Parameter
Definitive	r^2 = 0.85 to 1.0. The repeatability (RSD%) must be less than or equal to 10%, and inferential statistics indicate the two data sets are statistically similar.
Quantitative screening	r^2 = 0.70 to 1.0. The RSD% must be less than 20%, but the inferential statistics indicate that the data sets are statistically different.
Qualitative screening	r^2 = less than 0.70. The RSD% is greater than 20%. The data must have less than a 10 percent false-negative rate.

Lastly, a "site-specific accuracy" was calculated ((pXRF concentration/ICP-MS or DMA-80 concentration) × 100) and used to highlight method detection limits (MDLs) and concentration effect issues for the analysis of pXRF [11]. The MDL is defined as a threshold below which the analytes exhibit a region where there is no longer a linear relationship.

3. Results

3.1. Accuracy and Repeatability: pXRF vs. Certified Reference Materials (CRMs)

Accuracy refers to the degree to which a measured value for a sample agrees with a reference of true value for a CRM. An acceptable range of 80–120% of recovery with respect to the certified value was used to evaluate accuracy and two CRMs (PACS-3 and MESS-4) were analysed via pXRF for this purpose (Table 2). Except for Hg and Sb, which were not detected by pXRF, acceptable recoveries were obtained for Cr, Fe, Mn, Pb, and Zn. In the case of Cu, accuracy was acceptable only in the PACS-3, which has higher concentrations of Cu, and As was not acceptable in either, with the better recoveries on the MESS-4 than in the PACS-3 most likely due to interferences related to the relatively higher concentration of Pb in PACS-3. Repeatability expressed as RSD% was <10% for all the analytes, with the lone exception of Pb in the MESS-4, which showed a slightly higher value (13%). In the case of As, the accuracy was lower in PACS-3, which has a higher Pb content (As mean recovery = 164% with Pb concentration = 188 mg/kg) than in MESS-4, which, conversely, has a concentration of Pb one order of magnitude lower (As mean recovery = 121% and Pb = 21.5 mg/kg) because the As-K and Pb-L X-ray overlaps can be so severe that the resolution may not be enough to discriminate between the two elements [7], and the identification of As may be compromised. In fact, when the Pb:As ratio exceeds 10:1, As is not efficiently detected by means of pXRF [31].

Table 2. QA/QC of pXRF data from CRMs. Data presented in bold are out of the acceptable quality range.

Element	CRM Value (mg/kg)		Mean Accuracy—Recovery (%)		Mean Repeatability—RSD (%)	
	PACS-3	**MESS-4**	**PACS-3**	**MESS-4**	**PACS-3**	**MESS-4**
As	30.3	21.7	**164%**	**121%**	3.9%	6.1%
Cr	90.6	94.3	120%	106%	7.4%	4.1%
Cu	356	32.9	104%	**160%**	3.5%	2.4%
Fe	41060	37900	107%	102%	0.6%	1.4%
Hg	2.98	0.09	n.d.	n.d.	n.d.	n.d.
Mn	432	298	107%	103%	3.7%	3.4%
Pb	188	21.5	93%	93%	3.4%	**13.0%**
Sb	14.7	1.07	n.d.	n.d.	n.d.	n.d.
Zn	376	147	109%	102%	2.0%	3.3%

3.2. Validation Assessment: pXRF vs. ICP-MS and DMA-80

The comparability is determined by the degree to which the pXRF concentration of an element in a sample matches the concentration value obtained with the confirmatory analysis via reference methods. The comparability is assessed by the statistical equivalence of pXRF and ICP-MS (and DMA-80 for Hg) $\log_{10}$-transformed data and acceptable repeatability (RSD%) as described by the U.S. EPA [11], which indicates that pXRF results can reach definitive-, quantitative-screening-, or qualitative-screening-level criteria.

The first step in the evaluation of the quality of the pXRF analysis was performed under optimal sample preparation conditions ("lab-prepared" samples), where samples were finely ground and prepared in the same manner as samples for traditional laboratory analysis. The comparability between pXRF and confirmatory analysis on site-specific samples (soils, stream sediments, and mine wastes) are shown in the log-log plot in Figure 1 and in the statistical summary shown in Table 3.

The quality of pXRF analytical determination is variable among elements and matrices, in agreement to previous studies [13,27,32]. In general, a good comparability was found in both datasets for major elements as base metals (Table 3), according to previous investigations reporting significant correlations between digested samples through reference methods and pXRF for base metals [16,33]. In general, deviations from reference data may be due to uncertainties deriving from both pXRF and/or ICP-MS/DMA-80 analytical procedures, as demonstrated by the variability of the recovery for the different techniques (Table S1). Lead (Pb) was found to be the most accurate pXRF analyte and was the only element that reached the definitive data quality in both datasets among the nine elements investigated. Such high quality was the result of excellent comparability with ICP-MS analysis in a very wide concentration range, from 5 mg/kg to around 40,000 mg/kg (4 wt.%). Definitive quality levels were also obtained in the case of Zn in the Pb-Zn matrix and in the case of Sb in the Cu-Sb matrix. In addition, As, Fe, and Mn reached quantitative screening levels in both matrices, whereas Cu and Hg met the quantitative screening level only in the Cu-Sb-rich matrix due to the highest content of such metals in the host rocks and in the ore minerals [25,34].

In the case of As, results from pXRF were found to be slightly less correlated to ICP-MS results for the Pb-Zn site most likely due to the fact that As determination is affected by high Pb concentrations. The same issue was observed for the CRM analysis. Hence, for the Pb-Zn site, a better As determination was obtained by ICP-MS, e.g., [25], although statistics indicated that As could still be identified via pXRF at the quantitative screening level.

Chromium (Cr) and Hg (Table 3) reached low to very low concentrations in the Pb-Zn carbonate matrix. Their peaks were incorrectly interpreted by the factory calibration producing meaningless data (Figure 1). In the Pb-Zn site, Hg was in the 0.03–0.12 mg/kg interval according to the analysis performed by means of DMA-80, whereas the pXRF output was 33–280 mg/kg. The occurrence of false positives for Hg from pXRF is known to occur [18], and they can be removed after manual observation of the spectra. However, in the Cu-Sb site, Hg (up to 473 mg/kg—"quantitative") determination was better than Cr (up to 182 mg/kg—"qualitative").

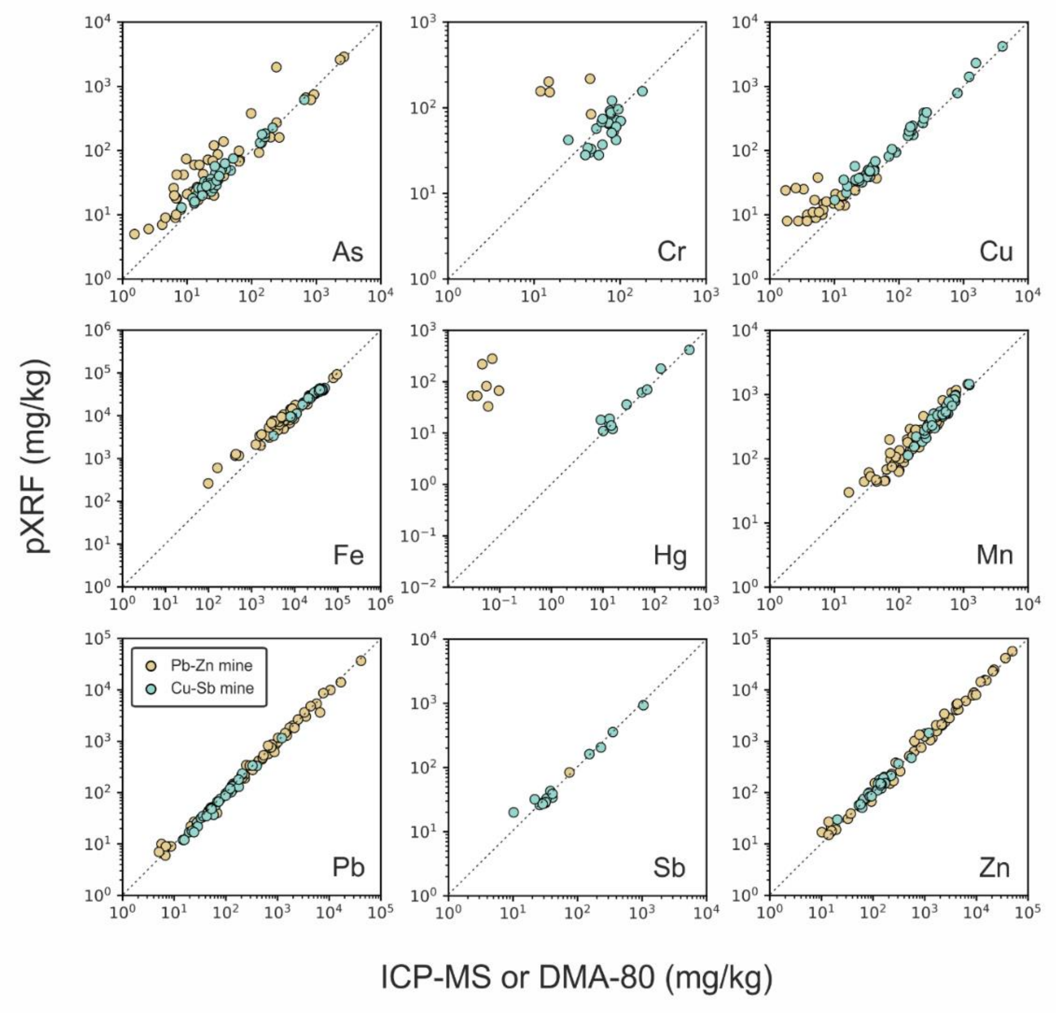

Figure 1. Comparison between pXRF and standard laboratory analyses (ICP-MS and DMA-80 for Hg) in "lab-prepared" samples (powders) of two datasets from Pb-Zn and Cu-Sb mining sites, marked using different colours.

Table 3. Statistical summary of comparability on “lab-prepared” samples (powders). Linear regression and *t*-test performed on $\log_{10}$-transformed data. n, number of data; Y-int, Y-intercept.

Matrix Type	Element	Data Quality [a]	n	Concentration Range ICP-MS—DMA	Concentration Range pXRF	RSD%	r^2	*t*-Test	Slope z-Test	Y-Int z-Test
				(mg/kg)	(mg/kg)				*p*-Value	
Cu-Sb	As	Quantitative	37	8.20–654	13–1057	7%	0.963 *	0.000	0.527	0.185
	Cr	Qualitative	25	6.91–182	28–156	12%	0.523 *	0.021	0.721	0.720
	Cu	Quantitative	37	10.1–4019	17–7739	8%	0.979 *	0.000	0.641	0.201
	Fe	Quantitative	37	3248–49,918	3405–44,504	1%	0.970 *	0.000	0.731	0.410
	Hg	Quantitative	11	0.04–473	11–720	14%	0.959 *	0.127	0.802	0.637
	Mn	Quantitative	37	138–1227	113–1452	3%	0.929 *	0.004	0.605	0.458
	Pb	Definitive	37	14.7–1216	12–1156	6%	0.988 *	0.760	0.770	0.524
	Sb	Definitive	15	1.64–1049	20–1627	9%	0.970 *	0.576	0.704	0.589
	Zn	Quantitative	37	20.3–1204	30–1462	4%	0.969 *	0.007	0.849	0.709
Pb-Zn	As	Quantitative	52	0.91–2693	5–2886	10%	0.856 *	0.000	0.383	0.051
	Cr	Qualitative	5	2.04–50.0	84–218	7%	0.100	0.007	0.035	0.000
	Cu	Qualitative	34	0.69–45.0	8–50	16%	0.358 *	0.000	0.024	0.001
	Fe	Quantitative	53	99–96,674	263–92,931	1%	0.952 *	0.000	0.201	0.003
	Hg	Qualitative	7	0.03–0.12	33–280	11%	0.050	0.000	0.537	0.017
	Mn	Quantitative	57	16.6–1239	30–1449	7%	0.895 *	0.003	0.917	0.747
	Pb	Definitive	58	5.05–41,436	6–36,853	5%	0.993 *	0.370	0.789	0.718
	Sb	Qualitative	2	0.05–75.0	21–84	-	-	-	-	-
	Zn	Definitive	58	10.2–49,752	15–56,400	4%	0.992 *	0.053	0.887	0.711

[a] Data quality levels are defined by [11]. * Significant for $p < 0.001$. Different colours identify the three data quality levels.

3.3. Low Concentration Effect

Results from this research indicate that the reliability of the pXRF analysis decreased at low concentrations for some elements, thus resulting in an overestimation, as in the case of As, Cu, and Fe. The results of the comparison considering “lab-prepared” samples from the two mining sites between confirmatory analyses (ICP-MS/DMA-80) and errors that are represented with a percent “site-specific accuracy” (pXRF analyte concentration/reference concentration × 100) are presented in Figure 2.

The field-based MDL was variable considering different elements. Regarding the pXRF analysis, acceptable results were obtained at concentrations of Fe > 10,000 mg/kg, As > 100 mg/kg, and Cu > 30 mg/kg, respectively. Below such MDLs, site-specific recoveries showed a non-linear increase, which started approximately from 120–130%, reaching almost 500% at very low concentrations. Method detection limits (MDLs) and overestimation observed in this research were consistent with previous studies reporting similar MDLs [11]. Especially for such elements, MDLs were found to be several orders of magnitude higher than the LOD indicated by the instrument documentation (LOD: Fe = 10 mg/kg, As = 1 mg/kg, Cu = 3 mg/kg, with a measurement time of 120 s/beam, against 20 s/beam of this study). The discrepancy is due to differences in counting time and to disparities in the developer’s definition of MDLs [11].

The concentration effect for Cu and Fe was mostly found in the Pb-Zn samples most likely due to a lower geogenic abundance of these two elements with respect to the other investigated site. Indeed, the geological matrices of the Cu-Sb site are constituted by higher background levels of Cu and Fe, and subsequently, such elements can be better determined by pXRF. The main reasons for the higher background in the Cu-Sb site are (1) dominance of silicate minerals in the host rock, which are in general characterised by higher concentrations in various elements, including Fe, with respect to carbonates (dolomite, calcite), which are the major mineralogical constituent of wall rocks and gangue in the Pb-Zn site, and (2) the natural enrichment, as in the case of Cu, related to the high and disseminated occurrence of Cu-bearing tetrahedrite minerals and possibly to the presence of a halo, which is the product of diffusion of trace elements related to the ore deposit during its emplacement or weathering. A similar concentration effect was also observed for the CRMs. The accuracy of the analysis in the case of Cu was found to be low in MESS-4, where Cu is <100 mg/kg (accuracy = 158–164% and Cu concentration = 32.9 mg/kg), whereas the opposite was observed in PACS-3, where Cu is >100 mg/kg (accuracy = 111–135% with Cu concentration = 372 mg/kg). Analytical issues in As determination in the Pb-Zn samples appeared to be influenced by both concentration effects and interferences with Pb, as described previously. However, interference caused by high concentrations of Pb appeared to be weaker as concentrations increased.

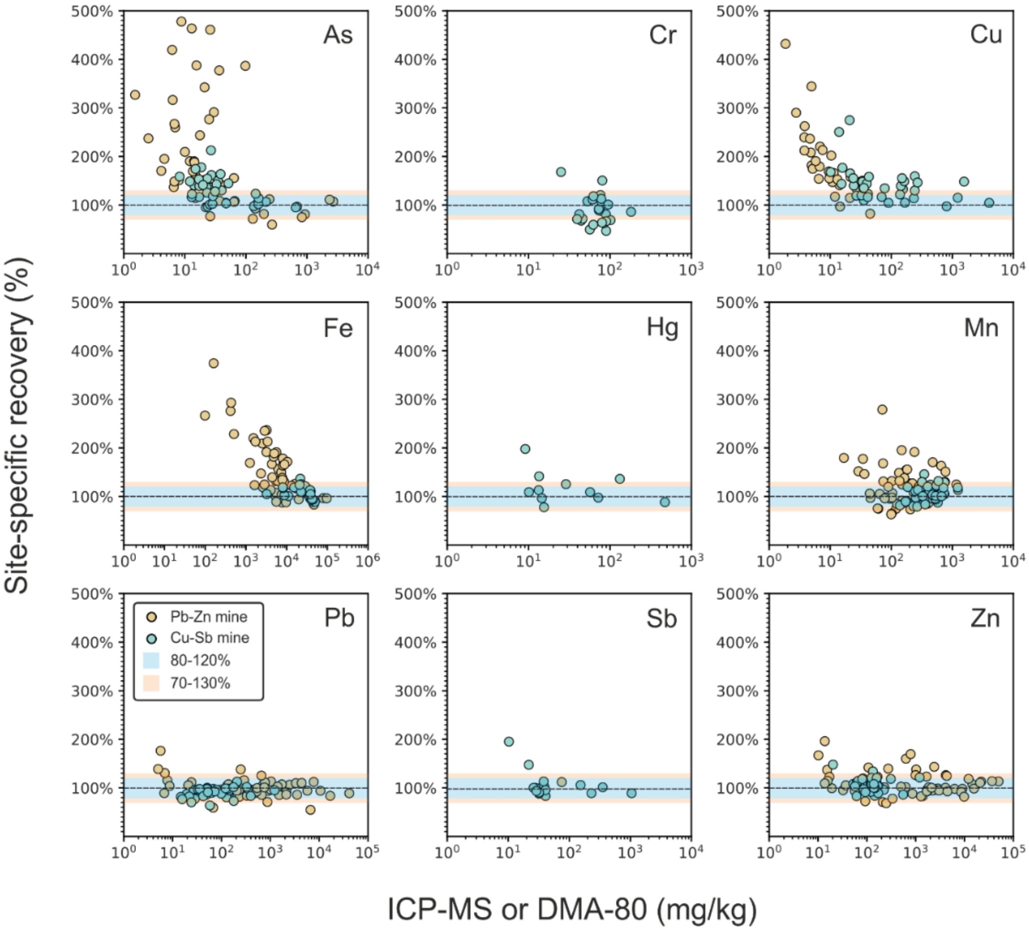

Figure 2. Concentration effect on pXRF data: site-specific recovery versus confirmatory analyses in "lab-prepared" samples (powders) of two datasets from a Pb-Zn and Cu-Sb mining sites, marked with different colours. Possible acceptance ranges are depicted in blue and yellow.

3.4. Effect of Sample Treatment

In order to evaluate the quality of the pXRF analysis, an additional QA/QC test was adopted in this study involving the potential influence of heterogeneity in samples prepared with a fast preparation procedure. The analytical procedure for pXRF analysis was not changed between "fast lab-prepared" aliquots (only dried and sieved <2 mm) and "lab-prepared" samples, as described previously. The results are presented in Figure 3 and Table S2.

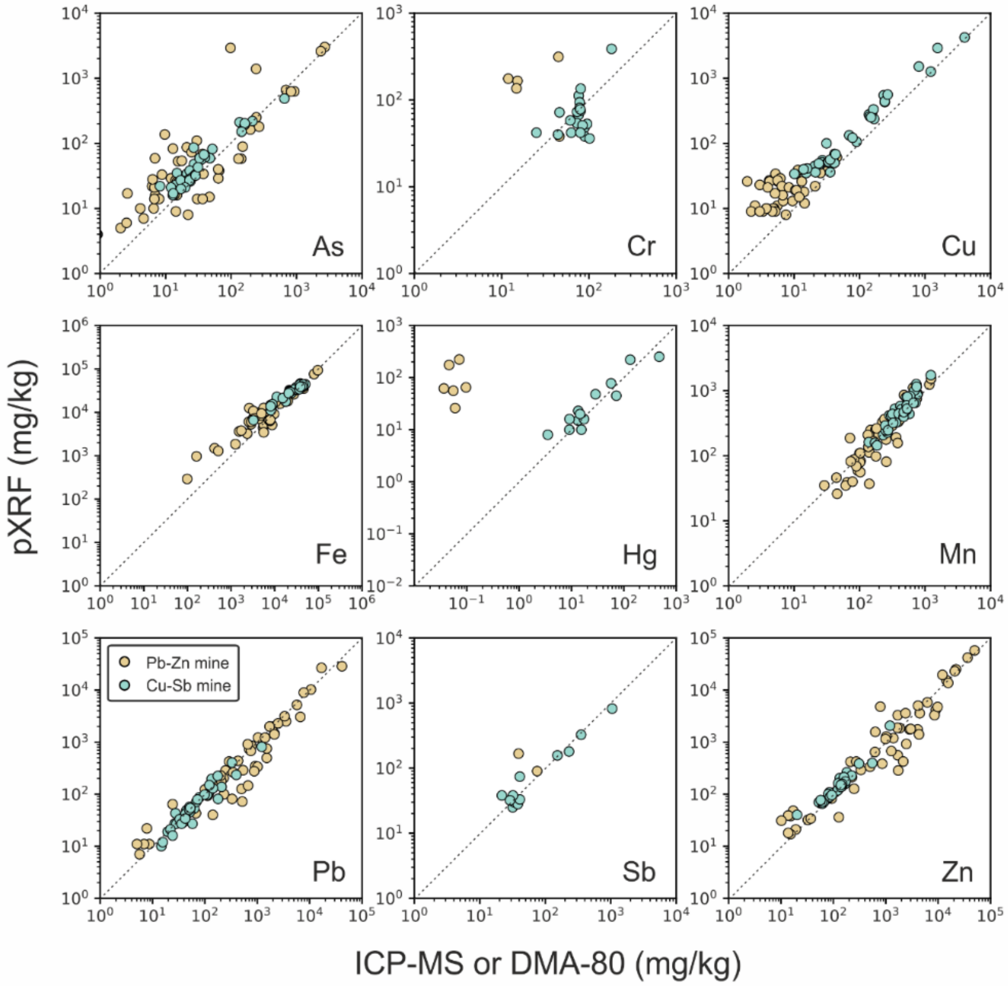

Figure 3. Comparison between pXRF and confirmatory data (ICP-MS and DMA) in "fast lab-prepared" samples (only dried and sieved < 2 mm) of two datasets from a Pb-Zn and Cu-Sb mining sites, marked with different colours.

In general, the scatterplots regarding "fast lab-prepared" aliquots (Figure 3) are similar to those reported for the "lab-prepared" aliquots (Figure 1). Most of the elements that were significantly correlated during the first validation step also maintained significant correlations for unground samples ($p < 0.001$). Those correlations were still robust, and the repeatability did not suffer heterogeneity as long as the sample was not displaced between each pXRF replicate analysis. For the data quality classification adopted [11], there were hardly any substantial upgrades or downgrades between the comparability of homogenised "lab-prepared" and "fast lab-prepared" heterogeneous samples.

However, some differences were observed. Indeed, the pXRF analysis of heterogeneous samples produced data that are slightly less correlated, more scattered, and less accurate. A moderate improvement in the pXRF data quality was observed; therefore, laboratory milling operations of field samples should be evaluated on the basis of the data quality desired.

4. Conclusions

In areas close to mining operations, the preliminary use of pXRF may be able to easily identify the location of the mining wastes characterized by the highest metal or metalloid concentrations, exploring even the occurrence of elements of potential economic interest. Conversely, users may encounter unreliable results when pXRF data are not validated, especially when dealing with low concentrations. Care must be taken regarding the concentration effects since the absence or occurrence of very low concentrations can be interpreted by pXRF as higher background levels and also regarding actual LODs, which may be higher than those indicated by the factory producer due to different operating conditions.

In this study, the overall analytical quality was found to be mainly influenced by the composition of samples due to interferences, matrix effects, and low concentrations more than the heterogeneity of the sample. Although milling is a highly time-consuming procedure, the sample preparation should be carefully defined according to the desired data quality. However, the loss in comparability due to "fast lab-prepared" samples was negligible in comparison to compositional differences. A summary of the results is presented:

- Lead (Pb), zinc (Zn), and manganese (Mn): the determination of these base metals by pXRF was often found to be successful (from quantitative to definitive quality levels), and no notable analytical issues related to interferences or concentration effects were observed;
- Arsenic (As): the element met the "quantitative" quality level in both datasets. However, better comparability is found in sites where Pb is not dominant, and As concentrations are elevated enough due to As-K and Pb-L X-ray overlaps, which reduce the accuracy of As determination, so that the traditional laboratory analysis may be preferential. A concentration effect was observed leading to a decrease in comparability for As < 100 mg/kg;
- Chromium (Cr): the metal showed moderate comparability between the two analytical approaches in the Cu-Sb matrix, characterised by relatively higher Cr concentrations and occurrence of false positives by using pXRF in the carbonate-hosted Pb-Zn samples that should be removed by the user via manual spectral interpretation. Overall, Cr never exceeded the "qualitative" level when determined via pXRF;
- Copper (Cu): comparability of pXRF with ICP-MS results was strongly dependent on the element concentration and acceptable for Cu > 100 mg/kg, whereas below such values, Cu concentrations detected via pXRF were false;
- Iron (Fe): similar to Cu, its detectability by pXRF was strongly dependent on the concentration. Comparability between the two analytical approaches was found to be optimal for values >10,000 mg/kg, which are common in many (but not all) natural samples;
- Mercury (Hg) and antimony (Sb): these trace elements were found quantitatively determined by pXRF only when occurring with concentrations > 10–20 mg/kg. Conversely, when the real sample concentrations were below such values, as in the case of Hg, pXRF produced false-positive results, which should be manually removed by the user via spectral interpretation. Unfortunately, this result reveals a serious limitation in using pXRF, as the operator may be precluded from detecting low concentrations of Hg in soils that exceed those threshold levels specified by national regulations that define the use of uncontaminated soil. This is the case with the Italian legislation, for instance, where the highest threshold level, defined by major land use, i.e., for commercial and industrial purposes, is fixed at 5 mg kg^{-1}, whereas for public, private, and residential use, it is 1 mg kg^{-1} (Italian Legislative Decree 152/06 [9]).

Overall, pXRF is a rapid and inexpensive technique, useful for preliminary quantification of element concentrations in contaminated solid matrices (e.g., soil, sediment, mining waste) without complex sample preparations followed by destructive standard laboratory analyses (e.g., ICP-OES, ICP-MS, DMA-80) and in a relatively short time interval. However, this study has shown that analytical results obtained using pXRF cannot be accepted outright, and they must be carefully evaluated, as interpretations should also take into consideration an initial accurate QA/QC protocol in addition to the skill and experience of the operator.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app122312189/s1; Table S1: Comparison of the accuracy of ICP-MS, DMA-80 and pXRF analysis; Table S2: Linear regression and *t*-test carried out on $\log_{10}$-transformed data.

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Abbreviations

CRM, certified reference material; DMA-80, Direct Mercury Analyser; ICP-AES, inductively coupled plasma atomic emission spectroscopy; ICP-MS, inductively coupled plasma mass spectroscopy; LOD, limit of detection; MDL, method detection limit; PTE, potentially toxic element; pXRF, portable X-ray fluorescence; QA/QC, quality assurance/quality control; RSD, relative standard deviation.

References

1. Crosera, M.; Baracchini, E.; Prenesti, E.; Giacomello, A.; Callegher, B.; Oliveri, P.; Adami, G. Elemental Characterization of Surface and Bulk of Copper-Based Coins from the Byzantine-Period by Means of Spectroscopic Techniques. *Microchem. J.* **2019**, *147*, 422–428. [CrossRef]
2. Pavoni, E.; Crosera, M.; Petranich, E.; Faganeli, J.; Klun, K.; Oliveri, P.; Covelli, S.; Adami, G. Distribution, Mobility and Fate of Trace Elements in an Estuarine System Under Anthropogenic Pressure: The Case of the Karstic Timavo River (Northern Adriatic Sea, Italy). *Estuaries Coasts* **2021**, *44*, 1831–1847. [CrossRef]
3. Pavoni, E.; Crosera, M.; Petranich, E.; Adami, G.; Faganeli, J.; Covelli, S. Partitioning and Mixing Behaviour of Trace Elements at the Isonzo/Soča River Mouth (Gulf of Trieste, Northern Adriatic Sea). *Mar. Chem.* **2020**, *223*, 103800. [CrossRef]
4. Sibilia, M.; Stani, C.; Gigli, L.; Pollastri, S.; Migliori, A.; D'Amico, F.; Schmid, C.; Licen, S.; Crosera, M.; Adami, G.; et al. A Multidisciplinary Study Unveils the Nature of a Roman Ink of the I Century AD. *Sci. Rep.* **2021**, *11*, 7231. [CrossRef] [PubMed]
5. Lemière, B. A Review of PXRF (Field Portable X-ray Fluorescence) Applications for Applied Geochemistry. *J. Geochem. Explor.* **2018**, *188*, 350–363. [CrossRef]
6. Higueras, P.; Oyarzun, R.; Iraizoz, J.M.; Lorenzo, S.; Esbrí, J.M.; Martínez-Coronado, A. Low-Cost Geochemical Surveys for Environmental Studies in Developing Countries: Testing a Field Portable XRF Instrument under Quasi-Realistic Conditions. *J. Geochem. Explor.* **2012**, *113*, 3–12. [CrossRef]
7. Kalnicky, D.J.; Singhvi, R. Field Portable XRF Analysis of Environmental Samples. *J. Hazard. Mater.* **2001**, *83*, 93–122. [CrossRef]
8. Horta, A.; Malone, B.; Stockmann, U.; Minasny, B.; Bishop, T.F.A.; McBratney, A.B.; Pallasser, R.; Pozza, L. Potential of Integrated Field Spectroscopy and Spatial Analysis for Enhanced Assessment of Soil Contamination: A Prospective Review. *Geoderma* **2015**, *241–242*, 180–209. [CrossRef]
9. Lgs, D. Decreto Legislativo n. 152 "Norme in Materia Ambientale". 88 Gazzetta Ufficiale Repubblica Italiana. 152/06, 14 April 2006.
10. Laiho, J.V.; Perämäki, P. Evaluation of Portable X-ray Fluorescence (PXRF) Sample Preparation Methods. *Spec. Pap.-Geol. Surv. Finl.* **2005**, *38*, 73.
11. *US EPA Environmental Technology Verification Report, Field Portable X-ray Fluorescence Analyzer*; Metorex X-MET 920-P; United States Environmental Protection Agency: Washington, DC, USA, 1998; EPA/600/R-97/146.
12. Pavoni, E.; Petranich, E.; Adami, G.; Baracchini, E.; Crosera, M.; Emili, A.; Lenaz, D.; Higueras, P.; Covelli, S. Bioaccumulation of Thallium and Other Trace Metals in Biscutella Laevigata Nearby a Decommissioned Zinc-Lead Mine (Northeastern Italian Alps). *J. Environ. Manag.* **2017**, *186*, 214–224. [CrossRef]
13. Hall, G.E.M.; Bonham-Carter, G.F.; Buchar, A. Evaluation of Portable X-ray Fluorescence (PXRF) in Exploration and Mining: Phase 1, Control Reference Materials. *Geochem. Explor. Environ. Anal.* **2014**, *14*, 99–123. [CrossRef]
14. Knight, R.D.; Kjarsgaard, B.A.; Russell, H.A.J. An Analytical Protocol for Determining the Elemental Chemistry of Quaternary Sediments Using a Portable X-ray Fluorescence Spectrometer. *Appl. Geochem.* **2021**, *131*, 105026. [CrossRef]
15. Migaszewski, Z.; Gałuszka, A.; Dołęgowska, S. The Use of FPXRF in the Determinations of Selected Trace Elements in Historic Mining Soils in the Holy Cross Mts., South-Central Poland. *Geol. Q.* **2015**, *59*, 248–256. [CrossRef]

16. Rouillon, M.; Taylor, M.P. Can Field Portable X-ray Fluorescence (PXRF) Produce High Quality Data for Application in Environmental Contamination Research? *Environ. Pollut. Barking Essex 1987* **2016**, *214*, 255–264. [CrossRef] [PubMed]
17. Rincheval, M.; Cohen, D.R.; Hemmings, F.A. Biogeochemical Mapping of Metal Contamination from Mine Tailings Using Field-Portable XRF. *Sci. Total Environ.* **2019**, *662*, 404–413. [CrossRef] [PubMed]
18. Spearman, S.; Bartrem, C.; Sharshenova, A.; Salymbekova, K.; Isirailov, M.; Gaynazarov, S.; Gilmanov, R.; von Lindern, I.; von Braun, M.; Möller, G. Comparison of X-ray Fluorescence (XRF) and Atomic Absorption Spectrometry (AAS) Results for an Environmental Assessment at a Mercury Site in Kyrgyzstan. *Appl. Sci.* **2022**, *12*, 1943. [CrossRef]
19. Lemière, B.; Melleton, J.; Auger, P.; Derycke, V.; Gloaguen, E.; Bouat, L.; Mikšová, D.; Filzmoser, P.; Middleton, M. PXRF Measurements on Soil Samples for the Exploration of an Antimony Deposit: Example from the Vendean Antimony District (France). *Minerals* **2020**, *10*, 724. [CrossRef]
20. Brigo, L.; Cerrato, P. Trace Element Distribution of Middle-Upper Triassic Carbonate-Hosted Lead-Zinc Mineralizations: The Example of the Raibl Deposit (Eastern Alps, Italy). In *Sediment-Hosted Zn-Pb Ores*; Fontboté, L., Boni, M., Eds.; Springer: Berlin/Heidelberg, Germany, 1994; pp. 179–197. ISBN 978-3-662-03054-7.
21. Barago, N.; Covelli, S.; Mauri, M.; Oberti di Valnera, S.; Forte, E. Prediction of Trace Metal Distribution in a Tailings Impoundment Using an Integrated Geophysical and Geochemical Approach (Raibl Mine, Pb-Zn Alpine District, Northern Italy). *Int. J. Environ. Res. Public. Health* **2021**, *18*, 1157. [CrossRef]
22. Henjes-Kunst, E.; Raith, J.G.; Boyce, A.J. Micro-Scale Sulfur Isotope and Chemical Variations in Sphalerite from the Bleiberg Pb-Zn Deposit, Eastern Alps, Austria. *Ore Geol. Rev.* **2017**, *90*, 52–62. [CrossRef]
23. Giorno, M.; Barale, L.; Bertok, C.; Frenzel, M.; Looser, N.; Guillong, M.; Bernasconi, S.M.; Martire, L. Sulfide-Associated Hydrothermal Dolomite and Calcite Reveal a Shallow Burial Depth for Alpine-Type Zn-(Pb) Deposits. *Geology* **2022**, *50*, 853–858. [CrossRef]
24. Brigo, L.; Dulski, P.; Möller, P.; Schneider, H.-J.; Wolter, R. Strata-Bound Mineralizations in the Carnic Alps/Italy. In *Mineral Deposits within the European Community*; Boissonnas, J., Omenetto, P., Eds.; Springer: Berlin/Heidelberg, Germany, 1988; pp. 485–498, ISBN 978-3-642-51860-7.
25. Brigo, L.; Camana, G.; Rodeghiero, F.; Potenza, R. Carbonate-Hosted Siliceous Crust Type Mineralization of Carnic Alps (Italy-Austria). *Ore Geol. Rev.* **2001**, *17*, 199–214. [CrossRef]
26. Brigo, L.; Kostelka, L.; Omenetto, P.; Schneider, H.-J.; Schroll, E.; Schulz, O.; Štrucl, I. Comparative Reflections on Four Alpine Pb-Zn Deposits. In *Time- and Strata-Bound Ore Deposits*; Klemm, D.D., Schneider, H.-J., Eds.; Springer: Berlin/Heidelberg, Germany, 1977; pp. 273–293, ISBN 978-3-642-66808-1.
27. Ross, P.-S.; Bourke, A.; Fresia, B. Improving Lithological Discrimination in Exploration Drill-Cores Using Portable X-ray Fluorescence Measurements: (1) Testing Three Olympus Innov-X Analysers on Unprepared Cores. *Geochem. Explor. Environ. Anal.* **2014**, *14*, 171–185. [CrossRef]
28. *US EPA Method 3052*; Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices; United States Environmental Protection Agency: Washington, DC, USA, 1996.
29. *US EPA Method 7473 (SW-846)*; Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry; United States Environmental Protection Agency: Washington, DC, USA, 1998.
30. Al-Musawi, M.; Kaczmarek, S. A New Carbonate-Specific Quantification Procedure for Determining Elemental Concentrations from Portable Energy-Dispersive X-ray Fluorescence (PXRF) Data. *Appl. Geochem.* **2020**, *113*, 104491. [CrossRef]
31. *US EPA Method 6200*; Field Portable X-ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soils and Sediment; United States Environmental Protection Agency: Washington, DC, USA, 2007.
32. Durance, P.; Jowitt, S.M.; Bush, K. An Assessment of Portable X-ray Fluorescence Spectroscopy in Mineral Exploration, Kurnalpi Terrane, Eastern Goldfields Superterrane, Western Australia. *Appl. Earth Sci.* **2014**, *123*, 150–163. [CrossRef]
33. Sarala, P. Comparison of Different Portable XRF Methods for Determining till Geochemistry. *Geochem. Explor. Environ. Anal.* **2016**, *16*, 181–192. [CrossRef]
34. Casari, L. Tetrahedrite-Tennantite Series in the Carnic Chain (Eastern Alps, Italy). *N. Jb. Miner. Mh.* **1996**, *5*, 193–200.