

Geochemical background of potentially toxic trace elements in soils of the historic copper mining area: a case study from Miedzianka Mt., Holy Cross Mountains, south-central Poland

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Abstract The aim of this study was to evaluate the geochemical background and spatial distribution patterns of selected trace elements (As, Cd, Cr, Cu, Mn, Ni, Pb, U and Zn) in 62 surface soil samples collected in the historic Cu mining area (Miedzianka Mt., Holy Cross Mountains, south-central Poland). In the study area the mining activity dates back to the fourteenth century. After the shutdown of mining operations in 1953, the soil was not remediated and neither its mineralogy nor chemistry was examined. The examined soils showed a high variability in the element concentrations. The threshold values defined as the upper limits of geochemical background range (mg kg^{-1} in parentheses) were Cr (63), Mn (2156), Ni (39), Cu (52), Zn (175), As (36), Cd (2), Pb (73) and U (1.9). A high percentage of the samples exhibited trace element concentrations above the upper limit of the geochemical background range. The threshold values were evaluated in this study with application of the iterative 2σ -technique. All of these values exceeded the standards recommended for soils in protected areas of Poland. The sampling points with anomalous concentrations of potentially toxic trace elements were located mostly in southern and western parts of the study area close to the sites of former mining activities. Very high concentrations of As, Cr and Ni at several sites may adversely influence the environment. High positive correlations between all the determined elements may be

indicative of a common geogenic source of these elements and their geochemical affinity.

Keywords Geochemical background · Historic mining areas · Trace elements · Soils · Poland

Introduction

In historic metal ore mining areas soils are usually enriched in potentially toxic trace elements. This enrichment results from natural (geochemical) processes like weathering of mineralized zones and from different forms of anthropogenic activities, including mining, processing, smelting of metal ores and disposal of mine wastes. The anthropogenic influence on soils can be more or less evident depending on the type and duration of metal ore extraction and also on efforts made to remediate soils after shutting down mining operations. However, no matter what precautions are taken, metal ore extraction and processing usually lead to multiple small-scale geochemical anomalies (Nannoni et al. 2011). The post-mining areas are often a source of serious environmental problems, caused, for example, by formation of acid mine drainage and consequently increased mobility of toxic metals (Nordstrom et al. 2000; García-Lorenzo et al. 2012). Other examples of environmental impact of the post mining areas are as follows: increased mobility of metals from sediments (Aleksander-Kwaterczak and Helios-Rybicka 2009), contamination of vegetables and herbaceous plants (Dudka et al. 1995; Bech et al. 2012). These areas create a health risk, for example, through a direct exposure to airborne soil and mineral particulates (Sing and Sing 2010).

Different approaches to soil remediation in historic metal ore mining areas have been tested, including (a) stabilization with municipal sewage sludge (Theodoratos et al.

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2000), (b) addition of different alkaline agents (Yukselen and Alpaslan 2001; Fernández-Caliani and Barba-Brioso 2010), (c) stabilization with mineral sorbents (García-Sánchez et al. 2002) and (d) phytoremediation (Abreu et al. 2008a). However, soil remediation is costly and often insufficient in areas where natural pollution sources prevail over anthropogenic ones (Hudson et al. 1997; Reimann and Garret 2005). Before remediation of soils in historic metal ore mining areas, it is important to establish a representative geochemical background range of metals in soils. Knowledge about the distribution of geochemical anomalies (values above the upper limit of geochemical background range) in the post-mining areas and evaluation of reliable threshold values could reduce the cost of cleanup operations and allows an indication of sites with the highest environmental and health hazard. The mobility and bioavailability of potentially toxic elements may be further examined with application of sequential extraction analyses (Fajković et al. 2011).

Since 2000, many authors have discussed the issues related to geochemical background and have proposed different methods of its evaluation (Matschullat et al. 2000; Li et al. 2003; Reimann and Garret 2005; Reimann et al. 2005; Gałuszka 2006, 2007; Gałuszka and Migaszewski 2011; Gustavsson et al. 2012; Rékási and Filep 2012). However, only very few publications have considered geochemical background of metals in soils of post-mining sites (Loredo et al. 2006; Teršič et al. 2009). In the historic mining areas the human-induced geochemical processes in the environment have been superimposed on the variable natural geochemical background where the abundances of chemical species can range over several orders of magnitude within several kilometer distances. These variations are inadequately documented and their existence is often overlooked in the establishment of land-use policy. Hudson et al. (1997) have criticized an approach of regulatory agencies to identification of the lowest concentrations of metals in different environmental samples collected in the post-mining areas as geochemical background values. These authors also stressed the need for recognition of site-specific background concentrations and development of guidelines for background characterization. The lack of uniform criteria for soil contamination assessment in areas with highly variable geochemical background has also been raised in scientific literature (Armiento et al. 2011).

The principal objectives of this study were as follows: (a) to characterize spatial distribution of nine trace elements (As, Cd, Cr, Cu, Mn, Ni, Pb, U, Zn) in soils of the historic Miedzianka copper mining area in south-central Poland; and (b) to evaluate site-specific geochemical background concentrations of these elements in the mine soils examined. The selection of the elements is based on their potential toxicity and/or on their occurrence in

minerals of the study area. The results obtained may serve as reference levels for future studies in other historic mining areas in the Holy Cross Mountains and at similar sites all over the world.

Materials and methods

Study area

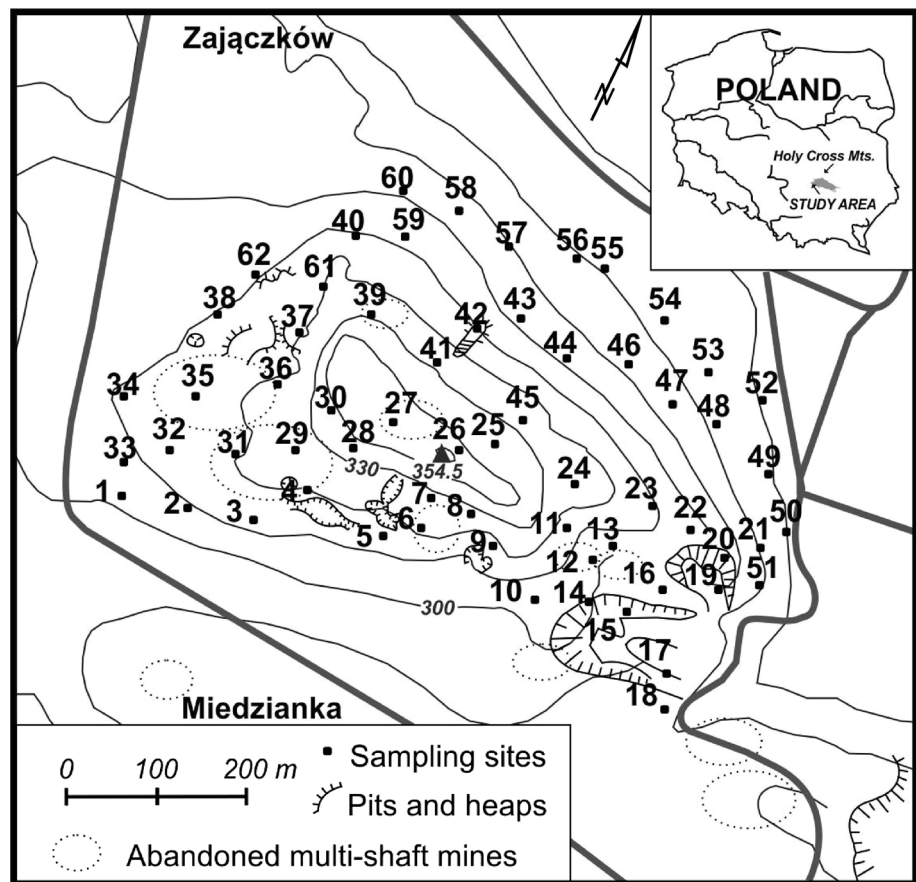
The study area is located in the southwestern part of the Holy Cross Mountains, south-central Poland. The soil samples were collected at Miedzianka Mt. (354 m a.s.l.) covering the area of about 25 hectares (Fig. 1). Only the highest cliffs lack a soil cover. In 1958 Miedzianka Mt. was established a nature reserve to conserve the geological heritage and to protect the xerothermic plant communities which are well developed on Rendzic Leptosols. The study area is located on a popular tourist trail. The mountain is partly surrounded by two villages: Miedzianka and Zajaczków. This reserve is frequently visited by speleologists who explore the abandoned mining workings.

Geology

The Miedzianka Mt. is located in the southwestern part of the parallel Chęciny Anticline. In general, this tectonic unit consists of the Lower Cambrian mudstone-sandstone core and the Middle and Upper Devonian limestones and dolomites cropping out on the northern and southern anticline flanks (Mastella et al. 2013). The towering Miedzianka Mt. is built of poorly bedded upper Givetian and Frasnian/Famennian limestones (Fig. 2). These massive organogenic limestones are locally pierced with calcite and Cu sulfide ore veins. The younger Frasnian/Famennian limestone series with calcareous-clayey shale lenses and interbeds are exposed in the southeastern part of Miedzianka Mt. The Lower Cambrian mudstones and sandstones adjoin this mountain to the north, whereas Lower Triassic sandstones, clayey shales and marls to the south and west. Few patches of uppermost Permian conglomerates occur in the northwestern part. Locally, these rock formations are covered with Pleistocene fluvioglacial sands with subordinate tills averaging 2 m in thickness, but in the northern part of the mountain foot reaching even 30 m. Intensive weathering of limestones has led to formation of residual clays and debris that fill sinkholes, fissures and other karst surface features.

According to Migaszewski et al. (1996) there were at least four major phases of Variscan and post-Variscan calcite mineralization in the study area. Metal ore mineralization formed in turn during three phases (Rubinowski 1971): (a) hydrothermal primary mineral ore formation

Fig. 1 Map of the study area with sampling sites



(Cu, Fe, Zn, Pb and Ni sulfides and sulfo-salts); (b) weathering and crystallization of secondary sulfides (chalcocite), and (c) remobilization and adsorption of copper ions onto residual clays (originated from limestone karstification) and, subsequently, generation of copper carbonates (malachite and azurite). Copper mineralization occurs in a longitudinal fault zone that developed in the southwestern part of the Miedzianka massif (Balcerzak et al. 1992). The Cu sulfide ore extraction was conducted mostly in the southeastern margin of the tectonic block (main mining field) and partly in the southwestern margin of Miedzianka Mt. The high-grade Cu sulfide ores containing up to 70 % Cu form veins within limestones.

Mineralogy The copper minerals reported from the study area are covellite, chalcocite, tennantite, native copper, and a long list of secondary minerals, including cuprite, tenorite, malachite, azurite, conicalcrite, cornubite, olivenite, zincian olivenite, tyrolite, hentschelite, pseudo-malachite, antlerite, brochantite and marshite (Wieser and Żabiński 1986; Bzowska et al. 2003; Karwowski 2009). Numerous minerals of metals other than copper have been identified from this locality, namely pyrite, goethite, hematite, adamite, austinite, gersdorffite, galena, anglesite,

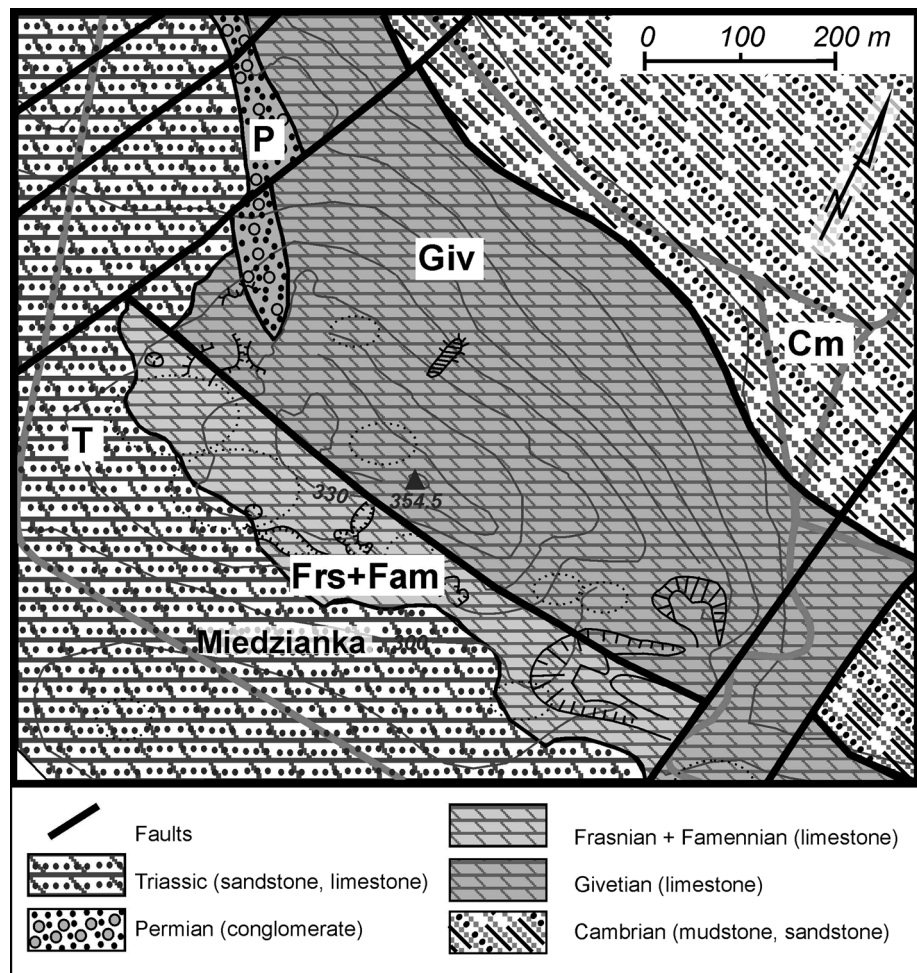
cerussite, pyromorphite, asbolane, native silver and gold (www.mindat.org/loc-2573.html, Accessed 1 Jan 2015).

The history of mining

Copper was intermittently extracted from the Miedzianka mineral deposit since the Middle Ages (fourteenth century) until 1953. The most intensive Cu ore extraction lasted from the fifteenth to the seventeenth century. Copper was extracted from numerous multi-shaft mines (Fig. 1) and from several underground mines. Multi-shaft mines were operating mostly at the beginning of Miedzianka mining history during the Medieval times. Additionally, in the southeastern part of the mountain, limestone was quarried and this mining activity is documented in two abandoned quarries.

A long history of copper ore and limestone mining impacted both geomorphology, bedrock and soils of the study area. All the underground workings are estimated to be about 4 km long. An interesting episode in the Miedzianka mining history is the invention of copper and zinc electrolytic extraction by Stanisław Łaszczynski, the former mine owner. This invention was patented in April 19 of 1904 by the US Patent Office (No. 757817).

Fig. 2 Geologic map of the study area (modified, after Rubinowski 1971)



Soils

In the upper parts of the mountain and in the vicinity of abandoned shafts and mine waste heaps the soils are shallow and weakly developed. The northern and north-western parts of the mountain have a dense plant cover. The soils of the study area can be classified according to the International Union of Soil Sciences Working Group (WRB 2006) as Leptosols (developed on Devonian limestones), Cambisols (developed on post-glacial Pleistocene sands) and Technosols. Rendzic Leptosols occur at lower elevations, whereas Lithic Leptosols can be found near the top. Cambisols predominate at the northern foot of the mountain. Technosols occur in the vicinity of abandoned shafts and mine spoils.

Soil sampling

Fieldwork was conducted in November of 2012. Soil samples were collected at 62 sampling sites in the historic copper mining area “Miedzianka Mt.”. A systematic

random sampling design was used for selection of sampling sites. Locations of sampling points were determined using a Global Positioning System with a precision of $\pm 4\text{--}5$ m and were used for plotting these points on a map (Fig. 1). About 2 kg of soil was collected per site from pits that were dug to a depth of about 0.5 m. Each composite soil sample consisted of 5–10 subsamples. The collected soil samples were placed in polyethylene bags and transported on the day of sampling to the laboratory. During sample collection, transport, storage and treatment, procedures were followed to minimize the possibility of contamination, i.e. talc-free disposable vinyl gloves were used during sampling and sample treatment, and samples were placed in polyethylene zip-lock bags and plastic trays to prevent accidental mixing.

Sample preparation and chemical analysis

In the laboratory, the soil samples were air dried for several days in a separate sample storage room with a limited access. After drying, the soil samples were sieved to obtain

<2.00 mm fraction and then disaggregated to pass a <0.063 mm sieve using a Pulverisette 2 Fritsch's blender and then Analysette 3 Spartan shaker.

The pH of soil samples was measured in water extracts in the laboratory. About 10 g of each sample was placed in a beaker and stirred vigorously with 25 mL of deionized water. The pH measurements were made in the filtered extracts after 24 h at a room temperature of about 20 °C. Granulometric analysis was performed by a standard sieve-pipette method.

Soil samples (0.5 g) were digested with aqua regia (6 mL HCl + 2 mL HNO₃) in a closed microwave system Multiwave 3000. The soil samples were analyzed for the following trace elements: As, Cd, Cr, Cu, Mn, Ni, Pb, U and Zn with the ICP-MS technique (instrument model ELAN DRC II, Perkin Elmer).

The standard reference materials (SRM) applied for measuring element concentrations were Certified Reference Material (CRM) NIST 2710a (Montana I Soil) and GSS4 (Chinese Academy of Geological Sciences). Quality control included both accuracy (CRM) and precision (triplicates). The average recovery of elements from the CRM was in the range of 81–96 %.

Lead isotope ratios (^{206/207}Pb and ^{208/206}Pb) were measured with a quadrupole ICP-MS (instrument model ELAN DRC II, Perkin Elmer) using the isotope ratio mode of analysis. A standard solution with known lead isotope ratios was prepared by dissolution of the NIST standard reference material 981 in a concentrated Suprapure HNO₃ (Merck). A 50 µg L⁻¹ solution of this standard was analyzed at a frequency of every third sample and the obtained results were used for mass bias corrections. The obtained correction factors varied from 0.970 to 0.999.

A single polished section of galena sample collected at the Miedzianka Mt. was analyzed for trace element concentrations by laser ablation ICP-MS (LA-ICP-MS). The ICP-MS model ELAN DRC II, Perkin Elmer was equipped with ablation system LSX-500 UV Nd:YAG (CETAC) operating at 266 nm wavelength. A matrix-matched reference material MASS-1 (polymetal sulfide, USGS) was used for calibration (Wilson et al. 2002). Ablation was performed with a single-point mode and a 50-µm beam size with a 70 % energy level. Analytical methodology was similar to that reported for pyrite samples analyses by Diehl et al. (2012).

Major element composition of the homogenized soil samples and trace elements in limestone and calcite samples were determined by the ED-XRF method using a FP-XRF instrument Niton XL3T Gold+ (Thermo Scientific) with an excitation source 50 kV X-ray tube with Ag anode.

Additionally, several mineral samples were examined with an optical stereoscopic microscope, Leica M205A. Mineral samples prepared as thin polished sections were analyzed by an electron microprobe (Cameca SX-100

equipped with four wavelength dispersive detectors) at the Faculty of Geology, University of Warsaw, Poland. The accelerating voltage was 15 kV and the probe current was either 10 or 20 nA.

All measurements, except for electron microprobe analysis, were done in the Geochemical Laboratory of the Institute of Chemistry, Jan Kochanowski University, Kielce, Poland.

XRD analyses

Bulk soil mineralogy of selected soil samples was assessed by the random powder X-ray diffraction (Thermo ARL SCINTAG X'TRA X-ray diffractometer with Cu K α irradiation). Clay mineral fraction <2 µm was obtained using sedimentation method. The samples were centrifuged twice for 15 min using a Sigma 4–15 centrifuge. The clay suspensions were pipetted onto a glass slide and left to dry at an ambient temperature. Clay mineral species were determined based on the oriented air-dried (untreated) samples, and ethylene glycol-solvated and heated (550 °C) samples according to the methods described by Moore and Reynolds (1989). Because the clay minerals peaks were well resolved, no treatment was necessary for the removal of carbonates or organic matter.

Measurements were done at 40 kV and 40 mA and scan rates from 3 to 30° 2 Θ (or from 2 to 30° 2 Θ) at 0.02° 2 Θ min⁻¹ step size. Phase identification and peak area determinations were done using the Win XRD software. The XRD analyses were performed in the Institute of Geology, Adam Mickiewicz University, Poznań, Poland.

Evaluation of geochemical background

Geochemical background represents a range of values in a geochemical dataset, which is usually considered as a natural concentration range of a specific chemical substance in a media examined, which is not influenced by the anthropogenic activity (Reimann and Garret 2005). The values that lie outside of this range (the so-called outliers) are considered either negative or positive geochemical anomalies. Of different statistical techniques that have been used for evaluation of geochemical background ranges (Matschullat et al. 2000; Reimann et al. 2005), the iterative 2 σ -technique was found plausible and realistic (Matschullat et al. 2000). This simple technique is based on the assumption that all values beyond the mean $\pm 2\sigma$ are omitted from the dataset and the new mean $\pm 2\sigma$ range is calculated using the reduced data. This procedure is repeated until all the values of the dataset lie within this range (approaching a normal distribution).

There are numerous examples of the use of iterative 2 σ -technique for evaluation of geochemical background of the

following: (a) trace elements in soils (Loska et al. 2005; Roca et al. 2012; Lecce and Pavlowsky 2014); (b) major ions and electric conductivity in groundwater (Urresti-Estala et al. 2013); (c) iron in fluvial sediments (de Lima Rodrigues et al. 2014) and (d) trace elements in soil, sediment and loess samples (Zgłobicki et al. 2011).

Results and discussion

Basic soil properties and mineral composition of soils

The selected properties of soil samples are presented in Table 1. The pH of soils was in the range of 5.6–7.3 with a mean of 6.2. The examined soils are coarse textured with fine and very fine-grained sand being dominant sub-fractions (Fig. 3). The mineral composition of <2 mm fraction showed enrichment in quartz with subordinate amounts of calcite, kaolinite, illite and feldspars (Table 2). In several samples quartz and kaolinite were the predominant minerals. Quartz, kaolinite and muscovite prevailed in <2 mm fraction of samples M19 and M28, in which a small admixture of phosphate minerals (probably fluorine apatite) was found (Fig. 4). In the soil clay fraction (<2 μm) kaolinite, smectite, illite, quartz, mixed-layer illite-smectite and kaolinite-smectite were identified.

Element concentrations, their possible sources and distribution in soils

The concentrations of trace elements and the summary statistics are presented in Tables 3 and 4. The distribution of trace elements is very heterogeneous as depicted in Fig. 5. In general, the highest element concentrations were found in the central, western and southern parts of the study area in the vicinity of abandoned multi-shaft mines. The elements showed the following threshold values (mg kg⁻¹ in parentheses): Cr (63), Mn (2156), Ni (39), Cu (52), Zn (175), As (36), Cd (2), Pb (73) and U (1.9).

Optical microscopic observations of minerals collected in the study area confirmed the presence of primary Cu minerals (tennantite) and secondary minerals (azurite, malachite and iron oxyhydroxides) (Fig. 6a, b). The presence of tennantite with subordinate chalcopyrite, pyrite and galena was also documented by the electron microprobe analyses (Fig. 6c, d), which also revealed the occurrence of secondary Cu-Fe-Zn arsenates that contained up to 19.8 % As and trace quantities of S (<1 %) (Fig. 6c). The limestone and calcite samples showed elevated levels of Mn (231–501 and 318–470 mg kg⁻¹), Ni (<20–143 and 101–166 mg kg⁻¹) and Cu (23–1020 and 37–444 mg kg⁻¹), respectively (Table 5). The results of chemical analyses of geologic samples from the study area

show that geogenic sources are responsible for contamination of soils with arsenic, copper, lead and nickel.

Chromium

The contents of chromium in soils strongly depend on mineral composition of the bedrock and the soil texture with the highest concentrations found in silty and loamy soils (Kabata-Pendias and Mukherjee 2007). The mobility of Cr in this medium is rather poor due to low solubility of its minerals. However, Cr contents in surface soil are affected by local geology and geomorphology (Petrotou et al. 2012). The pH and oxidation state have the highest influence on Cr mobility in soils. The solubility of Cr³⁺ dramatically decreases in the pH of above 3 and Cr⁶⁺ is practically immobilized in the pH range of 5.5–8 (Kabata-Pendias and Mukherjee 2007). Oxidation of Cr³⁺ and reduction of Cr⁶⁺ in soils can be simultaneous in the same redox conditions (Dhal et al. 2013).

The total concentrations of Cr in the present study varied from 5.2 to 221.2 mg kg⁻¹ with a mean of 39.5 mg kg⁻¹ (Table 4). In most soil samples the Cr concentrations were lower than the world median content of this element which is estimated to be 54 mg kg⁻¹ (Kabata-Pendias and Mukherjee 2007). The relatively low Cr contents (16–60 mg kg⁻¹) were reported from the post-mining soils from the High Moulouya Valley in Morocco (Iavazzo et al. 2012). The high Spearman's correlation coefficient values were found in the examined soils for Cr and Ni (0.88), Zn (0.81) and U (0.80) (Table 6). No Cr minerals have been reported from the study area, but this metal readily substitutes for Fe in tennantite, hematite, goethite, pyrite, and its geogenic source in the examined soils cannot be neglected. A strong correlation between Cr–Ni and Cr–U is common in soils (Salminen et al. 2005).

Manganese

Manganese is the most abundant trace element in the lithosphere and its natural content can be as high as 9000 mg kg⁻¹ in medium loamy and calcareous soils (Kabata-Pendias 2011). The world mean Mn soil concentration is 437 mg kg⁻¹ (Kabata-Pendias and Mukherjee 2007). Amorphous mineral phases, such as Mn oxides and hydroxides that are the most common forms of this metal in soils, play an important role in sorption of trace elements in soils.

Manganese showed a very broad range of concentrations in the examined soils (37–28,185 mg kg⁻¹, mean of 2463 mg kg⁻¹). The Mn concentrations above 1 % in samples M7, M30 and M61 are brought about by soil enrichment in Mn minerals. These samples had also the highest levels of Fe oxides (Table 1). Calcite and limestone samples collected in the study area are enriched in Mn. Occurrence of manganese oxides and hydroxides and asbolane has been

Table 1 The selected properties of the soil samples

	pH	Fe ₂ O ₃	CaO	K ₂ O
M1	5.6	1.6	0.2	1.7
M2	5.8	4.0	0.4	2.6
M3	5.8	1.0	0.2	1.1
M4	7.1	6.7	8.0	2.8
M5	7.1	6.3	2.2	2.9
M6	6.8	3.5	4.3	1.8
M7	6.7	10.6	4.2	2.6
M8	5.9	9.4	2.9	4.0
M9	6.4	3.6	0.9	2.1
M10	6.0	1.2	0.7	1.1
M11	6.5	5.0	1.5	2.8
M12	6.4	2.8	0.9	1.6
M13	6.0	2.6	0.6	2.7
M14	6.7	3.9	10.6	2.2
M15	6.5	4.5	4.0	2.2
M16	6.5	0.6	0.5	1.1
M17	6.7	0.5	0.5	1.0
M18	7.2	3.1	0.5	3.3
M19	7.3	4.3	3.9	3.1
M20	6.5	2.8	1.7	1.2
M21	6.0	2.0	1.5	1.1
M22	6.5	3.2	7.5	1.2
M23	6.2	0.6	0.4	1.1
M24	6.2	3.2	1.7	1.2
M25	6.0	1.9	0.7	1.3
M26	6.3	2.2	1.4	1.2
M27	5.8	1.3	0.6	1.2
M28	6.6	5.7	10.4	3.8
M29	7.2	5.7	3.6	3.4
M30	6.7	12.3	1.3	3.6
M31	6.5	2.0	0.2	1.7
M32	7.2	4.1	2.9	3.1
M33	6.8	2.2	0.6	2.0
M34	5.9	2.4	0.3	2.2
M35	6.9	2.7	2.7	2.7
M36	7.0	3.1	2.6	2.4
M37	5.7	4.5	0.6	3.1
M38	6.6	3.1	1.8	1.9
M39	6.4	2.7	1.1	1.4
M40	5.8	0.8	0.4	1.0
M41	6.5	2.1	3.3	1.3
M42	6.2	2.6	1.1	1.3
M43	5.9	1.1	0.6	1.0
M44	6.1	2.1	1.1	1.3
M45	6.2	2.7	1.0	1.3
M46	6.6	3.4	3.5	1.3
M47	6.4	2.2	2.3	1.2
M48	5.7	2.0	0.9	1.1

Table 1 continued

	pH	Fe ₂ O ₃	CaO	K ₂ O
M49	6.0	1.2	1.0	1.0
M50	6.5	3.0	1.7	1.0
M51	6.6	3.0	1.8	1.0
M52	6.5	0.5	0.3	0.8
M53	6.2	0.5	0.2	0.8
M54	6.1	0.4	0.3	0.8
M55	6.2	0.4	0.2	0.7
M56	6.1	0.3	0.2	0.9
M57	5.8	0.8	0.3	1.0
M58	6.6	3.4	1.5	1.5
M59	6.7	3.8	1.7	1.6
M60	6.2	2.2	1.1	1.3
M61	6.7	8.0	1.2	3.4
M62	6.5	4.2	2.4	3.1
Minimum	5.6	0.3	0.2	0.7
Maximum	7.3	12.3	10.6	4.0
Mean	6.2	3.1	1.9	1.8

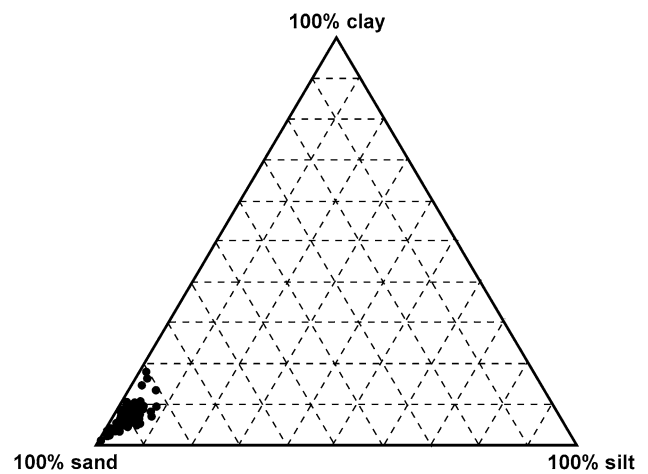


Fig. 3 A soil textural triangle

reported from the study area and this may confirm a geogenic source of this element. Manganese did not show a strong correlation with other elements, except for Ni, as evidenced from the Spearman’s correlation coefficient values (Table 6). A positive correlation between Mn and Ni may be explained by their co-occurrence in asbolane.

According to Kabata-Pendias (2011), Mn-rich surface soils exhibit Mn concentrations in the range of 5.5–13.6 %. The raised levels of Mn, 1446–4153 mg kg⁻¹, were found in surface soils (A-horizon) in the abandoned Miguel Vacas copper mine in SE Portugal (Abreu et al. 2008b). Similarly, high Mn concentrations in post-mining soils (400–4520 mg kg⁻¹) were reported from the High Mouloya Valley, Morocco (Iavazzo et al. 2012).

Table 2 Semi-quantitative mineral composition of selected soil samples based on XRD patterns

Sample no.	Fraction	Phyllosilicates						Cc	FSK	FAP	Q
		K	S	K/S	I/S	I	M				
M5	Bulk soil	tr				tr		+			+++
	<0.002 mm	++			+	++					
M7	Bulk soil	++				+					+++
	<0.002 mm	++			+	++					tr
M19	Bulk soil	++				+	++	+	+	+ (?)	+++
	<0.002 mm	++		+		++				+	+
M28	Bulk soil	++					++	++	+	+ (?)	+++
	<0.002 mm	++				+					tr
M35	Bulk soil	++				tr		+			+++
	<0.002 mm	+++		+		+					tr
M36	Bulk soil	++				++		+	+		+++
	<0.002 mm	+++		+		+					tr
M52	Bulk soil								+		+++
	<0.002 mm	+				+					+++
M53	Bulk soil								+		+++
	<0.002 mm	+	+			+			++		+++
M62	Bulk soil	+++				+++			+		++
	<0.002 mm	+++		+		+++			++		++

K kaolinite, *S* smectite, *K/S* kaolinite/smectite, *I/S* illite/smectite, *I* illite, *M* muscovite, *Cc* calcite, *FSK* K-feldspar, *FAP* fluorapatite, *Q* quartz, estimated proportion of minerals: +++ dominant, ++ moderate, + small, *tr* trace

Nickel

An average world abundance of Ni in soils is 29 mg kg⁻¹, but natural concentrations of this metal depend on the soil properties, being the highest in calcareous (18–92 mg kg⁻¹) and heavy loamy soils (23–50 mg kg⁻¹) (Kabata-Pendias 2011). The Ni concentrations in the examined soils were in the range of 1.4–127 mg kg⁻¹ with a mean of 28.5 mg kg⁻¹. The spatial distribution of Ni anomalies in the soils of the study area is similar to those of Mn (Fig. 5). This relationship may be explained by a high Ni sorption by Mn oxides and hydroxides, in which accumulation of Ni varies from 40 to 4900 mg kg⁻¹ (Kabata-Pendias and Mukherjee 2007). Nickel showed the high Spearman's correlation coefficient values with Cu (0.87), Zn (0.86), U (0.86) and Cd (0.80) (Table 6), which may be indicative of its geogenic origin in the soils examined. Nickel is a constituent of gersdorffite and asbolane that have been reported from Miedzianka and it also reveals high concentrations in calcite (101–166 mg kg⁻¹) and limestone (<20–143 mg kg⁻¹) (Table 5). The strongest correlation between Ni and Cu also supports a natural, geogenic source of this element in the study area.

The similar Ni contents (37–106 mg kg⁻¹) were also reported in the surface post-mining soils from the abandoned Miguel Vacas copper mine in SE Portugal (Abreu et al. 2008b). Somewhat higher Ni levels (5–353 mg kg⁻¹)

were found in soils from the former Cu ore mines in the Sudetes Mts, SW Poland (Karczewska et al. 2006).

Copper

Typical concentrations of copper in soils range from 14 to 109 mg kg⁻¹ being the highest in loamy soils, whereas they are the lowest in light sandy soils (Kabata-Pendias 2011). Although many soil samples of the study area showed even lower than typical Cu levels, this metal occurred in these soils in a very broad range of concentrations (1–5732 mg kg⁻¹) with a high mean of 927 mg kg⁻¹. The highest Cu contents were recorded in the southern and western parts of the study area with positive anomalies located in the vicinity of mine waste heaps and pits. The concentrations of Cu are strongly correlated with As (0.89), Ni (0.87) and U (0.86) (Table 6). A strong correlation between Cu and As can be explained by the co-occurrence of these elements in such minerals as conicalcrite, cornubite, olivenite, zincian olivenite, tennantite and tyrolite.

Metal ore mining usually leads to enrichment of soils with Cu, even if this metal is not directly extracted, because the majority of ores are polymetallic sulfides. For example, the Cu concentrations in the range of 17–225 mg kg⁻¹ were found in the abandoned mercury mining area in northern Spain (Loredo et al. 2006). Similarly, the contents of this metal ranged from 13 to

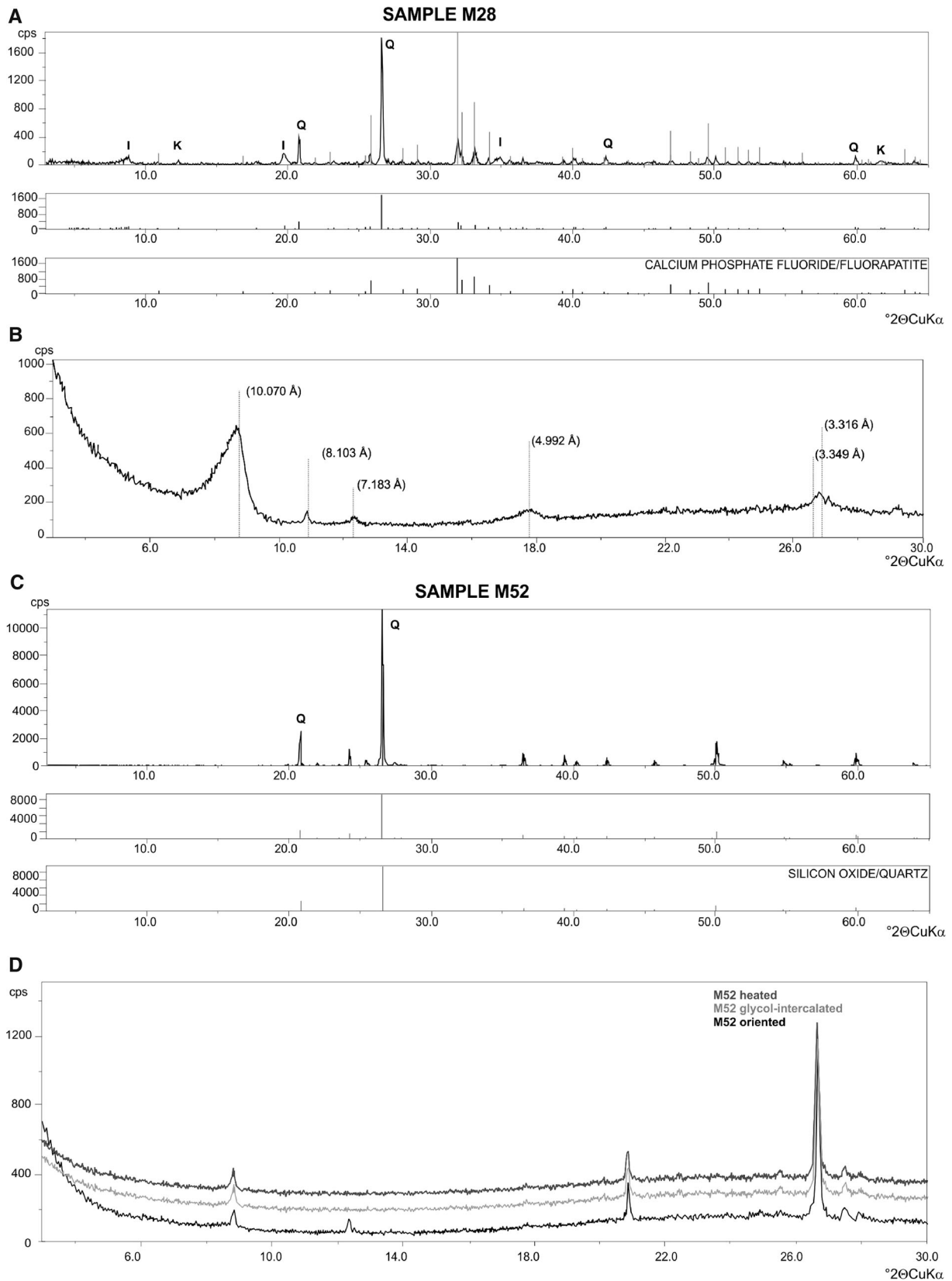


Fig. 4 Examples of the XRD patterns for samples M28 and M52. **a, c** Powder samples; **b, d** values for $<2\ \mu\text{m}$ fraction, oriented sample; **d** multiple diagram for $<2\ \mu\text{m}$ fraction; *Q* quartz, *K* kaolinite, *I* illite

Table 3 Concentrations of potentially toxic trace elements in the Miedzianka mine soil samples (values in bold exceed the upper limit of geochemical background range)

Sample	As	Cd	Cr	Cu	Mn	Ni	Pb	U	Zn
M1	39	0.752	19.3	30	745	5.5	57.8	1.36	51
M2	67	1.200	40.0	297	954	24.3	34.3	2.14	67
M3	332	0.769	12.9	112	1240	6.6	25.1	0.89	38
M4	630	4.119	52.3	3094	4907	62.0	138.9	4.77	249
M5	172	0.951	70.4	4824	2371	94.3	20.2	4.07	105
M6	339	2.697	37.1	2085	2371	36.4	54.6	2.37	124
M7	282	7.966	49.6	5732	28,185	127.0	32.9	8.05	232
M8	228	1.948	94.0	1412	3149	56.6	33.6	9.57	129
M9	174	1.388	35.5	1397	2785	36.1	27.9	3.14	77
M10	55	0.951	17.7	388	1338	11.2	32.6	1.06	66
M11	277	2.544	61.5	1440	2780	41.2	60.2	4.78	160
M12	104	1.388	29.4	422	1188	19.6	88.7	2.52	107
M13	176	0.805	37.1	586	659	19.2	52.3	2.20	53
M14	429	2.590	57.9	1158	1227	66.7	144.6	1.81	211
M15	100	1.636	67.3	361	890	43.5	57.4	3.20	129
M16	24	0.332	10.0	106	37	3.6	8.9	0.44	16
M17	17	0.371	9.1	39	155	3.0	9.4	0.46	13
M18	449	1.397	50.8	1158	913	34.6	618.8	2.16	107
M19	1234	3.619	49.9	2679	2663	57.1	628.2	3.61	212
M20	28	1.599	46.6	50	565	20.9	61.9	1.15	101
M21	16	1.175	33.4	20	780	13.3	57.0	0.75	67
M22	34	1.581	54.9	503	1746	22.5	67.7	2.11	108
M23	11	0.726	10.9	18	270	3.7	19.0	0.41	30
M24	28	1.603	54.1	183	2579	27.6	70.4	1.17	146
M25	21	0.963	29.0	163	1412	21.4	34.1	0.77	109
M26	22	0.849	30.4	61	389	13.4	44.4	0.71	125
M27	32	0.574	21.0	149	350	6.0	34.0	0.92	46
M28	383	9.003	86.4	5226	5081	106.5	33.5	11.75	396
M29	900	3.012	68.7	4361	3869	68.1	453.5	4.22	158
M30	1073	3.932	76.3	3539	20,043	109.9	42.9	7.05	227
M31	56	0.362	23.4	188	1366	7.3	12.4	1.85	13
M32	515	3.279	57.1	2382	3999	48.7	31.5	3.78	162
M33	190	1.522	21.4	912	1294	19.1	26.9	1.55	62
M34	88	1.304	28.2	299	918	13.4	37.5	1.88	56
M35	499	2.953	221.2	2121	1820	27.6	65.0	1.84	137
M36	1319	3.017	27.9	2505	1717	35.3	167.1	1.64	141
M37	80	0.845	56.6	561	1331	55.5	20.2	1.74	54
M38	278	2.209	34.8	35	2906	16.3	46.9	1.26	107
M39	48	1.275	31.1	345	1361	18.9	50.4	0.88	80
M40	9	0.516	12.6	5	641	3.0	21.1	0.45	39
M41	33	1.771	31.9	100	955	15.6	56.5	0.99	121
M42	46	1.738	35.9	133	1670	18.4	51.6	1.00	129
M43	11	0.556	15.6	30	1682	6.2	28.5	0.58	33
M44	19	1.429	27.5	231	2031	20.2	48.1	0.95	80
M45	46	1.127	30.2	807	3562	35.9	37.5	1.08	94
M46	19	2.663	40.1	352	7721	21.5	78.6	1.25	150
M47	13	1.256	29.4	31	1045	12.2	48.6	0.90	80

Table 3 continued

Sample	As	Cd	Cr	Cu	Mn	Ni	Pb	U	Zn
M48	15	1.261	32.4	48	742	14.0	56.2	0.86	82
M49	12	0.804	21.8	8	322	7.3	32.5	0.84	31
M50	17	1.598	52.3	12	1974	18.5	140.5	1.18	76
M51	20	1.493	39.5	26	491	21.2	53.7	0.82	81
M52	6	0.444	9.6	3	91	4.0	17.6	0.35	28
M53	7	0.437	9.1	2	114	2.8	22.3	0.39	17
M54	7	0.438	6.7	3	208	1.6	20.4	0.35	13
M55	4	0.161	5.6	1	61	2.7	7.5	0.32	7
M56	4	0.122	5.2	3	69	1.4	2.7	0.25	1
M57	7	0.246	10.4	4	180	2.5	12.8	0.43	19
M58	30	1.216	40.1	39	1468	20.3	38.6	1.08	83
M59	31	1.750	40.9	15	1743	17.9	55.7	1.34	90
M60	21	1.603	28.9	23	890	11.7	56.5	0.98	82
M61	713	4.536	65.9	2591	10,837	65.8	88.0	3.72	164
M62	775	4.503	42.3	2077	1835	36.6	177.7	3.06	145
Detection limit	0.1	0.005	0.1	0.01	0.5	0.01	0.01	0.01	0.1

Values are represented by mg kg⁻¹

Table 4 Descriptive statistics and geochemical background of potentially toxic trace elements in the Miedzianka mine soils

Parameters	As	Cd	Cr	Cu	Mn	Ni	Pb	U	Zn
Minimum	4	0.122	5.2	1	37	1.4	2.7	0.25	1
1st quartile	19	0.8	21	30	680	8.3	28	0.84	51
3rd quartile	278	2.14	52	1337	2371	36.3	59.6	2.33	129
Maximum	1319	9.0	221.2	5732	28,185	127	628	11.75	396
Mean	203	1.8	39.5	927	2463	28.5	75	2.1	99
Median	46	1.4	34.1	209	1334	19.4	46	1.2	82
Standard deviation	311	2	31	1417	4447	28	119	2	71
Upper limit of geochemical background range	36	2	63	52	2156	39	73	1.9	175
Soil quality standards for protected areas in Poland	20	1	50	30	–	35	50	–	100

– not regulated under current legislation. Values are represented by mg kg⁻¹

368 mg kg⁻¹ in soils of the post-mining site of the High Moulouya Valley in Morocco, where Pb was extracted (Iavazzo et al. 2012). Much higher Cu levels in surface soils (70–2231 mg kg⁻¹) were reported from the abandoned Miguel Vacas copper mine in SE Portugal (Abreu et al. 2008b) or other post-mining areas, where Cu ores were extracted, e.g. 15–7200 mg kg⁻¹ in Mexico (Razo et al. 2004) and 7–3430 mg kg⁻¹ in the Sudetes Mts, SW Poland (Karczewska et al. 2006).

Zinc

The average zinc content in soils is estimated to be 64 mg kg⁻¹ (Kabata-Pendias and Mukherjee 2007). The highest concentrations of Zn are typically found in calcareous and organic soils (up to 100 mg kg⁻¹) and the lowest in light sandy soils (31–61 mg kg⁻¹) (Kabata-Pendias 2011).

In the present study, Zn concentrations were in the range of 1–396 mg kg⁻¹ with a mean of 99 mg kg⁻¹, showing high Spearman’s correlation coefficient values with Cd (0.92), Ni (0.86) and Cr (0.81) (Table 6). Correlation between Zn and Cd results from similar geochemical behavior of these two metals. Surprisingly, the lower correlation coefficient (0.69) was found for As and Zn. These elements occur in some minerals of Miedzianka: adamite, austenite, tennantite and zincian olivenite. A relatively low number of Zn anomalies in soils of the study area occurs in the southern part of the study area.

Likewise, high Zn levels (53–211 mg kg⁻¹) were found in surface soils (horizon-A) of the abandoned Miguel Vacas Cu mine in SE Portugal (Abreu et al. 2008b) and soils of different post-mining areas, for example, 31–835 mg kg⁻¹ in France (Camizuli et al. 2014), 46–215 mg kg⁻¹ in northern Spain (Loredo et al. 2006) or

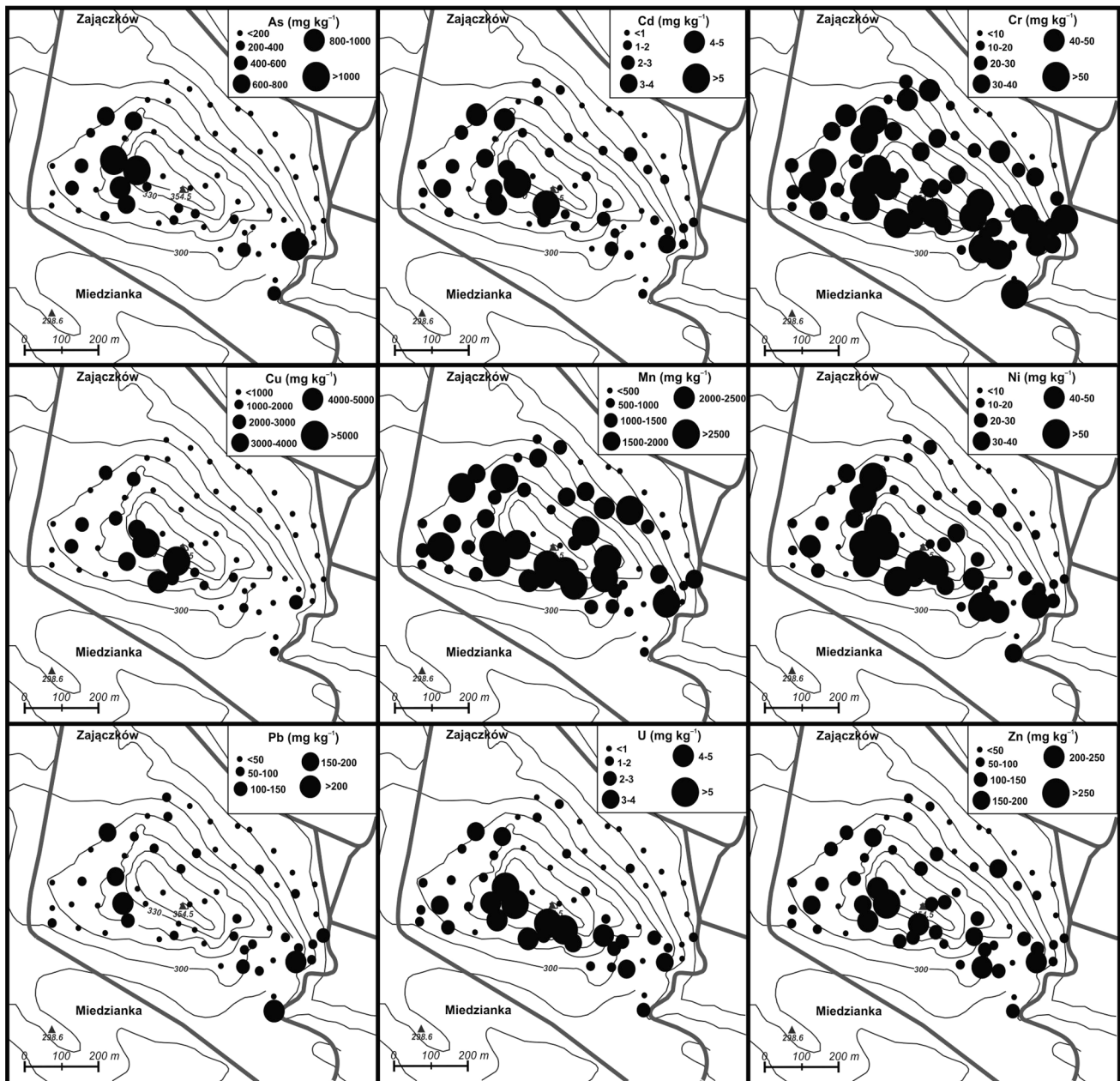


Fig. 5 Trace element distribution maps

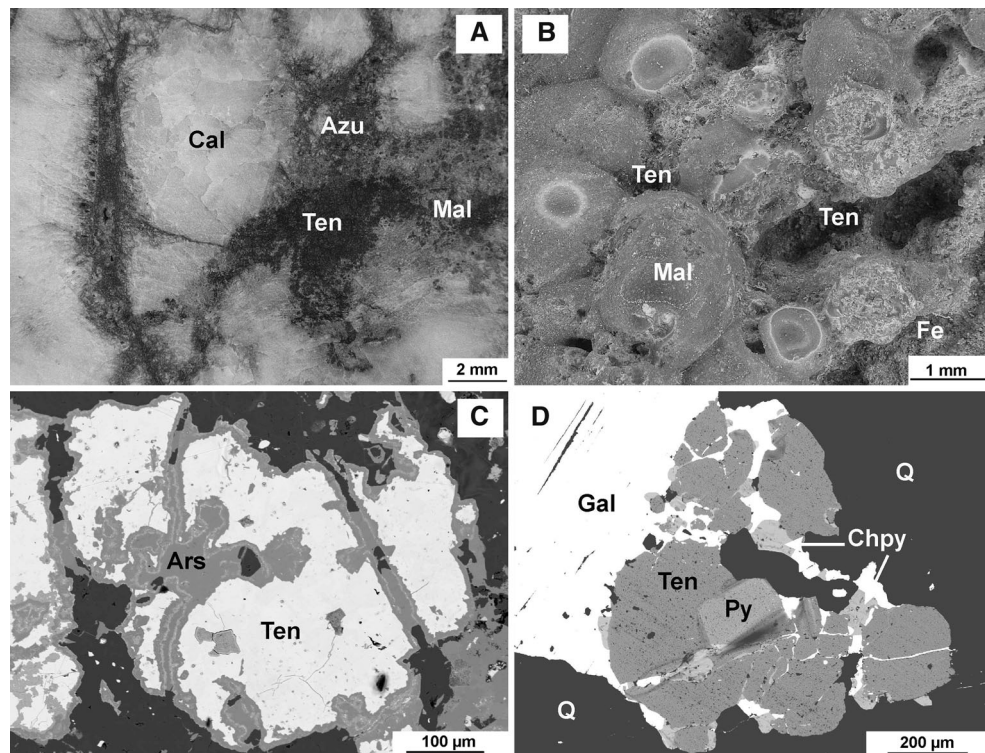
28–3660 mg kg^{-1} in the abandoned Cu mines in the Sudetes Mts SW Poland (Karczewska et al. 2006). Extremely high Zn concentrations (46–182,000 mg kg^{-1}) were reported in soils from the High Moulouya Valley in Morocco (Iavazzo et al. 2012) and from San Luis Potosi in Mexico (26–6270 mg kg^{-1}) (Razo et al. 2004).

Arsenic

Typical concentrations of arsenic in unpolluted soils are low, ranging from $<0.1 \text{ mg kg}^{-1}$ in sandy soils to 67 mg kg^{-1} in organic soils with an average world content of 6.83 mg kg^{-1}

(Kabata-Pendias 2011). Much higher levels of As in soils were found in post-mining areas throughout the world. The following concentration ranges of As in soils of the former mining sites were reported: 32–19,930 mg kg^{-1} (abandoned Hg-mining area in northern Spain) (Loredo et al. 2006), 2–262 mg kg^{-1} (post-mining soils of the High Moulouya Valley Morocco) (Iavazzo et al. 2012), 19–17,384 mg kg^{-1} (post-mining soils in Mexico) (Razo et al. 2004) and 50–17,400 mg kg^{-1} (former Sb mining area in Scotland) (Gal et al. 2007). The concentrations of As in the study area varied from 4 to 1319 mg kg^{-1} with a mean of 203 mg kg^{-1} .

Fig. 6 Optical microscope images: **a** Brecciated veined calcite (Cal) with tennantite (Ten) partially replaced by azurite (Azu) and subordinate malachite (Mal); **b** Botryoidal malachite (Mal) with relicts of tennantite (Ten) and iron hydroxides (Fe); BSEI images: **c** Tennantite (Ten) grain showing alteration into secondary Cu-Fe-Zn arsenate (Ars) that contains up to 19.8 % As and less than 1 % S; **d** Quartz veinlet with sulfide mineral concentrations: galena (Gal) with subordinate chalcopyrite (Chpy) filling fractures within tennantite (Ten) with a protruding grain of pyrite (Py)



The high Spearman’s correlation coefficient values between As and Cu (0.89) (Table 6) and elevated concentrations of arsenic at the mutli-shaft mining sites of the study area may be explained by the occurrence of tennantite $\text{Cu}_6[\text{Cu}_4(\text{Fe}, \text{Ag}, \text{Zn})_2]\text{As}_4\text{S}_{13}$ with subordinate secondary conichalcite $\text{Ca}(\text{Cu}, \text{Mg})[\text{OH}|\text{AsO}_4]$ in the mineral composition of the copper ore body. Analysis of galena samples from the study area showed an enrichment of PbS in arsenic with concentrations in the range of 161–904 mg kg^{-1} (Table 5).

Cadmium

According to Kabata-Pendias (2011), a global mean concentration of Cd in soils is 0.41 mg kg^{-1} , and typical Cd concentrations in uncontaminated soils occur in the range of 0.06–1.1 mg kg^{-1} (Kabata-Pendias and Mukherjee 2007). The Cd contents in soils in the former metal-ore mining areas are variable ranging, for example, from 0.3 to 1020 mg kg^{-1} (Iavazzo et al. 2012). In the study area the concentrations of Cd varied from 0.122 to 9.003 mg kg^{-1} (Table 3). High correlation coefficient values were noted between Cd and Zn (0.92) and to a lesser extent between Cd and Ni (0.80) (Table 6). Cadmium substitutes for Zn in its minerals, which explains the correlation between these two elements. As mentioned before, Zn occurs in the study area in numerous minerals. Cadmium minerals have not been reported from Miedzianka. The correlation between

Cd and Ni is probably caused by similar behavior of these elements in soil, where they show a strong affinity to organic matter.

Lead

The range and the mean world contents of lead in soils are 3–90 and 27 mg kg^{-1} , respectively (Kabata-Pendias 2011). The present and historic metal ore mining is considered as one of the most important source of soil contamination with Pb (Dudka and Adriano 1997).

As mentioned in the description of geology of the study area, lead sulfo-salts formed during hydrothermal mineralization phases. Surprisingly, Pb did not show a heavy enrichment in the soils examined and its concentrations were in the range of 2.7–628 mg kg^{-1} with a mean of 75 mg kg^{-1} . The threshold of Pb in the examined soils (73 mg kg^{-1}) is very close to the mean value of this metal. Geochemical anomalies of lead in the study area are located mostly in the eastern and south-western parts (sample sites M12, M14, M18, M19, M50 and M4, M29, M36).

Anomalous lead concentrations (in mg kg^{-1}) were reported for soils in historic mining areas in the following countries: France (41–4520 mg kg^{-1}) (Camizuli et al. 2014), Spain (20–142 mg kg^{-1}) (Loredo et al. 2006), Morocco (40–13,300 mg kg^{-1}) (Iavazzo et al. 2012), Mexico (31–3450 mg kg^{-1}) (Razo et al. 2004), SW Poland (5.8–2090 mg kg^{-1}) (Karczewska et al. 2006).

Table 5 Concentrations of trace elements in rock and mineral samples from the Miedzianka Mt.

Sample	As	Cd	Cr	Cu	Mn	Ni	Pb	U	Zn
Limestone	4	<12	<11	23	350	143	<5	<5	14
	11	<13	<12	60	384	101	13	6	20
	10	<12	<11	56	382	118	18	<5	16
	30	<12	<12	1020	423	99	35	6	24
	80	<13	<10	307	297	<20	56	<5	41
	13	14	<11	47	231	118	11	<5	42
	40	39	<11	181	501	120	32	<5	188
Calcite	13	22	<11	111	389	166	15	<5	32
	<4	<13	<11	37	318	118	<5	<5	<9
	6	<12	<10	44	409	142	11	<5	22
	16	13	<12	97	444	137	13	<5	36
	18	16	<11	444	470	119	24	<5	11
Galena	20	<13	<11	128	409	101	31	<5	16
	161	5	<5	n.d.	<1	1.5	n.d.	n.d.	n.d.
	425	7	<5	n.d.	2.3	16	n.d.	n.d.	n.d.
	655	6	<5	n.d.	<1	74	n.d.	n.d.	n.d.
	904	6	<5	n.d.	<1	182	n.d.	n.d.	n.d.
	338	7	<5	n.d.	<1	2.5	n.d.	n.d.	n.d.

Values are represented by mg kg^{-1}

n.d. not determined

Lead showed the lowest Spearman's correlation coefficient values compared with other elements (Table 6). This may suggest the influence of other than geogenic Pb sources or different behavior of this metal in surface soils of the study area. Comparison of lead isotope ratios ($^{206/207}\text{Pb}$ and $^{208/206}\text{Pb}$) suggests that lead in soil samples M19, M36 and M62 is genetically linked to galena (Table 7). This is also evidenced by the highest Pb concentrations in the range of 167–628 mg kg^{-1} (Table 3). In contrast, lead of the other samples, but especially M5, M7 and M28, exhibits a mixed geologic-anthropogenic origin. The most probable anthropogenic sources of this metal in the study area are residential combustion of bituminous coal and emissions coming from a cement plant located about 10 km south-west of the Miedzianka Mt.

Uranium

A range of 1.9–4.4 mg kg^{-1} is estimated to be a natural content of uranium in soils (Kabata-Pendias 2011). The concentrations of this element in the examined soils varied from 1.36 to 11.75 mg kg^{-1} (mean of 2.1 mg kg^{-1}), and only in 6 of 62 samples these levels were higher than 4.4 mg kg^{-1} . Uranium revealed the high Spearman's correlation coefficient values with Ni and Cu (0.86) and Cr (0.80) (Table 6). To the best of the authors' knowledge, no

Table 6 The values of Spearman's correlation coefficients between potentially toxic trace elements in the Miedzianka mine soils (significance level 0.05; $p < 0.05$)

Element	As	Cd	Cr	Cu	Mn	Ni	Pb	U	Zn
As	1								
Cd	0.69	1							
Cr	0.65	0.69	1						
Cu	0.89	0.69	0.69	1					
Mn	0.66	0.77	0.69	0.73	1				
Ni	0.78	0.80	0.88	0.87	0.78	1			
Pb	0.67	0.68	0.56	0.36	0.38	0.49	1		
U	0.72	0.74	0.80	0.86	0.75	0.86	0.44	1	
Zn	0.69	0.92	0.81	0.74	0.76	0.86	0.67	0.72	1

Table 7 Pb isotope ratios in selected soil samples and galena

Sample	$^{206/207}\text{Pb} \pm 0.001$	$^{208/206}\text{Pb} \pm 0.002$
M7	1.229	2.041
M19	1.178	2.078
M28	1.215	2.042
M35	1.185	2.131
M36	1.181	2.084
M52	1.183	2.109
M62	1.178	2.089
Galena	1.175	2.083

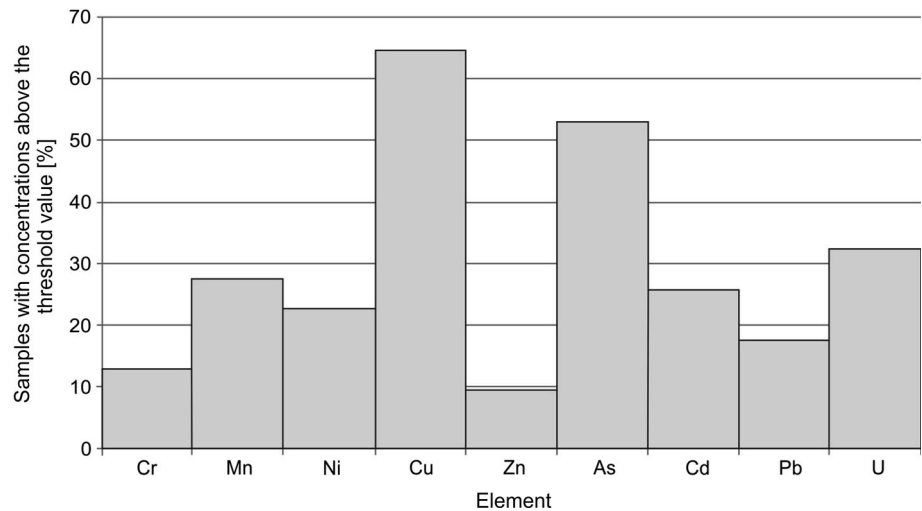
data about U minerals exist in the mineralogical literature of the study area. However, it should be stressed that for many years this information was classified in Poland. In a review paper about uranium mining in Poland, Borzęcki (2004) mentioned that the uranium ore containing about 400 g/Mg of U occurred in Miedzianka in 1951.

Little is known about U contents in soils of historic mining areas, except for these sites where U ores were extracted. One of the available data is derived from the abandoned Pb mining area in Morocco, where 1.1–2.3 mg kg^{-1} of uranium was found in soils (Iavazzo et al. 2012).

Geochemical background values and soil quality

An assessment of soil quality in the post-mining areas and distinguishing between natural (geologic) and anthropogenic influence on the soil chemistry is a very difficult task due to a physical disturbance of soil horizons and very high heterogeneity of contaminant concentrations in mine soils (Hudson et al. 1997). The regulatory standards in many countries, including Poland, differ for individual categories of soils depending on the type of area management and anthropogenic influence (e.g. residential soils, agricultural soils, technogenic soils, etc.). In case of soils in post-mining

Fig. 7 Percentage of samples showing element concentrations above the upper limits of geochemical background ranges



areas, especially in those where metal ore extraction ended a long time ago, categorization of the soil may be difficult. For example, according to the Polish regulations (The Regulation of the Minister of the Environment on the Soil Quality Standards 2002), soils of the study area should be assigned to soils in protected areas and should have the lowest permissible quality standards. These regulation standard values are presented in Table 3. Surprisingly, the quality standards for Cr and Ni are close to the upper limits of geochemical background range evaluated with the use of the iterative 2σ -technique (Table 3). However, the threshold values of the other elements were from 1.5 to 2 times higher than the quality standards included in the Polish regulations (The Regulation of the Minister of the Environment on the Soil Quality Standards 2002).

The upper limit of geochemical background range (threshold value) for As evaluated for the purpose of this study (36 mg kg^{-1}) is similar to the geochemical background value for As (39 mg kg^{-1}) that was established in the abandoned Hg-mining area in northern Spain (Loredo et al. 2006). The percentage distribution patterns of element concentrations above the upper limits of geochemical background ranges are depicted in Fig. 7. They represent positive geochemical anomalies (Gałuszka et al. 2013). The highest number of anomalous concentrations was recorded for Cu (64 %), As (53 %) and U (32 %). It is noteworthy that all the threshold values are higher than the recommended regulation standards for soils in protected areas of Poland (Table 3).

Conclusions

The study of the spatial distribution of selected nine trace elements in soils of the historic Miedzianka mining area in south-central Poland allows us to draw the following conclusions:

1. All the determined elements showed a high spatial concentration variability in surface soils with distinctive positive geochemical anomalies scattered around abandoned mine workings.
2. The element background concentrations, which were evaluated with application of the iterative 2σ -technique, exceeded the regulatory standards recommended for soils in protected areas of Poland.
3. The percentage of samples showing anomalous element concentrations was the lowest for Zn (10 %) and the highest for Cu (64 %). At above half of the sampling sites anomalous concentrations of As were detected.
4. There were many positive correlations between the determined elements, and the highest Spearman's correlation coefficient values were displayed by the following element pairs: Cd–Zn (0.92), Cr–Ni (0.88), As–Cu (0.89), Cu–Ni (0.87), Cu–U (0.86), Ni–U (0.86), Ni–Zn (0.86), Cr–Zn (0.81), Cd–Ni (0.80) and Cr–U (0.80). This may be indicative of a common geogenic source of these elements and their geochemical affinity.
5. Very high concentrations of As, Cr and Ni at several sites may adversely influence the environment, posing a potential health risk for inhabitants of the neighboring villages. However, considering the soil and bedrock properties (high pH, abundance of natural sorbents, such as clay minerals and iron oxides and hydroxides) that favor immobilization of the determined elements, the highest risk for human health appears to be a direct exposure to airborne soil and mineral particulates.

The Miedzianka Mt. is a popular local geologic, mining, botanic and historic highlight, the place which is frequently visited by tourists and scientists. For this and other reasons,

further studies should be conducted to assess the health hazard for humans. If the examined soils were to be remediated, the bioavailability tests should be performed and the mobility potential of hazardous elements showing anomalous concentrations in soils (considering soil properties) should be evaluated.

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