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Assessment of arsenic and toxic metal contamination in soils, pore waters and plants surrounding a historical mine site in Czarnów (SW Poland)

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Centuries of gold-arsenic ore mining activities in Czarnów village within the Evelinens glück mine (SW Poland) have left an enduring impact on the local environment, characterized by distinct geochemical anomalies and contamination in water and plants. We have comprehensively investigated the spatial distribution of arsenic and metals in soils, plants, and water in close proximity to post-mining dump sites. The findings reveal striking anomalies in the vicinity of the mine, notably elevated levels of arsenic, zinc, lead, copper and cobalt. The highest recorded arsenic content surpassed 290,000 ppm, with cobalt reaching almost 18,000 ppm and copper exceeding 21,000 ppm. This contamination was most pronounced around mining excavations and in the immediate vicinity of mining dumps. Additionally, pore water analysis from the study area uncovered elevated arsenic levels, surpassing permissible standards, with concentrations exceeding 600 ppb. Moreover, plant specimens (*Rubus idaeus, Deschampsia flexuosa, Dryopteris carthusiana*) in the region were observed to accumulate arsenic and other toxic elements, with *Rubus idaeus* recording the highest arsenic concentration at 19.0 ppm. These accumulations consistently exceeded established environmental norms. The presence of such elevated concentrations of toxic elements in both soil and plant life underscores profound concerns for human health, with potential implications for a range of health issues.

Key words: arsenic, mining, soil contamination, post-mining pollution.

INTRODUCTION

The phenomenon of arsenic migration in soils refers to the mobility of arsenic throughout the soil profile, which can occur naturally through processes such as leaching or erosion, or can be exacerbated by anthropogenic activity. Such processes can have a deleterious impact on local ecosystems, with abandoned or uncontrolled mining sites in particular having a profound and enduring effect on the environment (Salomons, 1995). During the exploitation of ore, large quantities of waste including gangue and barren rocks, sometimes with ore minerals, are exposed to surface weathering conditions. This material potentially leads to soil pollution by heavy metals via mechanisms such as mine tailings runoff and the exposure of primary minerals to atmospheric conditions. Mineral decomposition releases elements, which can then accumulate in soils, water, and plants across the affected area. Heavy metals and toxic elements commonly found in mining soil include lead, cadmium, arsenic, copper, zinc and mercury. Numerous studies have investigated the extent of heavy metal contamination in post-mining areas worldwide (e.g., Razo et al., 2004; Yabe et al., 2010; Li et al., 2014; Shaji et al., 2021; Chen et al., 2022) and in Poland (Karczewska, 2006; Sołek-Podwika et al., 2016; Lewińska et al., 2021; Szopka et al., 2021; Kałaska et al., 2022; Swęd et al., 2022; Derkowska et al., 2023). The Czarnów deposits have been studied in terms of both ore geology (e.g., Zimnoch, 1983; Mikulski 2007, 2010; Mochnacka, 2009), environmental concerns (e.g., Karczewska et. al., 2006; Mickiewicz and Marszałek, 2016; Dradrach et al., 2020) and most recently regarding the geophysical prospection of ore veins (Mikulski and Ostrowski, 2023). However, comprehensive multidisciplinary geochemical studies, including of plants, waters and soils around the Czarnów abandoned mine were not conducted prior to our current study.

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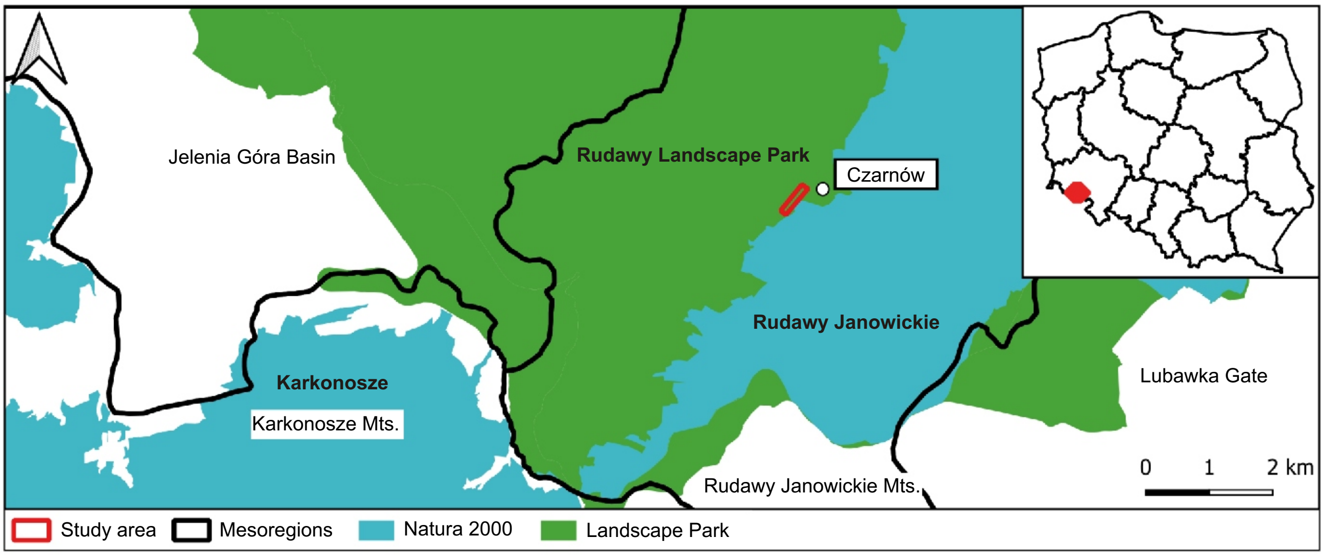

Fig. 1. The research area within the physiogeographical context of Poland within the context of protected areas (according to Solon et al., 2018)

The Czarnów mineral deposits are situated on the SE slope of Skalnik Mt. near Czarnów village within the Rudawy Landscape Park (Dolnośląskie Voivodeship, Eastern Sudetes). According to the physiogeographical division of Poland, this area is classified as part of the Rudawy Janowickie (Fig. 1). This deposit are known to be rich in arsenic, which is considered a highly hazardous element for both the environment and human health.

GEOLOGICAL SETTINGS

The As-Au deposit is situated within the Kowary–Czarnów unit (Kozdrój et al., 2017). Its western boundary is formed by the granite intrusion of the Karkonosze Mountains, while the eastern boundary follows the fault zone with the Leszczyniec unit. The Kowary–Czarnów unit primarily consists of Neoproterozoic-Cambrian metamorphosed rocks, including sedimentary and volcanic formations known as the “supracrustal series”. Additionally, it contains the Kowary orthogneisses, which mark the transition zone from the granite intrusion of the Karkonosze Mountains. The supracrustal series comprises mica-schists and phyllites with sporadic occurrences of graphite schist, marble, erlane, leptinite, and amphibolite (Fig. 2; Kozdrój et al., 2017).

During the Late Carboniferous, a granite pluton intruded within the metamorphic dome. The resulting thermal effects transformed the country rocks under conditions of the amphibolite hornfels facies along the entire contact zone in the Rudawy Janowickie region. As the intrusive body cooled, mineralized hydrothermal solutions circulated, and due to intense tectonic deformation of the host rocks, they migrated beyond the cooling batholith. Interaction of acid hydrothermal solutions with carbonate rocks along their pathway caused metasomatic alteration. The change in the chemical environment led to the precipitation of minerals ultimately forming the Czarnów deposit (Zimnoch, 1983).

The polymetallic ores are found within a quartz vein. The vein trends in a NE–SW direction, dipping at an angle of 80° south-east and exhibits a lenticular geometry. Its elevation ranges from 670 to 760 m a.s.l. Following its course, the vein is ~500 m in length, with a thickness varying from 0.5 m to as much as 3 m. The vein is heavily affected by tectonic deformation and intersected by numerous faults, with the most prominent faults trending NW–SE. The mineralized vein near Czarnów exhibits variations in terms of mineral composition and deposit thickness. Arsenopyrite zones typically have a thickness of no more than 0.2 m but can occasionally reach up to 1 m (Zimnoch, 1983; Mikulski, 2010). The predominant ore mineral in the deposit is arsenopyrite ($FeAsS$), accompanied by chalcopyrite ($CuFeS_2$), pyrrhotite (FeS), pyrite (FeS_2), and subordinate galena (PbS), sphalerite (ZnS), antimonite (Sb_2S_3), native gold (Au) and cassiterite (SnO_2; Mochnacka, 2009; Mikulski, 2010). Arsenopyrite within the mineralized quartz veins can occur in a nest-like form, with such ores exhibiting the highest concentration of arsenic, occasionally reaching up to 29% As. Lower concentrations of arsenic ores were found in mineralized veins cutting through amphibolites, with values fluctuating around 10% As. Additionally, apart from pure arsenopyrite ores, there are arsenopyrite-chalcopyrite ores, which may contain ~10% As and 12% Cu. Generally, arsenopyrite in the ore veins most commonly occurs as strongly fractured granular aggregates or in an automorphic form. The fractures within the arsenopyrite crystals are often filled with iron, copper, lead, zinc sulphides and bismuth minerals. The occurrence of arsenopyrite is closely associated with the most abundant gold-bearing ores (Mikulski, 2007, 2010).

MINING HISTORY

The oldest mentions of mines in Czarnów date back to the mid-18th century (Dziekoński, 1972). However, the remains of the oldest mining excavations indicate that the local mining industry is much older. The exploitation method employed, involving bell pits, is typical of medieval mining practices. Today, at the surface, there are perfectly preserved sequences of small depressions and collapsed bell pits. During the period from 1800–1825, the focus of the mining activities was on the extraction of arsenic, lead, copper and pyrite from the Rothezeche mine. Nonetheless, due to the mine’s fluctuating profitability, it was periodically opened and closed. It was not until 1838 that a significant breakthrough was made when the deposit was exploited in two new mines – Evelinens glück and Arnold

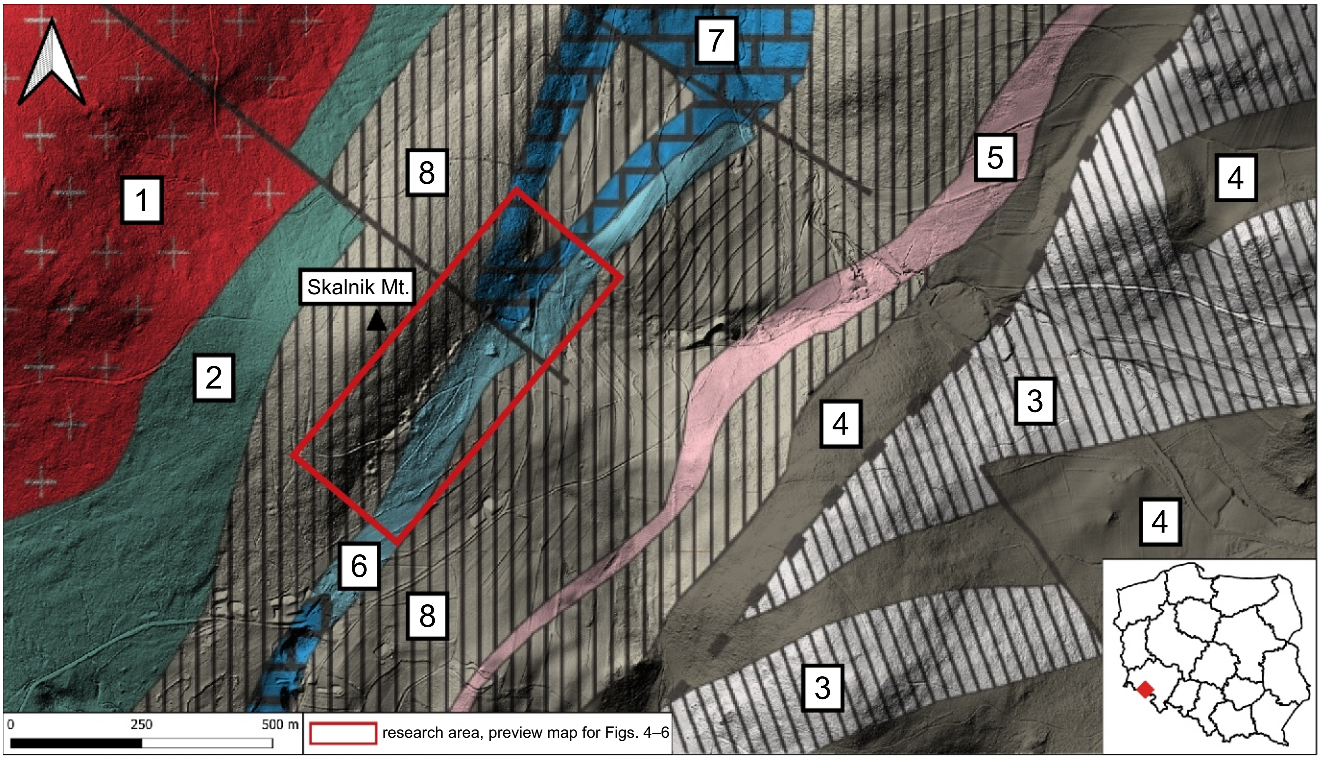

Fig. 2. Geological map of the Czarnów area (according to Kozdrój et al., 2017)

1 – granites (Carbon); 2 – granitogneisses (Cambrian); 3 – schists (Cambrian); 4 – amphibolites (Cambrian); 5 – gneisses (Cambrian); 6 – erlanes (Cambrian); 7 – marble (Cambrian); 8 – mica schists (Neoproterozoic)

(Zimnoch, 1983). The mining activities were conducted in five mining fields, over ten levels, reaching depths of 250 m (Mikulski, 2010). During this time, an ore processing plant was established in Czarnów to facilitate the extraction process. In the twentieth century, the production of ore concentrate reached between 500 to 1,000 tons per year. The deposit was exploited to a depth of ~250 m, with mining activities carried out across ten levels. However, due to the overproduction of arsenic concentrate and a subsequent drop in raw material prices during the economic crisis, the mines were finally closed in 1925 as they were no longer profitable (Zimnoch, 1983). After World War II, prospecting activities were conducted in Czarnów, but these efforts came to a halt in 1955 (Madziarz, 2009).

ARSENIC CHARACTERIZATION

Arsenic, a metalloid element, is the 20th most abundant element in the Earth's crust (Mandal, 2002). Despite its highly toxic nature, arsenic and its compounds have been utilized by human societies since antiquity. For instance, the earliest bronzes, dating back to 4,000 B.C., were likely made from alloys of copper and arsenic (Lechtman and Klein, 1999). Furthermore, arsenic sulphide, commonly known as orpiment, was used as a dye or an ingredient in medicinal preparations until the 19th century (Sambus and Willson, 2008). Arsenic exhibits a sulphophilic nature, indicating its high affinity towards sulphur, similar to other elements such as copper, silver, gold, zinc, bismuth, nickel and iron. In geological settings, arsenic is predominantly found as sulphides and sulphosalts or as secondary arsenates. More than 200 minerals contain arsenic as a component, with the most frequently occurring ones being realgar, aurypiment, arsenopyrite, lölingite and cobaltite (Maher, 1984; Niedzielski et al., 2000; Mandal, 2002).

When primary arsenic minerals, such as arsenopyrite, are exposed to atmospheric conditions through weathering processes or anthropogenic activities, soluble arsenite As(III), sulphate (SO_4), and ferrous iron can be released, as shown in Figure 3 and described by Equation 1. This process also causes a strong drop in pH. The presence of ferric ions can also hasten the weathering process (Cullen and Reimer, 1989). The rate at which these processes occur is reliant on the availability of oxygen, organic matter, pH, redox potential, and the sulphide oxidation rate (Mahimairaja et al., 2005). The arsenic released from these processes may undergo oxidation to arsenate As(V) due to biogenic activity (Garcia-Manyes, 2002; Mahimairaja et al., 2005; Violante et al., 2010).

$$FeAsS + 13Fe^{3+} + 8H_2O \quad 14Fe^{2+} + SO_4^{2-} + 13H^+ + H_3AsO_4\,(aq) \qquad [1]$$

As can exist in soil as inorganic forms, which are more mobile, such as arsenate – As(V) and arsenite – As(III), or as organic forms, such as methylarsenate (MMAA) and dimethylarsenate (DMAA). Trivalent As can exist as arsenous oxide (As_2O_3), arsenious acid ($HAsO_2$), arsenite and many other forms. Pentavalent As occurs as arsenic pentoxide (As_2O_5), orthoarsenic acid (H_3AsO_4), metaarsenic acid ($HAsO_3$) and arsenate ions (Turpeinen et al., 1999; Mahimairaja et al., 2005). These chemical species show the ability to form complexes with other potentially toxic elements, such as copper, lead, zinc and cobalt, and have a high solubility in water. Consequently, plants and other living organisms can readily take up

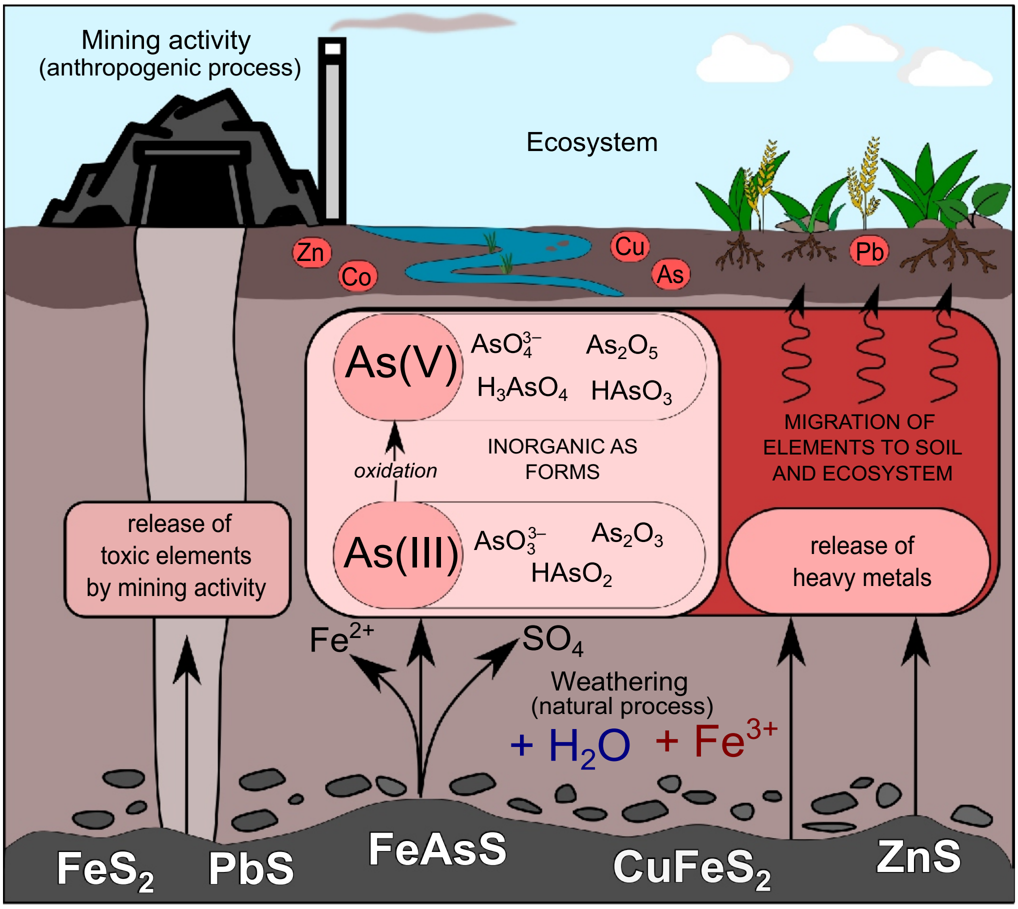

Fig. 3. Arsenic migration in soils (after Mahimairaja et al., 2005)

these species, leading to potential contamination of the food chain. The specific arsenic species present in soil play a critical role in determining its potential toxicity, mobility and bioavailability. The speciation of arsenic is influenced by various environmental factors, including pH, redox potential, organic matter and biological activity.

In soils, the average concentration of arsenic can vary from 0.2 to 40 ppm. The average As content in the Earth's mantle is ~2 ppm, which may increase up to 3,000 ppm under highly reducing conditions. In uncontaminated soils, As concentration is typically around 5 ppm (Hooda, 2010). Sandy soils tend to have the lowest As concentrations, ranging up to 4.4 ppm, whereas clay-silty soils may exhibit higher As concentrations, up to 8.4 ppm due to As binding by clay minerals (Kabata-Pendias, 2010). However, in certain areas affected by anthropogenic activities such as mining, As concentrations may be significantly higher. Due to its easy solubility, this element can easily enter aqueous solutions, leading to potentially high concentrations in both water and marine organisms (Maher, 1984; Niedzielski et al., 2000).

Arsenic concentration in plants growing on non-contaminated soils usually varies from 0.009 to 1.5 ppm of dry weight (DW) (Kabata-Pendias and Pendias, 2001). The role of arsenic in plant metabolism has still not been thoroughly clarified, but most studies indicate that As is a non-essential element for plant growth and toxic when it accumulates in plant tissues (Farooq et al., 2016; Chandrakar et al., 2018). All plant species take up As from the environment and its concentration in plants increases proportionally to the content of As in a soil, although many species have developed strategies reducing acquisition and toxicity of that element (Li et al., 2015). Uptake of arsenic from soil depends not only on the plant species, but also on edaphic factors controlling arsenic mobility, e.g. soil pH, organic matter, microbial activity, presence of iron and phosphorous (Krysiak and Karczewska, 2007; Ociepa-Kubicka and Ociepa, 2012). Arsenic accumulates in plants mostly in roots, stems and old leaves, while seeds usually have the lowest content of As (Kabata-Pendias and Pendias, 2001). Concentration of As in a plant biomass reaching 5–20 ppm DW has toxic effects for most species, but even lower contents can reduce plant growth, and yield in cultivated plants (Kabata-Pendias and Pendias, 2001). However, tolerance mechanisms towards high As concentrations in tissues have been revealed in some plant species e.g. in the grasses *Holcus lanatus* and *Agrostis tenuis* (Porter and Peterson, 1970). Moreover, extremely large concentrations of As, reaching 23,000 ppm DW, were found in *Pteris vittata,* which is an example of a As hyperaccumulator as are several other fern species (Zhang et al., 2002), and in brassica *Isatis cappadocica* (Souri et al., 2017).

MATERIALS AND METHODS

Soil samples were systematically collected within a grid pattern that corresponds to the field complexity. A total of 236 samples were obtained from two distinct levels (Fig. 4 – soil sampling points). The documentation points were spaced at 20-metre intervals. For the first level probes, sampling was con-

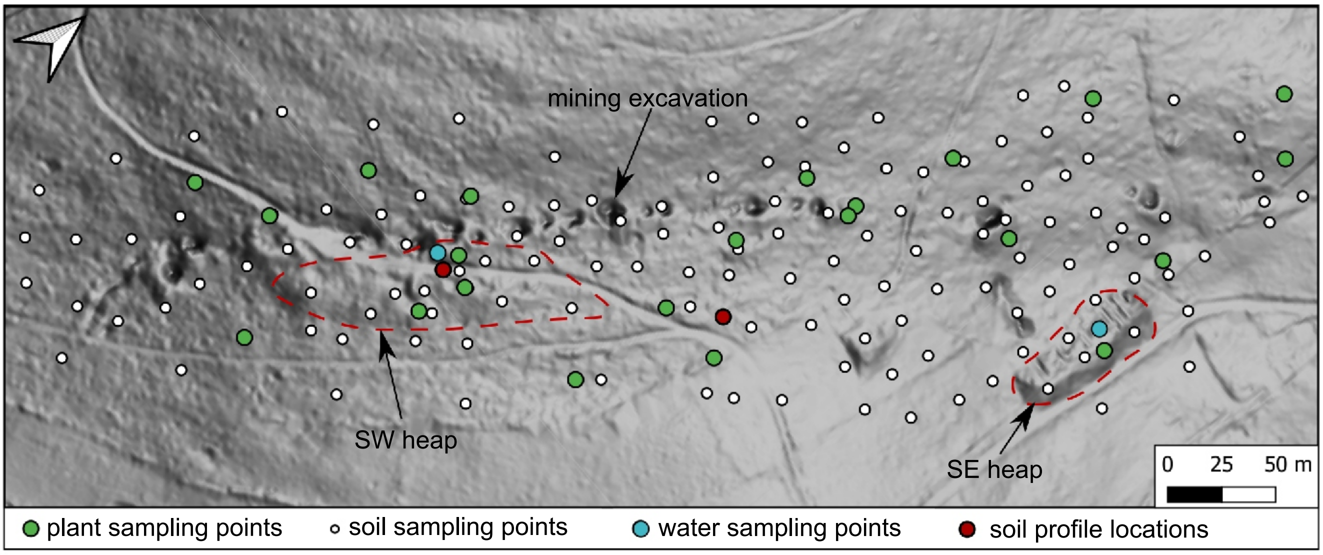

Fig. 4. Sampling points in the vicinity of the mine in Czarnów

ducted at a depth of 15–20 cm below the ground, while the second level probes were collected at a depth of 50–60 cm. Twelve soil probes were collected from various locations within the soil profile for two specific localities. Probes were taken from the southwestern mine dump, and from the natural soil profile located near a road ditch (Fig. 4 – soil profile location). All the samples collected underwent a drying process in ambient temperature for approximately one week, followed by sieving to ensure material homogeneity.

All samples collected were analyzed using the XRF model *MinPal 4 by PANalytical*. The analysis was performed with a current of 150 mA and a voltage of 14 kV. Each sample underwent a measurement time of 60 seconds. The elements assessed during the analysis included Ti, P, Fe, As, V, Cr, Co, Ni, Cu, Zn, Ag, Ba and Pb. Concentrations of these elements were reported in parts per million (ppm). Selected data were visualized as interpolation maps created using *Surfer 25* made by *Golden Software*, Inc., and *QGIS Development Team, 2023*, *QGIS Geographic Information System*, software.

Fourteen soil samples were dissolved in deionized water and left for 24 hours. Subsequently, pH measurement was carried out using *Elmetron CPC-411* pH/conductivity meter equipment.

For analyses of arsenic and heavy metal contents in plant biomass three species were selected, which were relatively most common in the study area and that represent different taxonomic groups: red raspberry *Rubus idaeus* L. (present throughout the study area), wavy hair-grass *Deschampsia flexuosa* L. (synonym *Avenella flexuosa* (L.) Drejer, present mostly in open habitats in the study area), and narrow buckler-fern *Dryopteris carthusiana* (Vill.) H.P. Fuchs (occurring in a forested part of the study area). Plant material samples were collected from 22 sampling points situated at various distances from former mining sites (Fig. 4 – plant sampling points). Two of the selected species were present in each sampling point, besides four plots where only one species occurred. At each point, leaf samples were obtained from a 25 m^2 area, comprising 8–12 shoots with a combined mass of ~20–30 g per species. We selected only green, mature leaves, without signs of yellowing, disease or soil contamination. In total, we collected 20 samples of *R. idaeus*, 10 samples of *Deschampsia flexuosa*, and 10 samples of *Dryopteris carthusiana*. In the laboratory these samples underwent a drying process at a temperature of 100°C for 48 hours. After homogenisation ~0.3 g of the material was mineralized following the digestion procedure of Nawrocka et al. (2022). This process was conducted with an UltraWave (Milestone, Sorisole, Italy) microwave digestion system instrument. Subsequently, measurements of arsenic, lead, zinc, cadmium, cobalt, and copper content in the digested plant samples were made with an ICP-MS spectrometer *NexION 300D* (PerkinElmer, Schwerzenbach, Switzerland). All the laboratory analyses of biomass samples were performed in the Laboratory of Biogeochemistry and Environmental Conservation in the Biological and Chemical Research Centre, Faculty of Biology, University of Warsaw. For pairs of species co-occurring in the same sampling location (*R. idaeus* vs. two other species) a paired t-test was performed to check whether the contents of arsenic and heavy metals differed between species. Moreover, using interpolation maps created using the results of soil analyses and *QGIS* software, values of As, Co, Cu, Zn, Cd, and Pb contents in the soil were obtained for each point where plant material was collected. Then, simple linear regression analysis was applied to test the relationship between the content of those elements in the soil (independent variables) and plant biomass (dependent variables). Soil pH was additionally included in the models to check for possible interactions between soil acidity and element uptake by plants, but in none of the cases was the interaction term significant. Thus, only the results of simple linear regression analysis were reported. All the statistical analyses were performed in the *R* programme (R Core Team, 2022).

A total of six suction lysimeters were deployed in the field to collect pore water samples. Throughout a period of one year, an adequate amount of water for geochemical analysis was only obtained in two lysimeters positioned on the mining dumps (SW and NW dump, Fig. 4 – water sampling points). Physichochemical analysis was conducted in-situ for the water samples using *Elmetron CPC-411* pH/conductivity meter equipment. Samples were preserved by one drop of pure nitric acid. The water samples collected were subjected to analysis using the ICP-MS (Inductively Coupled Plasma Mass Spectrometry) method at the Hydrogeochemistry Laboratory in the Faculty of Geography and Earth Sciences at the Adam Mickiewicz University.

Two samples of soil with the highest arsenic concentrations (from the SW dump) were collected to analyse their phase composition. The presence of all minerals was confirmed by powder X-Ray diffraction (PXRD). Identification of these minerals was performed using a powder X-ray diffractometer *X`Pert PRO MPD* by the DSH method. The parameters of the X-ray beam were as follows CoK : wavelength, finally monochromatized by parabolic X-ray mirrors, emitted from the X-Ray tube with 40 mA and 40 kV current applied. X-ray patterns was recorded in the 2.5 to 75.99°2 range, with a step size of 0.02°2 . The results were processed using the X-ray analysis software *X`Pert Plus HighScore* (ver. 2.2e) and the ICDD PDF-2 database.

RESULTS

SOIL

The analysis of soil arsenic content revealed notable patterns across two different soil levels (Tables 1 and 2). In the first soil level, the minimum concentration of arsenic was 53 ppm, while in the second soil level, it was slightly lower at 42 ppm. The maximum concentrations were significantly higher, reaching values of 298,957 and 231,480 ppm for the first and second soil levels, respectively. Elevated values, exceeding 100,000 ppm, were recorded for a total of 11 samples. Examining the central tendencies, the median concentration of arsenic in the first soil level was 420 ppm, while in the second soil level, it was slightly lower at 346 ppm. The mean values also differed between the two soil levels, with arsenic concentrations averaging 21,776 ppm in the first soil level and 18,245 ppm in the second soil level.

Table 1

Statistical presentation of analytical results from the first soil level in Czarnów [ppm]

	As	Co	Cu	Pb	Zn
Min.	53	20	12	22	16
Max.	298957	17923	21589	1150	1542
Mean	21776	1764	1067	140	216
Median	420	233	44	67	129
Std. error	5311	358	261	18	22
Stand. dev.	62387	4206	3071	206	253
25 percentile	185	168	27	47	103
75 percentile	2302	412	308	99	193

Table 2

Statistical presentation of analytical results from the second soil level in Czarnów [ppm]

	As	Co	Cu	Pb	Zn
Min	42	14	11	19	62
Max	231480	14958	12870	1253	1690
Mean	18245	1488	1018	120	233
Median	346	195	52	48	153
Std. error	4926	336	238	21	25
Stand. dev	49262	3341	2384	211	247
25 percentile	150	112	29	36	118
75 percentile	1495	382	344	71	230

The variability in the data was assessed using the standard deviation, which was found to be 62,387 ppm for the first soil level and 49,262 ppm for the second soil level. Additionally, the 25th percentile indicated that 25% of the data fell below values of 185 ppm in the first soil level and 150 ppm in the second soil level. In contrast, the 75th percentile revealed that 75% of the data fell below values of 2,302 ppm in the first soil level and 1,495 ppm in the second soil level. These results emphasize the significant variability in arsenic content within the soil levels examined.

In the first soil level, the minimum values were observed for Co (20 ppm), Cu (12 ppm), Pb (22 ppm) and Zn (16 ppm). Comparatively, the second soil level exhibited lower minimum values for Co (14 ppm), Cu (11 ppm), Pb (19 ppm), and higher for Zn (62 ppm). Analysing the medians, the first soil level had median values of Co (233 ppm), Cu (44 ppm), Pb (67 ppm), and Zn (129 ppm). By contrast, the second soil level displayed lower median values for Co (195 ppm), Cu (52 ppm), Pb (48 ppm) and Zn (153 ppm). These statistics indicate variations in element concentrations between the two soil levels. The first soil level generally exhibited higher minimum and median values for Co, Cu, Pb and Zn compared to the second soil level. This suggests potential differences in element availability and distribution between the two soil layers.

The distribution of elements in the environment reveals distinct anomalies (Fig. 5). The most significant anomalies are associated with the SW and SE mine dumps, as well as the mining excavations, particularly in the central part of these excavations. There is a strong similarity between arsenic and cobalt, as their distributions in the research area are almost identical. The distributions of copper, lead and zinc also show prominent anomalies on the mine dump and within the excavations, although there are some differences compared to the distributions of arsenic and cobalt.

Soil samples obtained from the SW heap for phase analysis revealed the existence of iron arsenates. The samples include scorodite ($Fe^{3+}AsO_4{\cdot}2H_2O$) and zýkaite, a rare arsenic secondary mineral ($Fe^{3+}{}_4(AsO_4)_3(SO_4)(OH){\cdot}15H_2O$) previously identified in the nearby location in Radzimowice (Siuda and Januszewska, 2022). These minerals are formed during alteration of pyrite and arsenopyrite, constituting integral components of the arsenic-enriched soil. In the second soil level (Fig. 6), the distribution of arsenic is similar to that of the first level, but it shows larger anomalies in the vicinity of the SW mine dump.

The pH measurements obtained span a range of 3.7 to 5.6 across the entirety of the research site (Fig. 7). The aggregate soil specimens are uniformly indicative of acidic pH levels. Of particular note is the identification of the lowest pH values within regions characterized by the highest concentrations of arsenic, namely the SW dump and the mining excavations.

The arsenic distribution in the soil profiles highlights the impact of the mine dump on contamination levels, the dispersal of arsenic in the surrounding natural soils, and the contrasting arsenic distribution in a purely natural soil profile (Fig. 8). The first soil profile (Fig. 8A) represents the anthropogenic heap deposits (anthropogenic soil). The second profile (Fig. 8B) depicts natural soils characterized by a sandy composition and a lack of well-defined diagnostic levels. These soils fall into the category of arenosoil.

In the first profile, located on the mine dump, the highest concentration of arsenic is observed in the central part of the profile within the heap deposits, reaching >250,000 ppm. This extremely high level of arsenic indicates severe contamination

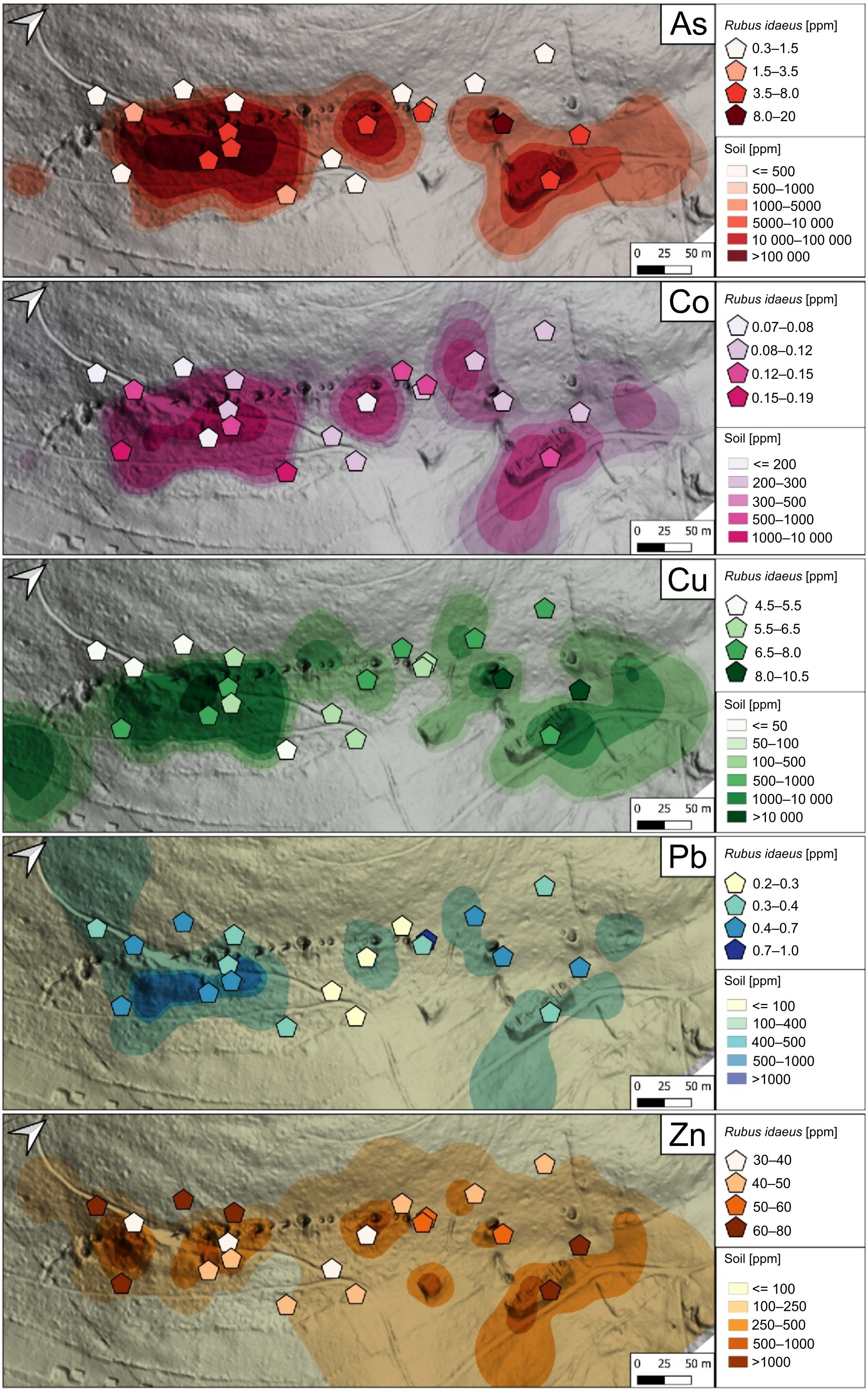

Fig. 5. Element distribution in soils and leaves of *Rubus idaeus*

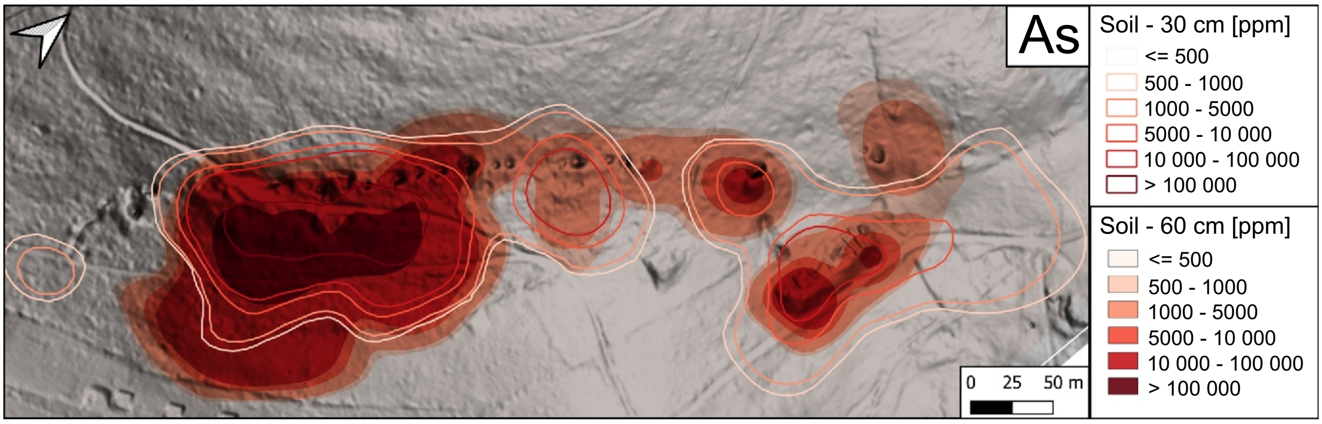

Fig. 6. Arsenic distribution in soil of the first and second level

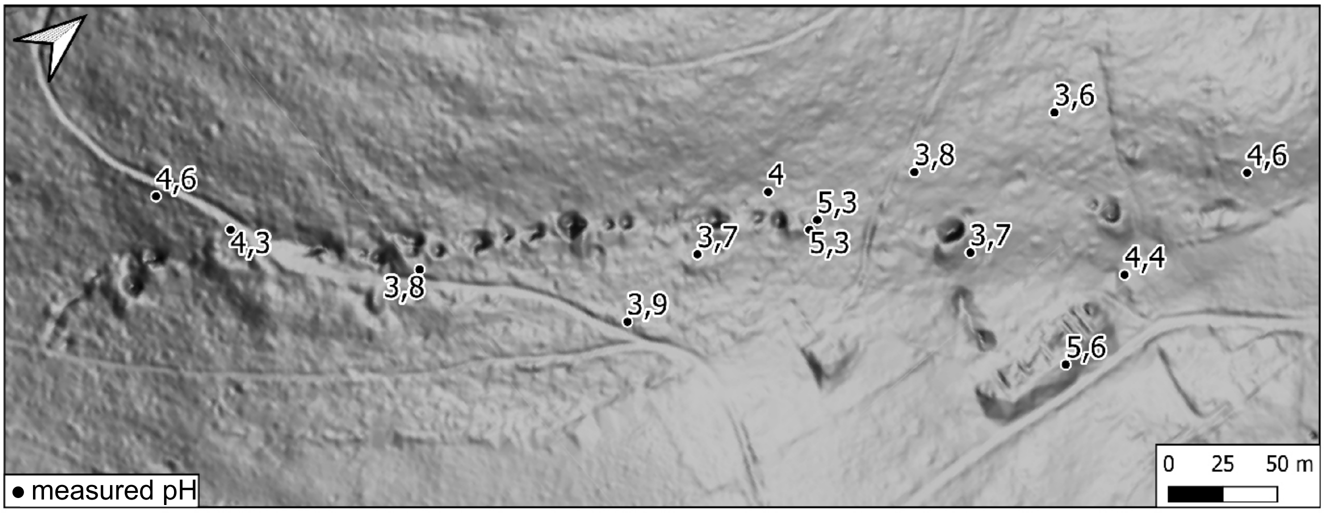

Fig. 7. Measured pH of the soils in the vicinity of the mine in Czarnów

in that area. The natural soils above the heap are also enriched in arsenic, although at a lower level of 4,000 ppm. Beneath the mine dump, the arsenic concentration remains relatively high, averaging around 4,880 ppm. In contrast, the second profile, situated within the natural soil profile, does not show such high concentrations of arsenic. The highest level of arsenic is found at the top of the profile, measuring 340 ppm. The values throughout the rest of the profile are around 100 ppm, showing no significant diversity.

PLANTS

The As content in all plant material collected ranged from 0.26 to 19.02 ppm DW (mean = 3.40, median = 1.46). Among the heavy metals, Zn had the highest content in the plant samples (28.44–107.77 ppm DW, mean = 55.44), followed by Cu (3.94–10.40 ppm DW, mean = 6.46), Pb (0.23–4.12 pm DW, mean = 0.81), Cd (0.03–1.21 ppm DW, mean = 0.35), and Co (0.05-0.43 ppm DW, mean = 0.16). *Rubus idaeus* and *Deschampsia flexuosa* samples had higher maximum contents of As than did *Dryopteris carthusiana* (Table 3). But, there was no significant difference between the mean content of As in *R. idaeus* and in two other species (Table 4). By contrast, such differences were found for heavy metals, except Zn (Table 4). *Deschampsia flexuosa* accumulated less Cu and Cd, and more Pb, than *R. idaeus*, while *Dryopteris carthusiana* accumulated more Co, Pb and Cd than *R. idaeus* (Table 4).

The arsenic content in the soil had a significant impact on the As content in plant biomass in all species studied, with the strongest relationship found for *Deschampsia flexuosa* (R^2 = 0.75) and *Dryopteris carthusiana* (R^2 = 0.66) (Table 5 and Fig. 9). The only relationships between the soil and plant biomass heavy metal contents were found for *Deschampsia flexuosa* (Table 5). Interestingly, in that species the contents of Co and Pb in plant biomass related negatively to the contents of these elements in the soil (Table 5).

PORE WATER SAMPLES

The pore waters of the mine dumps show elevated concentrations of arsenic. The SW heap shows an arsenic content of 651.4 ppb, while the SE dump exhibits a slightly lower concentration of 638.8 ppb (Table 6). These findings suggest a significant presence of arsenic in the water samples, which can have potential environmental and health implications.

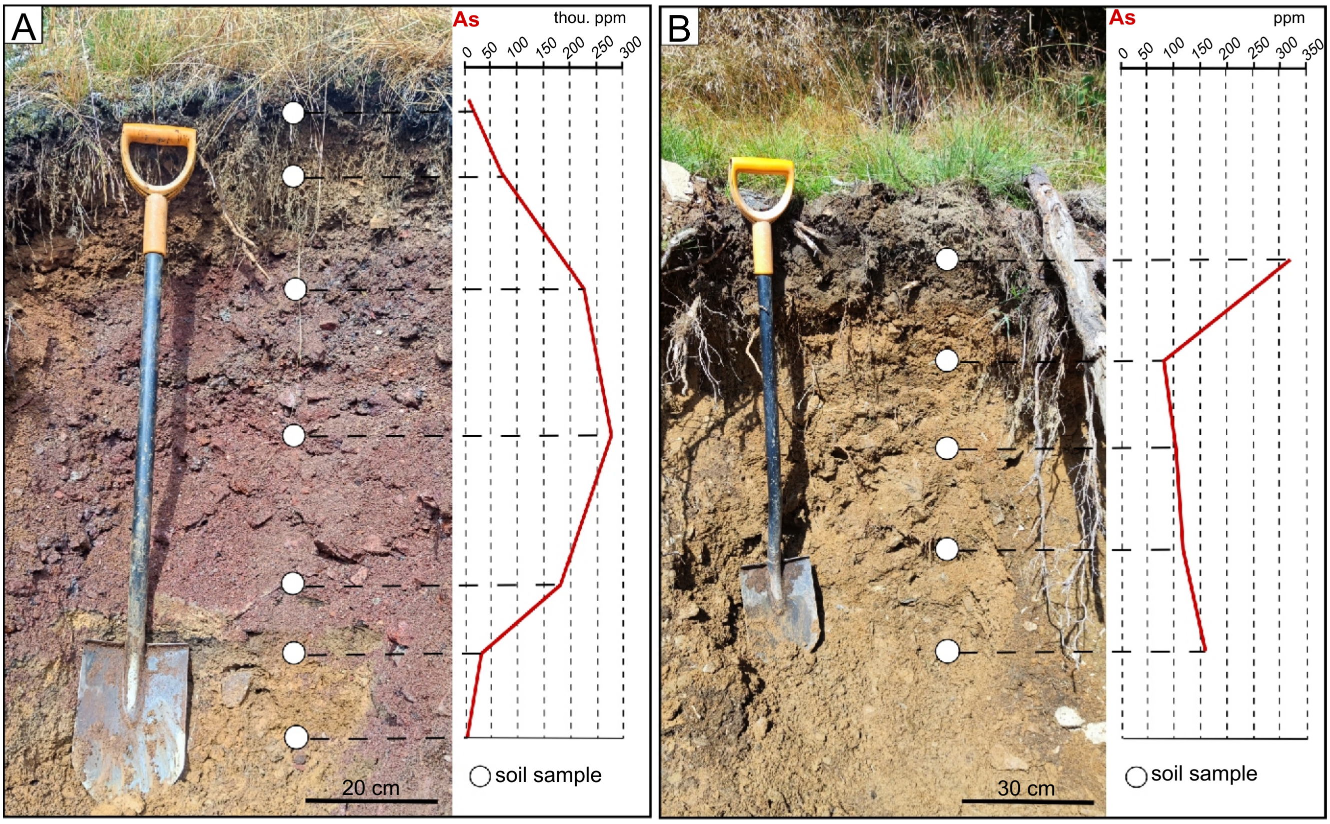

Fig. 8. Distribution of arsenic in the soil profiles

A – SW heap deposits; **B** – natural soil; thou. – thousand

Table 3

Summary statistics of arsenic and heavy metal contents in leaves (in ppm/DW) of *Rubus idaeus* (raspberry, n = 20), *Deschampsia flexuosa* (grass, n = 10), and *Dryopteris carthusiana* (fern, n = 10) in Czarnów

	Min.	Max.	Mean	Std. error
Rubus idaeus				
As	0.32	19.02	3.73	4.23
Co	0.07	0.19	0.12	0.03
Cu	4.72	10.40	6.70	1.40
Zn	31.64	78.87	51.17	14.28
Pb	0.23	1.07	0.42	0.18
Cd	0.11	0.83	0.31	0.16
Deschampsia flexuosa				
As	0.39	14.74	4.17	5.30
Co	0.05	0.19	0.10	0.04
Cu	3.94	7.00	4.71	0.89
Zn	32.70	50.06	39.96	5.19
Pb	0.32	1.76	1.00	0.51
Cd	0.03	0.22	0.08	0.05
Dryopteris carthusiana				
As	0.26	9.49	2.00	2.72
Co	0.09	0.43	0.29	0.12
Cu	6.33	9.80	7.72	1.06
Zn	28.44	107.77	79.44	22.01
Pb	0.35	4.12	1.41	1.16
Cd	0.46	1.21	0.71	0.23

In terms of the environmental conditions, the pH of the SE dump was measured at 9.4, indicating alkaline water. The temperature was recorded as 12°C, and the redox value as 153 mV. Additionally, the conductivity of the water sample was 354 μS . The SW dump displays a pH value of 7.5, suggesting more acidic conditions compared to the SE dump. The temperature remains consistent at 12°C, and the redox value was recorded as 166 mV, and the conductivity as 258 μS.

Table 4

Results of paired t-test on arsenic and heavy metal contents in leaves of *Deschampsia flexuosa* vs. *Rubus idaeus* (n = 10), and *Dryopteris carthusiana* vs. *R. idaeus* (n = 8) occurring within the same sampling points in Czarnów

	Deschampsia flexuosa–Rubus idaeus		*Dryopteris carthusiana–Rubus idaeus*	
	Mean diff.	*p*	Mean diff.	*p*
As	1.67	0.19	–2.97	0.24
Co	–0.03	0.16	**0.19**	0.00
Cu	**–1.39**	0.00	0.42	0.47
Zn	–10.05	0.06	21.87	0.12
Pb	**0.58**	0.00	1.12	0.04
Cd	**–0.25**	0.01	**0.37**	0.00

Mean difference unit is ppm DW; significant relationships (*p*-value <0.05) are marked in bold

Table 5

Results of linear regression analysis performed for arsenic and heavy metal contents in soil and in leaves of *Rubus idaeus* (raspberry, n = 20), *Deschampsia flexuosa* (grass, n = 10), and *Dryopteris carthusiana* (fern, n = 10) in Czarnów

	Rubus idaeus			*Deschampsia flexuosa*			*Dryopteris carthusiana*		
	Coef.	R^2	*p*	Coef.	R^2	*p*	Coef.	R^2	*p*
As	**0.21**	**0.23**	**0.03**	**0.41**	**0.75**	**0.00**	**0.61**	**0.66**	**0.00**
Co	–0.05	0.09	0.21	**–0.16**	**0.67**	**0.00**	–0.28	0.18	0.22
Cu	0.04	0.14	0.10	0.02	0.04	0.57	0.05	0.32	0.09
Zn	–0.02	0.00	0.89	–0.24	0.39	0.05	–0.40	0.33	0.08
Pb	–0.05	0.02	0.57	**–0.52**	**0.65**	**0.01**	–0.35	0.04	0.60
Cd	–0.01	0.00	0.95	–0.15	0.03	0.61	–0.01	0.00	0.90

Significant relationships (*p*-value <0.05) are marked in bold

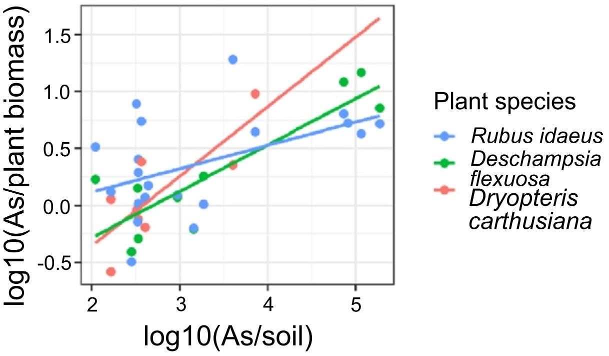

Fig. 9. Relationships between arsenic content in the soil and in the plant biomass of three species (raspberry *Rubus idaeus*, grass *Deschampsia caespitosa* and fern *Dryopteris carthusiana*) studied in Czarnów

Lines represent simple linear regression lines fitted to the data for each plant species

DISCUSSION

The arsenic content in the soils greatly exceeds the permissible limit of 100 ppm (Regulations, 2016), with the highest concentrations exceeding it many times (Table 7). Additionally, the median value for arsenic is also four times higher than the permissible limit. The highest concentrations of arsenic in the soil, exceeding 100,000 ppm, correlate with the presence of iron arsenates that have crystallized within the dump deposits.

Compared to other mining localities such as Miedzianka, Złoty Stok, Żelaźniak and the Upper Silesian Industrial District, the maximum arsenic content in the soils is significantly higher (Karczewska and Bogda, 2006; Krysiak and Karczewska, 2007; Pasieczna et al., 2018). Furthermore, the cobalt content in the first soil level surpasses the permissible limit and, compared to other localities, it is also considerably higher. However, the median content of other elements in the soils does not exceed permissible limits, and in some cases, their concentrations are even lower than in other localities compared, with a few exceptions. Our findings highlight the alarming levels of arsenic and cobalt in these soils, which indicate potential environmental concerns.

The elevated cobalt content is associated with the primary ore mineral, arsenopyrite, known for its high cobalt levels (Mikulski, 2010). The distribution of both minerals corresponds to a common source of ions, namely the weathering of arsenopyrite.

The pH measurements of the soils provides evidence for a link between the oxidative degradation of ore minerals and the ensuing lowering of soil pH within the confines of the mining area. The weathering of ore minerals therefore seem to result in the acidification of the surrounding pedosphere.

Research into the soil profiles indicates that the presence of the mine dump significantly affects the arsenic levels in the soil, resulting in extremely high concentrations within the dump materials and gradually decreasing concentrations on moving away, suggesting a localized contamination source associated with the mine dump. The natural soils above the dump also show elevated levels of arsenic, albeit lower than within the dump deposits. This indicates the potential dispersal of arsenic beyond the immediate vicinity of the dump.

All species of plants studied are good indicators of bioavailable As in a soil and their mean contents of As were >1.5 ppm DW, thus higher than average values in plants from non-contaminated sites (accordingly to the range reported by Kabata-Pendias and Pendias, 2001). However, neither *Deschampsia flexuosa* nor *Dryopteris carthusiana* reached such high contents of As in biomass as the maximum values reported for *Deschampsia flexuosa* and *Dryopteris* ssp. from arsenic-polluted sites in the Sudety Mts. by Dradrach et al. (2020). Also, the median of As content in the plant biomass studied was lower than reported by Dradrach et al. (2020) for 13 plant species collected in Złoty Stok, Radzimowice and Czarnów (median = 8.9 ppm). But, in the current study in Czarnów, plant samples were collected along a gradient of pollution, not only directly from mining dumps or their very close surroundings.

Table 6

Water analysis from two locations

[ppb]	**Na**	Mg	Al	K	Ca	Fe	As	Co	Cu	Zn	Pb	Ni
SW dump	912.4	12597.8	145.6	7450.5	14925.7	236.3	651.4	0.4	24.0	5.1	2.8	5.2
SE dump	656.8	7076.2	34.9	3649.0	5972.3	64.2	638.8	0.5	9.3	4.2	2.0	1.6

Table 7

Comparison of the contents of As, Co, Cu, Pb, Zn with those from other locations in Poland, as well as with the regulations of the Polish Ministry of Environment (Regulation, 2016)

[ppm]	Czarnów		Regulation (2016)	Karczewska and Bogda (2006)	Krysiak and Karczewska (2007)		Pasieczna et al.(2018)
	Min-max	Median	The permissible content	Miedzianka, Rudawy Janowickie	Złoty Stok	Żelaźniak, Radzimowice	The Upper Silesian Industrial District
As	*53–298,957 *42–231,480*	420 346	100	n.d.	272–43,500	100–9,650	10–5,288
Co	*20–17,923 *14–1, 958*	233 195	200	n.d.	n.d.	n.d	1–218
Cu	*12–21,589 *11–12,870*	44 52	600	180–460	5–100	7–3,430	53–13,230
Pb	*22–1,150 *19–1,253*	67 48	600	139–348	45–320	5.8–2,090	4–54,940
Zn	*16–1,542 *62–1,690*	129 153	2,000	213–698	51–280	28–3,660	8–55,460

* – first soil level in Czarnów; second soil level in Czarnów is marked in italics

The As content in *R. idaeus* leaves was higher than contents detected by Kotuła et al. (2022) in wild and cultivated raspberries in non-contaminated areas of Poland (mean content in leaves of a wild crop was 0.12–0.40 depending on the year). The arsenic content of raspberry leaves in Czarnów was also higher than in Złoty Stok mining dumps, where the As content was 1.3 ±0.1 ppm DW (Jedynak et al., 2012). Leaves of *R. idaeus* are often used for herbal infusions. The maximum allowed level of As contamination in a tea is 0.01 ppm DW. Despite only 40% of a tea or herb contaminant, on average, migrating into an infusion, regular drinking of herbal tea prepared from *R. ideaus* leaves with As contents as detected in Czarnów may pose a health risk (Wojciechowska-Mazurek et al., 2010).

Kotuła et al. (2022) found similar or even lower contents of heavy metals in raspberry leaves than in those growing in Czarnów. Populations of plants occurring in sites highly contaminated with heavy metals often exhibit higher tolerance to the metal stress than populations from non-contaminated sites (Ernst, 2006). Plants may limit uptake of heavy metals from a soil and their transport to the aboveground biomass (Viehweger, 2014). But, many such mechanisms are activated only when metal stress thresholds are exceeded (i.e. metal contamination reaches extremely toxic levels) as such defence mechanisms require energy and resources e.g. for synthesis of phytochelatins and hormones (Viehweger, 2014). Thus, the relationship between the soil heavy metal contents and those in plants is not always straightforward, as indicated also by very weak relationships in the case of almost all heavy metals and species studied in Czarnów. Defense mechanisms under metal stress are particularly well-developed in *Deschampsia flexuosa*, a relatively common species which is known as a dominant species in other sites rich in heavy metals e.g. in the Harz region (Ernst et al., 2004) and in Slovakia (also in places of historical mining activities; Banásová et al., 2006). Although, no typical obligatory metallophytes grow on the mining dumps (Ernst, 2006), other species tolerating heavy contamination by As were present, such as *Agrostis capillaris* (Dradrach et al., 2020).

The study area is quite heterogeneous in terms of topography, vegetation cover and land use. It is mostly covered by a beech forest (in the NE part), and herb and shrub vegetation typical of forest clearings (in the SW part). The pH of soil in the study area varied from 3.6 to 5.6 (Fig. 7). Although we did not confirm the influence of soil pH on heavy metal uptake by plants in the study area, other environmental factors like organic matter, phosphorus and iron content in soil might impact heavy metal bioavailability (Ociepa-Kubicka and Ociepa, 2012), and obscure the relationship between soil and plant biomass contents of heavy metals. Also, plants can increase bioavailability of heavy metals in the rhizosphere by releasing a variety of root exudates, which have pH-lowering effect (Dalvi and Bhalerao, 2013). Finally, different element species can vary in their bioavailability, as is often reported e.g. in the case of Pb (Brown et al., 1999) and may explain the negative relationship between soil and plant biomass content of Pb in our study. Both in the past and at present, afforestation of the area with coniferous species (including spruce) was carried out, which can promote further acidification of soils and may lead to future local changes in uptake of As and heavy metals by plants (Dradrach et al., 2019).

Water samples were collected from two distinct dumps, denoted SW and SE. Discrepancies in pH values were observed between the respective sample solutions, a phenomenon likely attributed to the composition of the materials deposited on each dump. The SW dump predominantly features materials reflecting ore exploitation, and material analysis reveals the presence of coal fragments, related to fire-extraction of metal from ore. Conversely, the SE heap includes more waste material, comprising carbonate rocks. Variation in the material deposited has significantly influenced the physicochemical characteristics of the water samples collected. Alkalinity is positively correlated with waste rock presence, leading to higher pH levels, whereas acidity is associated with ore-derived materials, resulting in more acidic water conditions.

Arsenic concentrations in pore waters from mineralized soils in SW England range from 93–240 ppb (Haswell et al., 1985), which is lower than the concentrations found in the SW and SE dumps in the Czarnów mining area. Pore waters near Giant Mine, Yellowknife Bay, Canada, shwo an arsenic content of 585 ppb (Andrade et al., 2010), indicating comparatively lower contamination. However, at the old mining site of Jedová jáma in the Czech Republic, the arsenic content in pore waters reaches around 4,600 ppb after rainfall, which is significantly higher than the concentrations in the SW and SE dumps (Drahota et al., 2016).

In terms of surface waters in Poland, the highest concentrations of As are found in Złoty Stok with 6,830 ppb (Marszałek and Wąsik, 2000) and the Trująca stream with a significantly elevated arsenic content of 3,778 ppb (Komorowicz and Barałkiewicz, 2016). These levels are much higher than those observed in the waters from Czarnów. Conversely, Złotoryja (0.41 ppb), Legnica (0.21 ppb), and Wałbrzych (0.25 ppb) demonstrate considerably lower arsenic concentrations compared to the mine dumps of our study, indicating less contamination of their water sources (Komorowicz and Barałkiewicz, 2016).

According to the Regulations of the Polish Ministry of Health, the acceptable limit for arsenic content in drinking water is set at 10 ppb (Regulation, 2017). However, the water testing results from the SW and SE dump reveal that arsenic levels in the pore waters far exceed the acceptable limit for drinking water. Such high concentrations of arsenic can pose potential health and environmental risks. Mickiewicz and Marszałek (2016) also found increased arsenic contents in groundwater (springs) and surface water (streams) in the Czarnów area. But the content of this element there was many times lower than in the pore water analyzed in this work.

Our findings underscore the imperative for stringent control measures over post-mining pollution within the study area. Notably, elements such as arsenic and cobalt emerge as particularly hazardous, warranting continuous monitoring efforts. To effectively remediate contaminated soils, several methods may be employed. One such approach is phytoremediation, which leverages plants with the ability to sequester toxic elements, and has proved to be efficient (Wei et al., 2006; Martínez-López et al., 2014; Lopes et al., 2016). Chemical methods (immobilization, soil washing) can be applied to hinder the dissolution of arsenic. Furthermore, bioremediation presents advantages in this context and can be employed in conjunction with other remediation techniques (Wan et al., 2020).

SUMMARY

Mining operations spanning centuries in the Czarnów region (SW Poland) have played a significant role in shaping a distinct geochemical anomaly. The highest concentrations of metals and arsenic are observed in soils developed directly on post-mining dumps or in their immediate vicinity. In the study area, the SW dump region stands out, where the highest concentrations of elements such as arsenic, lead, copper and cobalt were found. No clear correlation was observed between the concentration of elements and depth in the soil. This may indicate far-reaching migration processes of elements deep into the soil profile. The content of arsenic and other toxic elements in pore water collected from the soils also exceeds the permissible standards. The acidic nature of the local soils promotes the penetration of these elements into pore water. In the study area, accumulation of As and other toxic elements by plants was observed. Arsenic contents were high in the plant biomass of all three species studied and were positively related with As contents in the soils. The highest maximum values were found in raspberry (*Rubus idaeus*) leaves. The element contents detected in plant biomass exceed the permissible environmental norms. Such high concentrations of toxic elements may pose a real threat to human health, and exposure to these hazardous substances may lead to a range of health concerns. As a result, it is imperative to closely monitor and address these geochemical anomalies to safeguard the well-being of the local population and ecosystem.

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