

The use of FPXRF in the determinations of selected trace elements in historic mining soils in the Holy Cross Mts., south-central Poland

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In this study, concentrations of As, Cu, Mn, Pb, and Zn were determined in 231 samples of mine soils and spoils by field portable X-ray fluorescence (FPXRF), and by inductively coupled plasma-mass spectrometry (ICP-MS) as a comparison method. The use of both spectrometric methods allows for comparison of the total and *aqua regia*-extractable contents of elements. The study areas encompassed three historic metal-ore mining sites and one abandoned mine tailings site in the Holy Cross Mountains, in south-central Poland. Sample collection in these areas, which are characterized by various bedrock mineralogy and lithology and different anthropogenic impacts, enabled us to test the FPXRF performance for a wide range of element concentrations. The results of FPXRF and ICP-MS determinations were found to be significantly correlated with the highest r^2 (coefficient of determination) value of 0.987–0.991 for Pb, irrespective of the soil mineralogy, bedrock lithology or concentration levels of this element. Overall, the FPXRF showed excellent performance in determining selected trace elements in contaminated soils.

Key words: historic mining sites, mine soils, trace metals, FPXRF, ICP-MS.

INTRODUCTION

Modern analytical laboratories offer different instrumental methods that enable the routine determination of trace metals in soils, including: atomic absorption spectrometry (AAS), inductively coupled plasma-optical emission spectrometry (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS), X-ray fluorescence spectrometry (XRF), and instrumental neutron activation analysis (INAA). Although these laboratory methods allow us to obtain very low limits of detection at the concentration level of ppb ($\mu\text{g}/\text{kg}$) or even ppt (ng/kg), they are generally time-, energy-, and reagent-consuming and usually require a laborious physical and/or chemical sample preparation. In addition, they require the use of hazardous reagents, such as strong acids, for analyte extraction. For example, a commonly used extraction agent in soil sample analyses is *aqua regia* (Sastre et al., 2002). All of the features mentioned above make these methods less environmentally-friendly, and not in agreement with the current trend in analytical chemistry towards green analytical chemistry (Gałuszka et al., 2013). Another disadvantage of the lab-based instruments is that they are not mobile and cannot be applied in the field for real-time measurements of element concentrations and on-site pollutant

screening especially in vast post-mining areas, or in urban and industrial brownfields. The field portable X-ray fluorescence spectrometry (FPXRF) is a method that can both meet these performance requirements and bring the laboratory to the field (Kalnicky and Singhvi, 2001).

FPXRF spectrometry is a rapid, low cost, multi-element, and nondestructive method that can be employed for both *in situ* and *ex situ* measurements. The modern models of FPXRF analyzers are characterized by low detection limits below regulatory levels, e.g. Polish soil quality standards (Wcisło, 2012), high sample throughput, and the capability to determine a broad range of target elements varying from Mg to U. Typically, these instruments exhibit the superior performance on heavy elements. Improved detector performance, for example, the application of Geometrically Optimized Large Drift Detector (GOLDD™) technology, reduces most inter-element interferences and overlaps. This new technology and the application of helium purge allow the detection limits of most elements to be lowered to less than 10 mg/kg. Quantification of the results is possible with official methods such as EPA Method 6200 (26 elements in soil and sediments; USEPA, 2007) and National Institute for Occupational Safety and Health (NIOSH) Method 7702 (Pb in air filters; NIOSH Method 7702).

Apart from chemical matrix effects (spectral interferences, X-ray absorption, and enhancement effects), the accuracy of soil and sediment measurements decreases when the sample is: not homogenized (physical matrix effect), the moisture content exceeds the range of 5 to 20%, and when there is no direct contact between the sample surface and the probe window (USEPA, 2007). Another minor disadvantage is that the rapid

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Fig. 1. Location of the study areas

change of ambient temperature (e.g., 7 °C per hour) may cause an instrument drift. To improve the quality of data, it is recommended that soil and sediment samples be fine-grained, uniform, homogenized, dried, have smooth surfaces (X-rays penetrate to a depth of about 1.2 to 2 mm), and cover the whole probe window (about 1 cm in diameter).

The FPXRF analysis has found applications in many areas, including determinations of trace elements in various environmental compartments, including soils (Drake et al., 2003; Melquiades and Appoloni, 2004; Mäkinen et al., 2005; Kilbride et al., 2006; Carr et al., 2008; Hürkamp et al., 2009; Radu and Diamond, 2009; Higuera et al., 2012; Stamm and Hoogstraat, 2012; Bosco, 2013). Many theoretical and practical aspects of this analytical method can be found in the superb compendium by Potts and West (2008).

The principal objective of this study was to compare the results of the determinations of selected trace elements (As, Cu, Mn, Pb, and Zn) by the FPXRF and ICP-MS methods in topsoils, technogenic soils (spolic technosols), and mine spoils of three historic mining areas of the Holy Cross Mountains, in south-central Poland, in order to find the advantages and limitations of the FPXRF method. These methods also enabled determination of the total concentrations (FPXRF) of selected trace elements and their *aqua regia*-extractable fractions (ICP-MS). We also aimed to find a relationship between the mineralogy/lithology of bedrock, soils or alien waste material, and element concentration levels and their influence on the FPXRF performance.

MATERIALS AND METHODS

LOCATION AND GEOLOGICAL FRAMEWORK

The study was conducted in three remote historic metal-ore mining areas: (1) Miedzianka Mt. (copper mines), (2) Karczówka Mt. (lead mines), and (3) Rudki (iron-uranium mine) and Serwis (low-grade iron ore tailings pile; Fig. 1). The intensive metal-ore extraction is reflected by numerous multi-shaft mines with underground workings and spoil heaps. Miedzianka Mt. is built of uppermost Middle and Upper Devonian limestone

formations, cut by calcite CaCO_3 and Cu sulfide ore veins. Soils are represented by rendzinas with a variable admixture of sand, locally lithosols, and arenosols.

Karczówka Mt. consists of Upper Devonian limestones, cut mostly by galena and calcite veins. Soils are represented by sandy rendzinas, and in places by arenosols and lithosols.

The pyrite-hematite-siderite-uranium mineral deposit of Rudki is genetically linked to the deep-rooted Łysogóry Fault that separates Silurian clayey shales with subordinate mudstones, sandstones, and greywackes from Middle Devonian dolomites and clayey shales. The surficial workings at Rudki and the nearby mine tailings site at Serwis were covered with an alien material composed of clays and sands, with an admixture of mining wastes.

SAMPLING

The soil sampling was conducted on November 15–16 and 27 of 2012 (Karczówka and Miedzianka) and on May 31 and June 1 of 2013 (Rudki and Serwis). A total of 231 soil samples were collected (number of samples in parentheses): Karczówka (69), Miedzianka (72), Rudki (63), and Serwis (27) using systematic random (Karczówka, Miedzianka and Rudki) and three-transect (Serwis) sampling plans. At each site, pits were dug to a depth of about 0.3–0.5 m. Each soil sample (weighing about 2 kg each) consisted of 5–10 subsamples. The soil samples were placed in polyethylene bags for selected element determinations. During sample collection, transport, storage, and preparation, procedures were followed to minimize the possibility of contamination, i.e. talc-free disposable vinyl gloves were used during sampling and sample treatment, samples were placed in polyethylene zip-lock bags and plastic trays to prevent accidental mixing, and samples were stored in a separate sample storage room with limited access before analyses. A set of soil samples included 4 replicates for each sampling series.

SAMPLE PREPARATION AND ANALYSES

After removing any miscellaneous material (leaves, twigs, etc.), the soil samples were dried for a week at an ambient temperature of about 20 °C, sieved to obtain <2 mm fractions, and

then disaggregated to pass a <0.063 mm sieve using a *Pulverisette 2* Fritsch's blender and then an *Analysette 3 Spartan* shaker. Each soil sample (0.5 g) was digested with *aqua regia* (6 mL HCl + 2 mL HNO₃) in a closed microwave system (*Multiwave 3000*; 100 mL vessels, power 1000 W, time 65 min., T 220 °C, p 60 bars, p growth rate 0.3 bar/s) and replenished up to 25 mL with distilled water.

For the purpose of this study, all the homogeneous soil samples were placed in thin polyethylene sampling bags and then analyzed for 5 trace elements (As, Cu, Mn, Pb, and Zn) using a portable XRF analyzer (model *Thermo Scientific NITON XL3t 960 GOLDD+*) with an excitation source 50 kV X-ray tube with Ag anode. The time of FPXRF analysis was 120 seconds; measurements were done in triplicates and precision was expressed as 2 standard deviations of the mean values, and the detection mode was set on "soil". The limit of detection (LOD) for As, Cu, Pb, and Zn was 10 mg/kg, and for Mn it was 70 mg/kg. The average precision was the highest for As (10 mg/kg), lower for Zn (15 mg/kg), Cu, and Pb (20 mg/kg), and the lowest for Mn (150 mg/kg). The emission spectra were transferred to the PC and appropriately processed with the use of the *Niton Data Transfer* software.

The comparison analysis encompassed the same trace elements using an ICP-MS instrument (model *ELAN DRC II, Perkin Elmer*). Instrumental and data acquisition parameters of the ICP-MS instrument were as follows: sweeps/reading – 20, readings/replicate – 3, replicates – 4, nebulizer gas flow – 1.03 L/min, plasma gas flow – 15 L/min, lens voltage – 7.50 V, plasma power – 1275 W. The measurements were done in the peak hopping mode and the dwell time was 50–150 microseconds, depending on the analyte. Two internal standards were utilized: Rh and Ir. The ICP-MS instrument was optimized with a standard daily procedure. For trace element determinations, a series of mixed element calibration standards at appropriate concentrations were prepared in 2% HNO₃ from *Perkin Elmer ICP-MS Multielement Calibration Standard 3*. The detection limits for ICP-MS analysis were (in mg/kg) 0.01 for Cu and Pb; 0.1 for Zn and As; 0.5 for Mn, respectively.

The standard reference material (SRM) applied for measuring element concentrations by the FPXRF method was Certified Reference Material (CRM) NIST 2709a (San Joaquin soil). For the quality control of the ICP-MS analysis, CRM NIST 2710a (Montana I Soil) and GSS4 (Chinese Academy of Geological Sciences) were used. Quality control included both accuracy (CRM) and precision (triplicates). The average percentage recovery of elements from the SRM and CRM was in the range of 87–109% (FPXRF) and 92–110% (ICP-MS), whereas the uncertainty of the method ($U_c^2 = u_{RM}^2 + u_d^2 + u_m^2 + B^2$, $U_e = 2 U_c$)¹ was below 10%. The RSD values were <4% for most of the samples analysed. The chemical analyses of collected samples were performed in the Geochemical Laboratory of the Institute of Chemistry, Jan Kochanowski University in Kielce.

RESULTS

The results of As, Cu, Mn, Pb, and Zn determinations in the soils of four sites (Serwis, Rudki, Karczówka, Miedzianka) by the FPXRF method are summarized in Table 1. The highest concentrations of As and Cu (geom. mean of 52 and 201 mg/kg) occur in the Miedzianka soils, which are related to

tennantite (Cu,Fe)₁₂As₄S₁₃ and other secondary Cu-As minerals predominating in a copper sulfide ore.

The Rudki technosols contain in turn the highest levels of Mn, Pb, and Zn (geom. means of 2543, 672 and 215 mg/kg, respectively). These technosols represent a more homogeneous alien material composed of clays, silts, and sands mixed with pieces of carbonate (mostly dolomite) and terrigenous rocks. They comprise inclusions of Fe- and Mn-oxides and -oxyhydroxides, galena PbS and sphalerite ZnS.

It is interesting to note that Karczówka topsoils contain lesser amounts of Pb (geom. mean of 380 mg/kg) in the form of galena and anglesite PbSO₄. However, this site is highlighted by maximum values (10,780 mg/kg), which were recorded near mine workings with associated tailings piles. In contrast, the Serwis pyrite- and siderite-bearing technogenic soils are generally depleted in these trace elements.

DISCUSSION

ANOMALOUS ELEMENT CONCENTRATIONS

Geochemical anomalies, i.e. values above the upper limit of geochemical background range, commonly occur in post-mining areas (Gałuszka, 2007). The typical concentrations of lead in soils are in the range of 3–90 mg/kg (Kabata-Pendias, 2011). However, in soils influenced by present and historic metal-ore mining, Pb occurs at much higher levels, for example, in Karczówka soils in the range of 40–10,780 mg/kg. The anomalous Pb concentrations in post-mining soils have also been reported from many countries, including (in mg/kg): Mexico (31–3450; Razo et al., 2004), Spain (20–142; Loredo et al., 2006), Morocco (40–13,300; lavazzo et al., 2012), and France (41–4520; Camizuli et al., 2014).

Zinc showed concentrations of at least twice the detection limit, for example, in Rudki soils from 30 to 750 mg/kg. Even in soils that are depleted in Zn, namely light sandy soils, concentrations of this metal are in the range of 31–61 mg/kg (Kabata-Pendias, 2011). High Zn levels in soils were also reported from different historic mining areas, for example, from the abandoned Miguel Vacas Cu mine in SE Portugal (Abreu et al., 2008), where Zn concentrations were in the range of 53–211 mg/kg.

The range of natural Mn contents in soils is very broad and the maximum concentrations of this metal can reach several thousands of mg/kg (Kabata-Pendias, 2011). The mean Mn content in soils is estimated to be 437 mg/kg (Kabata-Pendias and Mukherjee, 2007). The soils examined are heavily enriched in Mn. Although the mean Mn concentrations are similar to those reported from the studies conducted in different post-mining areas, for example, in Portugal 1446–4153 mg/kg (Abreu et al., 2008) and in Morocco 400–4520 mg/kg (lavazzo et al., 2012), the maximum values at Miedzianka (31,880 mg/kg) and Rudki (20,050 mg/kg) represent anomalous enrichment in this metal.

The Miedzianka soils display the highest levels of Cu in a wide range of <10 to 7680 mg/kg (mean of 984 mg/kg). Similar concentrations of this metal were found in soils of other historic Cu-ore mining areas, including (in mg/kg): Mexico (15–7200) (Razo et al., 2004), Portugal (70–2231; Abreu et al., 2008), and the Sudetes in southwestern Poland (7–3430; Karczewska et al., 2006).

¹ u_{RM} – reference material uncertainty, u_d – sample digestion uncertainty, u_m – measurement uncertainty by ICP-MS, B – error of the obtained result relative to the certified value, U_c – composite uncertainty, U_e – expanded uncertainty significant at 0.05 probability level (extension coefficient $k = 2$)

Table 1

Summary statistics of the results obtained by the FPXRF method

Locations	Miedzianka	Karczówka	Rudki	Serwis
Number of samples	72	69	63	27
Element	As			
Minimum [mg/kg]	<10	<10	<10	<10
Maximum [mg/kg]	1520	110	90	30
Arithmetic mean [mg/kg]	173	13.4	26	15
Geometric mean [mg/kg]	52	8	17	13
Median [mg/kg]	30	5	20	10
Standard deviation	292	20.8	23	7
Number of results below detection limits	8	45	20	3
Element	Cu			
Minimum [mg/kg]	<10	<10	10	<10
Maximum [mg/kg]	7680	90	170	50
Arithmetic mean [mg/kg]	984	15	66	31
Geometric mean [mg/kg]	201	10	60	27
Median [mg/kg]	185	5	60	30
Standard deviation	1610	17	28	12
Number of results below detection limits	8	42	0	3
Element	Mn			
Minimum [mg/kg]	<70	<70	130	160
Maximum [mg/kg]	29,220	1850	20,050	8560
Arithmetic mean [mg/kg]	2462	403	3862	2000
Geometric mean [mg/kg]	1851	311	2543	1337
Median [mg/kg]	1185	330	2460	1550
Standard deviation	5157	296	3945	1952
Number of results below detection limits	5	1	0	0
Element	Pb			
Minimum [mg/kg]	<10	40	10	20
Maximum [mg/kg]	660	10,780	2390	210
Arithmetic mean [mg/kg]	74	1144	910	76
Geometric mean [mg/kg]	43	380	672	53
Median [mg/kg]	50	200	830	40
Standard deviation	116	1991	532	61
Number of results below detection limits	3	0	0	0
Element	Zn			
Minimum [mg/kg]	20	30	30	50
Maximum [mg/kg]	450	790	750	320
Arithmetic mean [mg/kg]	139	152	247	113
Geometric mean [mg/kg]	110	124	215	98
Median [mg/kg]	130	110	250	90
Standard deviation	92	121	121	70
Number of results below detection limits	0	0	0	0

The FPXRF may also be very useful in determining concentrations of As in soils of the post-mining areas, where anomalously high concentrations of this element are very common, e.g. <10–1520 mg/kg in Miedzianka soils, and even higher, including (in mg/kg): Spain (32–19,930; [Loredo et al., 2006](#)), Portugal (19–17,384; [Abreu et al., 2008](#)), and Scotland (50–17,400; [Gal et al., 2007](#)). However, its application in the study of unpolluted soils may be problematic because typical As contents in these soils are in the range of <0.1–67 mg/kg,

with an average of 6.82 mg/kg (below the limit of detection which is 10 mg/kg). The determination of accurate As values in the presence of high Pb concentrations (if Pb:As concentration ratio is greater than 10:1) in contaminated soils may be difficult and requires spectrum evaluation due to the spectral overlap of the L- for Pb and K- for As line. However, the inbuilt deconvolution procedure used in the instrument's software effectively corrected for this interference in the present study.

ELEMENT COEFFICIENTS OF DETERMINATION VERSUS CONCENTRATION PATTERNS

Lead exhibited both high coefficients of determination (r^2) varying from 0.987 to 0.991 ($P < 0.05$) and a nearly perfect overlap between Pb concentrations determined by the FPXRF and ICP-MS methods (Figs. 2 and 3). It is noteworthy that the highest coefficient of determination was found in soils of Miedzianka, highlighted by the lowest Pb contents (Fig. 2A). The reason for this may be linked to corrections, i.e. the combination of fundamental parameters (FP) mode with Compton normalization, in the soil detection mode that was used in this study (Radu and Diamond, 2009). The other studies conducted in the post-mining or heavily polluted areas also confirmed excellent correlation ($r^2 = 0.99$) between Pb concentrations derived from parallel soil sample analyses by the FPXRF and ICP-OES methods ($r^2 = 0.97$) (Kilbride et al., 2006) or by the FPXRF and AAS methods (Radu and Diamond, 2009). In case of homogeneous material, Pb screening may be performed in the field, for example Hürkamp et al. (2009) determined the concentrations of Pb in floodplain alluvial deposits of the historic mining area at the Vils River near Freihung (Eastern Bavaria, Germany). These authors obtained a high coefficient of determination (0.94) between *in situ* and laboratory measurements.

Zinc also exhibited high coefficients of determination between FPXRF and ICP-MS measurements. These values varied from 0.910 (Karczówka) to 0.994 (Serwis). Paradoxically, the highest r^2 values in the technogenic soils of Serwis and Rudki ($r^2 = 0.971$) were associated with the most distinct discrepancies between Zn concentration profiles derived from

these two analytical methods. The best agreement of the FPXRF and ICP-MS profiles was recorded in the Miedzianka and Karczówka soils (Fig. 4).

The third element, Mn, showed high coefficient of determination values in the range of 0.886 (Rudki) to 0.997 (Miedzianka). Of the four sites examined, the Miedzianka soils (Fig. 5A) revealed a nearly perfect overlap of Mn concentration patterns derived from FPXRF and ICP-MS measurements. The Karczówka soils exhibited a distinctly worse overlap of these two patterns (Fig. 5B).

Copper displayed a diverse relationship between the coefficients of determination and the concentration levels at different sites. The relatively low r^2 values in the technogenic soils of Serwis (0.722) and Rudki (0.826) are mostly linked to the low contents of Cu, with a geometric mean of 27 mg/kg at Serwis and somewhat higher contents (geom. mean of 60 mg/kg) at Rudki. In contrast, the Cu-bearing soils of Miedzianka, genetically linked to Cu-sulfide mineralisation, were highlighted by both the high coefficient of determination (0.985) and the nearly excellent overlap of concentration profiles derived from these two analytical methods (Fig. 6A).

The Miedzianka soils revealed much higher contents of arsenic (geom. mean of 52 mg/kg) combined with high r^2 (0.971) and almost the same concentration patterns determined by these two methods (Fig. 6B). Very low concentrations of this element (geom. mean of 13 mg/kg) and a corresponding low coefficient of determination ($r^2 = 0.585$) were noted in the Serwis technogenic soils.

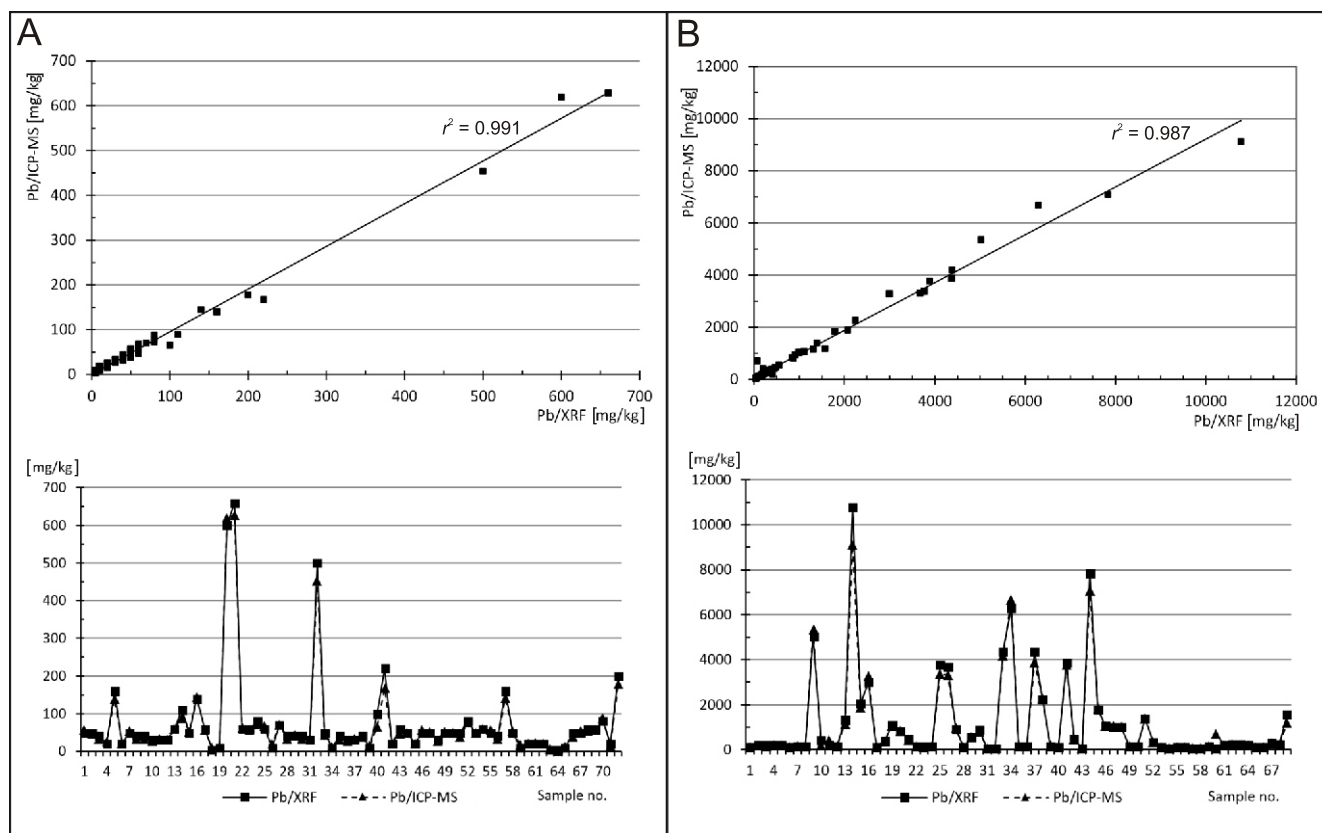


Fig. 2. Correlations and concentrations of Pb in historic mining soils derived from FPXRF and ICP-MS analyses: A – Miedzianka Mt.; B – Karczówka Mt.

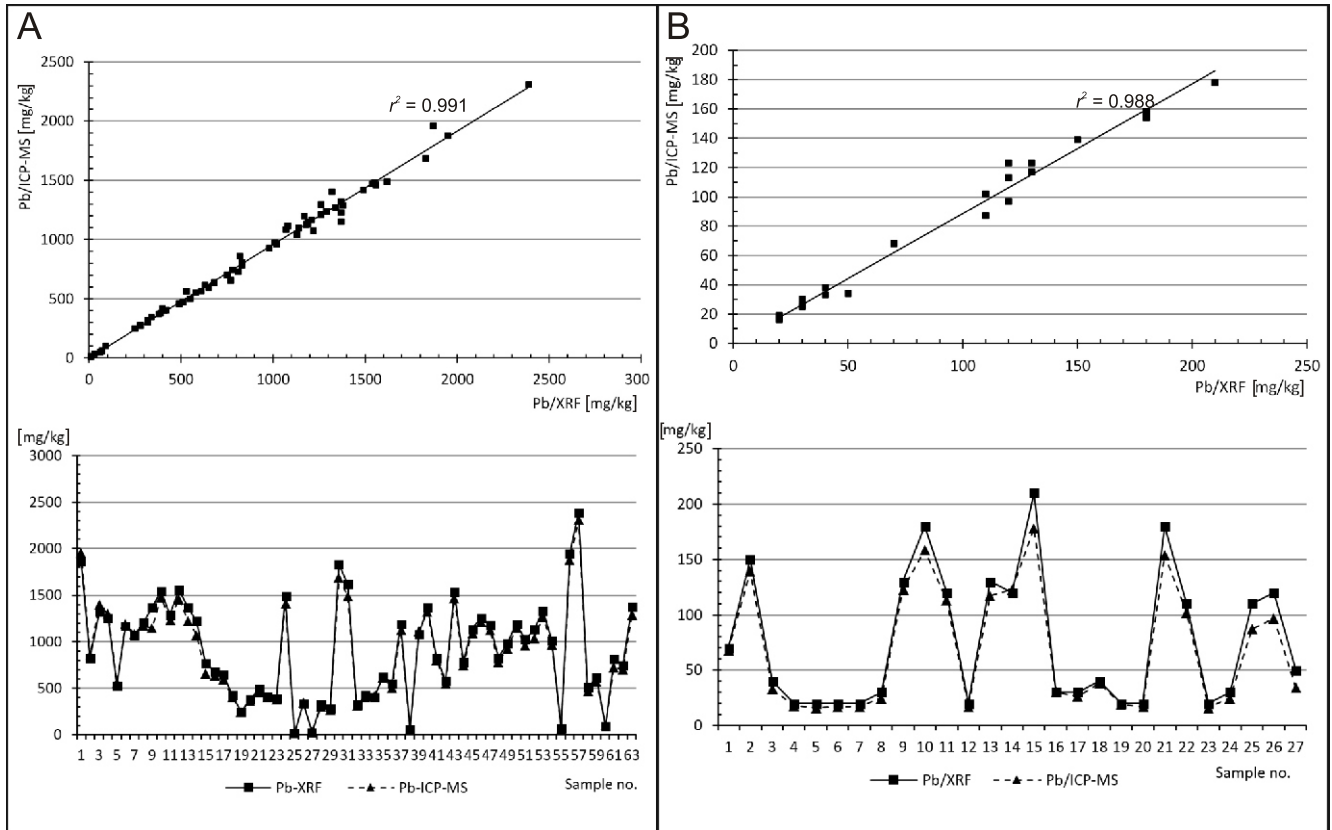


Fig. 3. Correlations and concentrations of Pb in historic mining soils derived from FPXRF and ICP-MS analyses: A – Rudki reclaimed mining area; B – Serwis mine tailings site

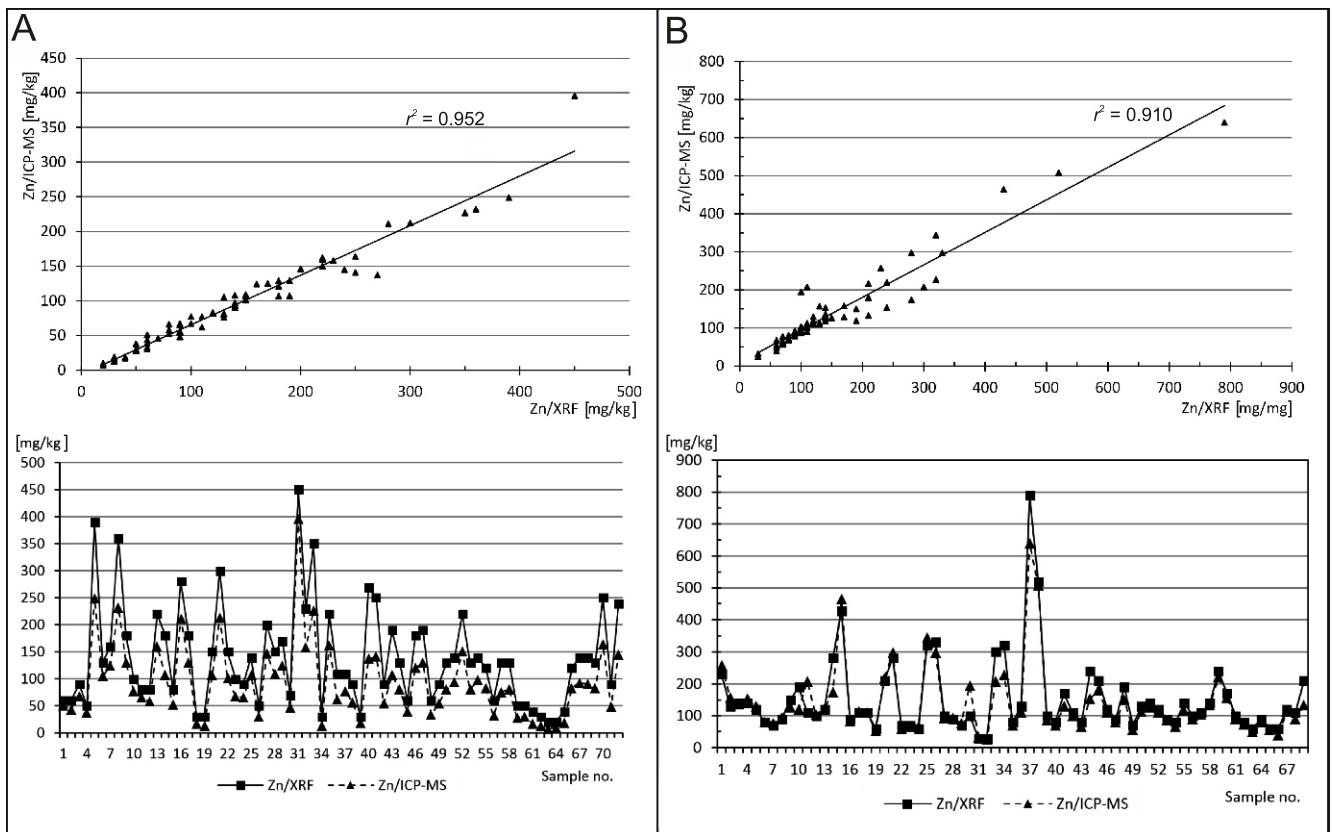


Fig. 4. Correlations and concentrations of Zn in historic mining soils derived from FPXRF and ICP-MS analyses: A – Miedzianka Mt.; B – Karczówka Mt.

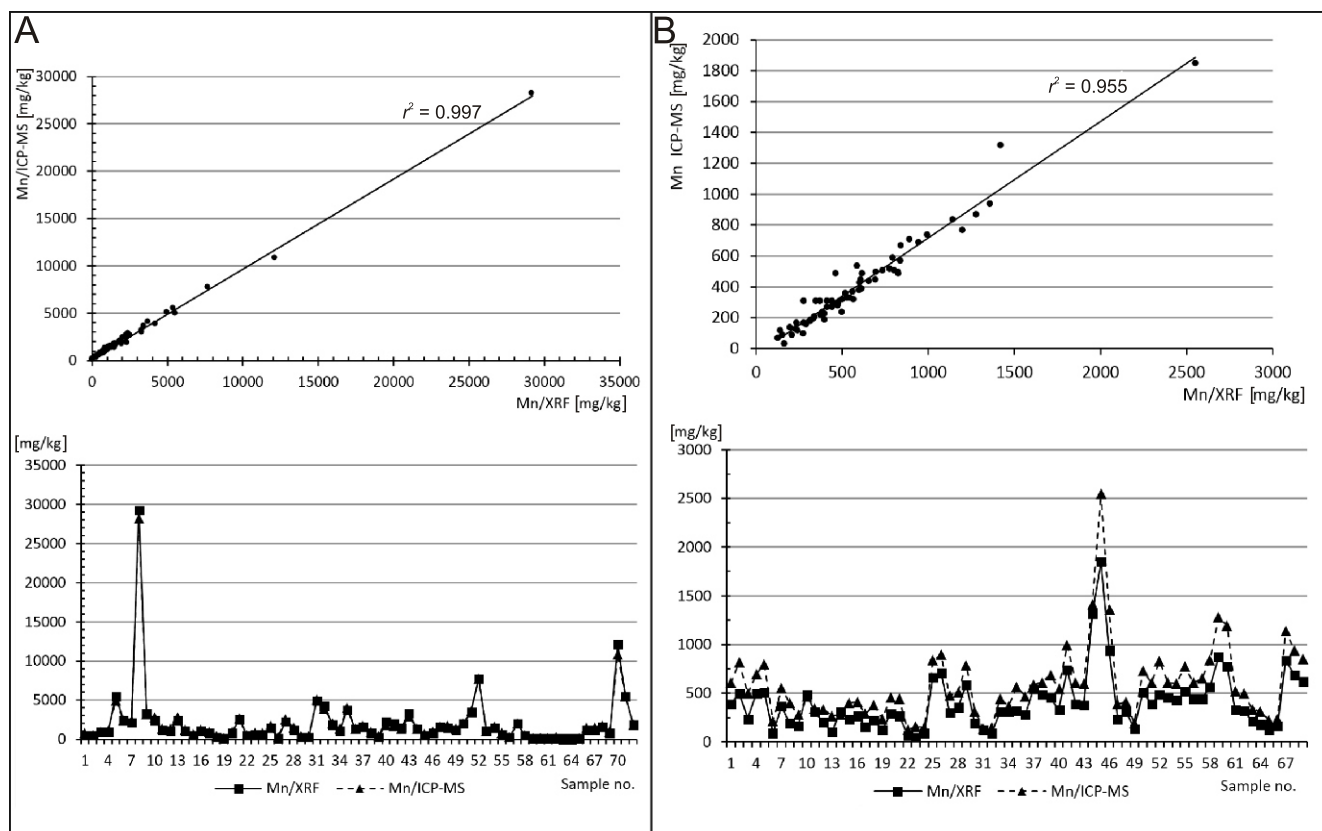


Fig. 5. Correlations and concentrations of Mn in historic mining soils derived from FPXRF and ICP-MS analyses: A – Miedzianka Mt.; B – Karczówka Mt.

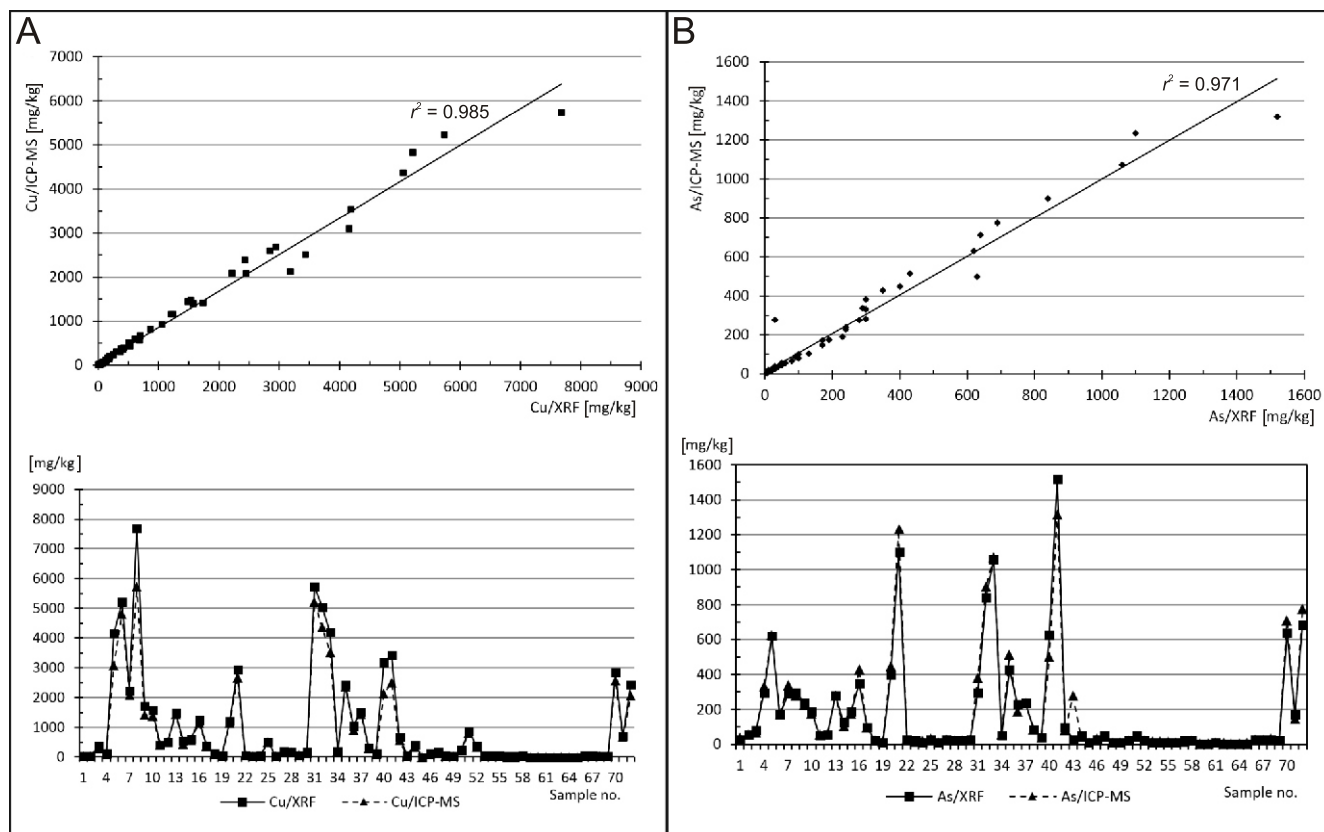


Fig. 6. Correlations and concentrations of (A) Cu and (B) As in historic mining soils of Miedzianka Mt. derived from FPXRF and ICP-MS analyses

LESSONS DRAWN FROM FPXRF AND ICP-MS MEASUREMENTS

Soils in the post-mining areas examined showed much diversified spatial distribution of the trace elements that originated primarily from mineralised bedrock, as well as from mining and processing activity. The concentrations of trace elements in these soils ranged over several orders of magnitude within short distances. This study showed that the FPXRF spectrometer was a handy instrument that enabled fast measurements, providing valuable data, especially for soils showing a high heterogeneity due to physical disturbance and natural contamination. However, the results derived from screening on-site measurements of trace elements in heterogeneous soils should be used with caution. In order to obtain more reliable results, soil samples must be homogenized through grinding and sieving prior to the FPXRF analysis. For example, Glanzman and Closs (2007) have shown that there is about 20% difference in As concentrations in soil determined by FPXRF in homogenized and in inhomogenized samples. The study of Markey et al. (2008) has demonstrated that sieving to <125 µm improved the accuracy of FPXRF lead determinations. According to the U.S. EPA Method 6200, soil and sediment samples should be sieved to 250 µm.

Another advantage of the FPXRF spectrometer was that this instrument allowed us to perform a large number of measurements in a very short time. However, the application of this method for quantitative analysis was problematic for those elements occurring in soils at levels close to detection limits. This is why the best-correlated results were obtained in soils rich in trace metals, such as the Karczówka soils, in which the minimum Pb concentrations were 4 times higher (mean of 40 mg/kg) than the detection limits of FPXRF (10 mg/kg).

This and other studies have shown the potential of FPXRF spectrometry for the determination of Pb concentrations in contaminated soils from areas influenced by metal-ore mining and processing, irrespective of the soil mineralogy, bedrock lithology or concentration levels of this element (Drake et al., 2003; Raab et al., 2005). Determinations of Pb by the FPXRF and ICP-MS methods both revealed similar coefficients of determination and nearly identical concentration levels of this element. The results derived from this study also showed an excellent performance of FPXRF over a wide range of Pb concentrations in soils. The same trend was displayed by As, Cu, and Mn of the Miedzianka soils. Different studies have shown that sulfide mineral phases undergo easy decomposition in oxidizing conditions, releasing different metal(loid)s into the environment (Smith and Huyck, 1999). Due to the karstification of limestones, the Miedzianka soils contain a variety of clay minerals and Fe-oxides and oxyhydroxides that scavenge elements released from decomposed sulfides. This specific soil matrix and a lack of metal(loid)s-bearing resistates (minerals resistant to weathering) also favor the desorption of trace elements at a lower pH. This is the reason why Pb, As, Cu, and Mn are easily *aqua regia*-extractable from Miedzianka soil samples, giving

nearly the same concentrations as those derived from the FPXRF measurements.

In contrast, As, Cu, Mn, and Zn concentrations of the remaining sites showed a distinct difference between the total and extractable concentrations. The specific lithology, mineralogy, and chemistry of these sites prevent the release of these elements; for example, the technogenic soils of Serwis and Rudki comprise Mn and Zn that occur in poorly dissolved carbonate minerals (siderite FeCO₃, Fe-rich dolomite) or Fe-oxides (e.g., hematite -Fe₂O₃), which host these elements mostly in their crystal lattices (substituting for Fe²⁺ or Fe³⁺). However, it should be stressed that mineralogical features and the insufficient extraction of metal(loid)s in *aqua regia* for ICP-MS, combined with FPXRF determinations, provide information about the presence or lack of resistates as well as about subtotal concentrations and the mobility of these elements in soils.

CONCLUSIONS

Our study shows that the FPXRF spectrometer can successfully be applied for the determinations of trace metal(loid)s in soils at historic mining sites. The following conclusions can be drawn from the geochemical data derived from this study:

1. The field portable XRF method shows excellent performance for Pb determinations in soils, irrespective of the bedrock lithology, mineralogy or concentration levels of this element, and confirms efficient lead extraction from soil samples prior to ICP-MS analyses.

2. Both FPXRF and ICP-MS methods give similar patterns over a wide range of other trace metal(loid) concentrations. The critical factor that leads to differences in element contents is the mineral and chemical characteristics of mine soils and spoils.

3. Except for Pb and partly As, Cu, and Mn (Miedzianka soils), the total element concentrations measured by the FPXRF spectrometer were generally higher than those determined by the ICP-MS instrument, indicating that the *aqua regia* extraction was insufficient to dissolve all mineral phases.

Because the FPXRF spectrometry is less time and reagent consuming, more cost-effective, and more environmentally friendly, its use for multi-element analyses of contaminated soils, such as these in the post-mining areas, is recommended. However, to obtain comparable data to ICP-MS, the soil samples require a simple treatment (sieving, drying), especially when they contain gravel and have a high humidity.

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