Abstract: This study, carried out in Radzimowice, a historical As mining site, analyzed the speciation and mineralogical As forms in soils, in different locations, as related to rock weathering processes and associated environmental risk. Four soil groups, including those on mine dumps, and in the stream valley, as well as stream sediments, were examined. The screening performed on 52 samples showed an extremely low actual As solubility, except for soils at reducing conditions. Nine samples were subjected to mineralogical analysis by microscopy and X-ray diffraction (XRD), and sequential extraction according to Wenzel. The results indicated that in all samples, As was associated mainly with amorphous Fe oxides, that constituted up to 66% of total As. Scanning electron microscopy–energy-dispersive spectroscopy (SEM-EDS) analysis performed on 3 representative samples revealed that the dump material contained the grains of primary As minerals, mainly arsenopyrite and loellingite, rimmed and encrusted with goethite. Stream sediments and the alluvial soil contained large amounts of (hydroxy)Fe-oxides, in which As was present in sparse scorodite grains and in highly dispersed forms associated with goethite and amorphous compounds of various compositions. The diversity of As species makes forecasting of its environmental fate difficult, therefore further research should focus on As transformations, particularly under reducing conditions.

Keywords: mine dump; alluvial soil; sediment; speciation; solubility; arsenopyrite; goethite; SEM-EDS; sequential extraction

1. Introduction

Arsenic, a toxic metalloid, is often present as an associating element in metal ores, and it usually accompanies gold. Various ores were mined in the past in several sites in the Sudetes, a mountain range in SW Poland, to produce gold, non-ferrous metals and arsenic itself. The largest arsenic mines operated in Złoty Stok, formerly the main European center of its processing [1–4], and Radzimowice, a village situated on the slopes of the Żeleźniak hill [5–10].

The toxicity of arsenic and its compounds has been known since ancient times. It is well known that arsenic present in the soil environment may enter the geochemical cycle, posing a threat to biota, including humans. This risk depends not so much on the total content of this element in soils as on the species in which it occurs. Its solubility, speciation and bioavailability in soils depends on numerous factors, including its origin and primary mineralogical forms, soil properties, such as pH, texture and the content of organic matter,
and redox potential, the presence of competing compounds in soil pore water, as well as on various biochemical processes that can facilitate or hinder arsenic mobilization [11–20].

Strong enrichment of soils in arsenic in the areas of former ore mining and processing occurs mainly in soils that develop on mining and processing dumps, however, the various mechanisms have caused the spread of arsenic and other potentially toxic elements in the environment, and their secondary accumulation in distant sites. Arsenic-bearing waste material was for many years used for backfilling workings, ground leveling and road hardening [4,7]. Environmental pollution in those areas was also caused by the emission of pollutants into the atmosphere from local smelting facilities [5,7,8]. The weathering of mine waste material associated with transformation of minerals and leaching processes together with acid mine drainage (AMD) and acid rock drainage (ARD) [7,21–24] should be considered as the main processes responsible for spreading contaminants in the surroundings of former mining sites and their secondary accumulation in the environment. Therefore, it can be expected that the stream sediments in the areas of former ore mining as well as alluvial soils along the streams can be highly enriched in potentially toxic metals and metalloids, including arsenic. Such enrichment was confirmed by numerous authors [25–27].

The aim of this study was to examine the concentrations of arsenic as well as its speciation and mineralogical forms in soils differing in properties, situated in various geomorphological and topographic settings, in the area of the former arsenic ore mining and processing in Radzimowice. The results on As speciation were analyzed and discussed in relation to various processes of weathering, transport and accumulation of minerals in the environment, as well as to potential environmental risk.

2. Materials and Methods

2.1. Soil Samples and the Scope of Examination

Soil samples were collected from the surface layer of soil (0–20 cm) in various places in the area affected by the former mining and ore processing in Radzimowice (Figure 1). Additionally, the samples of bottom sediments of the Olszanka watercourse were included in the study. The stream, called also the Yellow Stream, has its source below the mine dumps and is supplied by acid rock drainage (ARD) and periodically also by acid mine drainage (AMD) flowing out from the adit of former Arnold mine [7–9]. The samples of stream sediments were collected in various locations where transported solid material was accumulated in the stream bed.

In the study area, four different groups of settings were chosen, that differed in geomorphology and soil origin (Table 1). The distinguished groups were: soils situated in the vicinity of mine dumps built of mine waste rich in As, used as meadows or arable fields (I), soils that developed on the mine dumps (II), alluvial soils and other types of soil in the valley of the Olszanka stream (III), and soils located on forested slopes enriched in arsenic inherited from the parent rock, and additionally, probably via air pollution caused by metallurgical processes (IV). The sediments collected from the Olszanka stream along its course were analyzed as a separate group (V); these samples were marked with the symbol (S). In the first stage of research, screening examination was carried out, in which all the samples (N = 52) were analyzed on the concentrations of total As and its potentially and actually soluble, susceptible to extraction with appropriate solutions. The samples taken from the field were crushed, sieved on site to remove stones and large gravel (>5 mm) and then brought to the laboratory, air-dried, homogenized, and sieved to 2 mm. The fine fraction was subjected to screening analyses of basic properties by standard methods used in soil science [28].
Based on the results of a screening stage, nine samples were selected for a detailed analysis. The samples chosen for this part of the study were representative for five groups of settings. Additionally, we examined those samples that contained exceptionally high concentrations of As. The detailed study involved determination of texture, chemical properties including As speciation in the solid phase by sequential extraction, as well as mineralogical composition examined by optical microscopy and X-ray diffraction (XRD). The purpose of those analyzes was to recognize and assess the progress of the weathering processes in soils and/or possible re-precipitation of As in sediments and soils in the form of various secondary minerals. In order to ensure high homogeneity of those samples, they were powdered in an agate mortar prior to chemical and mineralogical analyses.
2.2. Basic Properties and Chemical Analyses

The texture of soils and sediments was determined by a sieve-and-hydrometer method. Soil pH was measured potentiometrically in 1M KCl (1:2.5, v:v). The content of organic carbon (Corg) in soils and sediments was analyzed on the CS-MAT 5500 instrument (Strohlein, Ströhlein, Kaarst, Germany). “Total” concentrations of As in soils were measured after digestion of samples with aqua regia (concentrated HCl + HNO₃, 3 + 1) in microwave oven, according to ISO 14466 [29]. Potentially and actually soluble forms of As were extracted with 0.43 M HNO₃ and 1 M NH₄NO₃, respectively, according to the ISO procedures 17402 [30], and 19730 [31]. Concentrations of As in soil digests and extracts were determined by inductively coupled plasma – atomic emission spectroscopy ICP-AES, on iCAP 7400 (Thermo Scientific, Waltham, MA, USA). Validation of analytical methods involved the analysis of two certified reference materials CRMs, certified for total concentrations of trace elements, acquired by aqua-regia digestion (freshwater sediment CNS 392 and contaminated soil CRM 027, provided by Sigma-Aldrich Poland, Poznań). Because of the lack of appropriate certified materials, the accuracy of As determination in the case of its extractable forms was verified via standard addition.

Speciation of As in the solid phase of soils and sediments was determined using a sequential extraction method according to Wenzel et al., 2001 [32] in which five operationally defined As fractions were distinguished. They are believed to represent non-specifically-bound (F1), specifically-bound (F2), amorphous hydrous oxide-bound (F3), crystalline hydrous oxide-bound (F4) and the residual (F5) species of As in soils and sediments. In each case, the sequential extraction was performed in duplicate, of which the mean values were reported in the paper. Briefly, the procedure involves five extraction steps and washing following the steps 3 and 4 (Table S1 in Supplementary Materials). After each extraction or washing step, the tubes were centrifuged (15 min, 1700 × g), and supernatants were filtered through 0.45 µm filter paper and immediately analyzed by ICP-AES. Blanks were subjected to the same procedure. Recoveries of sequential extractions, calculated as differences between total As (determined via aqua regia digestion) and the sums of five fractions, ranged between 85% and 112%. Those differences were cured by the adjustments made proportionally to the fractions F3, F4, and F5.

2.3. Mineralogical Analyses

Microscopic studies of soil samples were performed in transparent and reflected light (ZEISS JENA POL, Carl Zeiss AG, Jena, Germany). Identification of crystalline phases in bulk soil samples was undertaken by XRD. Analyses were performed with a Thermo Electron (ARL X’tra) diffractometer, using CuKα radiation. XRD data were collected in the range 3 to 65° 2θ using a step scanning technique with a fixed counting time of 2 s per 0.01° step. Win XRD software was used for identification of minerals. Analyses were made in the XRD-laboratory, Institute of Geology Adam Mickiewicz University in Poznań.

Three samples, No. 2, 5(S) and 6, were selected for more detailed analysis with scanning electron microscopy coupled with energy dispersive spectral analysis SEM-EDS (SU3500, Hitachi, Tokyo, Japan), in the Science and Technology Park in Poznań. Operating conditions for analysis were: 15.0 kV, P = 70 Pa, detector BSE-COMP, detector EDS–Ultra Dry Silicon Drift X-ray Detector (SDD) (Thermo Fisher Scientific). The scanning electron microscopy–energy-dispersive spectroscopy (SEM-EDS) analysis allowed to obtain the data on associations of elements in the samples, including associations of arsenic with other elements.

2.4. Statistics

Collections of samples that represented particular settings in the screening stage of the study were subjected to basic descriptive statistical analyzes aimed to compare the ranges and medians of properties in the groups. As the data did not show normal patterns of distribution, and they could not be normalized by common methods, non-parametric statistics were applied. The correlations between the parameters were determined by
calculating the Spearman correlation coefficient. The differences of soil properties among the groups were analyzed by a two-sample Kolmogorov–Smirnov test. All the analyses were performed using the software Statistica, version 13.0 (Dell Inc., Round Rock, TX, USA).

3. Result

3.1. Screening

The properties of soils within individual groups of settings showed large differentiation (Table 1). The total As content in all tested samples (N = 52) was within a very wide range of 89–156,000 mg/kg, with the highest medians for the group II, i.e., soils developed on mining dumps (8160 mg/kg), and the group III, i.e., alluvial soils in the Olszanka valley (5170 mg/kg As). The median value of As concentrations in bottom sediments (V) was even higher, 9630 mg/kg As (Table 1), which indicates that the main mechanism leading to enrichment of alluvial soils is the input of material transported by the stream, rich in arsenic, and its sedimentation or secondary precipitation. At this stage of the study it was not possible to identify the main source of As-bearing minerals in the sediments of the Olszanka stream, which could be both the leaching of As from the waste rocks rich in sulfidic minerals (ARD) and the release of As from the mine via open adits (AMD) [9]. An additional source of enrichment could be the mechanical transport of particles from waste material disposed in the site of a very likely location of former calciner that was probably situated in the upper part of the Olszanka valley [5,8], and not—as previously believed—in the village Radzimowice itself.

Potential and current solubility of As in the groups of settings also showed a large variation, both in terms of extractable amounts expressed in mg/kg and their share in the total content (Table 2). The share of potentially soluble forms of As, extractable with 0.43 M HNO₃, ranged from 1.7–44.7% of the total As, and was generally the highest in soils formed on dumps (II), and the lowest in forested weathering soils on the slopes (IV), with corresponding median values: 20.3% and 6.5%, respectively.

Table 2. Potentially and actually soluble forms of As in soils, extractable with 0.43 M HNO₃ and 1 M NH₄NO₃, respectively.

| Group | 0.43 M HNO₃—Extractable As | 1 M NH₄NO₃—Extractable As |
|-------|--------------------------|--------------------------|
|       | mg/kg | Percent of Total As | mg/kg | Percent of Total As |
| I     | 14–3320 | 32 | 4.1–23.4 | 13.0 | 0.05–0.78 | 0.07 | 0.01–0.25 | 0.03 |
| II    | 5.2–2890 | 1360 | 4.8–44.7 | 20.3 | 0.06–1.56 | 0.23 | <0.01–0.05 | 0.01 |
| III   | 6.2–18,900 | 504 | 3.0–39.6 | 13.9 | 0.02–63.2 | 0.65 | <0.01–0.75 | 0.02 |
| IV    | 9.5–179 | 20 | 1.7–22.6 | 6.5 | 0.10–4.63 | 0.30 | <0.01–1.28 | 0.02 |
| V     | 206–2740 | 1330 | 4.7–23.4 | 16.2 | 0.20–1.78 | 0.34 | <0.01–0.02 | <0.01 |

It should be emphasized, however, that the differences between the groups were not statistically significant. Potential solubility of As in general should be assessed as relatively high, as some authors reported much lower values, for instance approximately 1% in mining tailings [33]. The current solubility of As in soils and sediments remained generally very low, and in none of the sample, the share of 1M NH₄NO₃-extractable As exceeded 0.03% of the total concentration. Absolute concentrations of actually soluble As were higher than 1 mg/kg in only 20% of the samples. Only 3 samples, that represented alluvial soils (III), contained 1M NH₄NO₃-extractable As in the amounts higher than 10 mg/kg, with maximum 63.2 mg/kg (Table 2). These exceptionally high concentrations of currently soluble As in soils can be probably explained by reducing conditions, as the related soils had in the field the distinct redoximorphic features.
3.2. Detailed Chemical Analysis of Representative Samples

3.2.1. Basic Properties

The properties of 7 soil samples and 2 samples of stream sediments, chosen as representative for the groups of settings, are presented in Table 3. Despite the very large morphological and typological differentiation of soils in the area covered by the study (not presented in this paper), the earthy parts of all these soils showed a similar texture of sandy loams (SL) and the only one sample No 6, with the highest As concentration, contained lower amount of silt (0.002–0.05 mm), in favor of the sand fraction, so that its texture was classified as a loamy sand (LS). The samples of stream sediments No. 4 (S) and 5 (S), as well as mineral components of the organic soil No. 8 had also the textures of sandy loams (SL).

Table 3. Properties of soils and sediments selected for detailed analysis.

| Group | Soil No. | Texture | C$_{org}$ g/kg | pH | As, mg/kg | 0.43 M HNO$_3$—Extractable | 1 M NH$_4$NO$_3$—Extractable |
|-------|----------|---------|----------------|----|-----------|-----------------------------|-------------------------------|
| I     | 1        | SL      | 33.4           | 3.6| 14,200    | 3320                        | 0.78                         |
| II    | 2        | SL      | 12.2           | 6.9| 8670      | 953                         | 0.48                         |
|       | 3        | SL      | 12.2           | 6.9| 8670      | 953                         | 0.48                         |
| III   | 6        | LS      | 31.6           | 4.6| 156,200   | 18,900                      | 63.2                         |
|       | 7        | SL      | 88.0           | 6.0| 4770      | 2160                        | 25.6                         |
|       | 8        | SL      | 254.0          | 4.3| 16,400    | 649                         | 0.04                         |
| IV    | 9(S)     | SL      | 42.0           | 3.1| 737       | 145                         | 1.48                         |
| V     | 4(S)     | SL      | 21.5           | 6.9| 8950      | 814                         | 0.34                         |
|       | 5(S)     | SL      | 20.8           | 6.7| 28,400    | 1330                        | 1.78                         |

3.2.2. Total and Extractable As

All the representative samples showed a significant enrichment in As (Table 3), but their concentrations of As differed considerably, in the range from 737 mg/kg in a forest soil (No. 9) to 156,200 mg/kg in the most enriched alluvial soil (No. 6). Two alluvial soils (No. 6 and 7) contained exceptionally high concentrations of easily soluble As, extractable with 1M NH$_4$NO$_3$: 25.6 mg/kg and 63.2 mg/kg, respectively, which, as mentioned earlier, should probably be explained by temporal waterlogging and anoxic conditions. Rather unexpectedly, the lowest concentration of easily soluble As was found in the third soil collected in the Olszanka valley, that had a total As concentration of 16,400 mg/kg, and was very rich in organic matter (C$_{org}$: 254 g/kg). A potential solubility of As in that soil, revealed by extraction with 0.43 M HNO$_3$, was also very low: 649 mg/kg, which corresponded to only 4% of the total As. Similarly low shares of potentially soluble As, below 10% of total As, were also found in stream sediments, i.e., in samples No. 4 (S) and 5 (S).

3.2.3. Sequential Extraction of As

The results of As speciation revealed by the sequential extraction according to Wenzel et al. [32] show that the main As fractions were those associated with (hydroxy)Fe-oxides, i.e., F3 and F4 (Figure 2). The forms associated with amorphous oxides (F3) constituted 34–68% of the total As, and predominated over the crystalline fraction F4 except for the forest soil No. 9, where As bound to crystalline (hydroxy)Fe-oxides was clearly the main species of this element.

The highest shares of the F3 fraction—in the light of sequential extraction—were found in stream sediments (67–68% of total As), and in the soils of the III group (alluvial soils in the Olszanka valley): 60–67%. Easily soluble As (F1), considered to be the fraction that indicates the real environmental risk [32], constituted a very low share of As: 0.03–0.89% of its total concentrations, but it was much higher than that determined based on the extraction of 1M NH$_4$NO$_3$ (Figure 3). The results of both extractions were highly correlated with each other, and the Spearman correlation coefficient was R = 0.965. Particularly high concentrations of As in the F1 fraction were found in the soils with hydro morphic features:
No. 6 and 7 (43 and 224 mg/kg, respectively), revealing a considerable environmental risk. The correlation between the sum of F1 + F2 fractions, believed to indicate the potential ecological risk, according to Wenzel et al. [32], and 0.43 M HNO$_3$-extractable As, was poorer than that determined for actually soluble As (R = 0.722). The absolute content of As in the sum of F1 + F2 fractions was the lowest (60 mg/kg) in the forest soil (No 9), while in the remaining soils it was in the range of 267–2260 mg/kg, indicating a considerable potential risk [33]. The share of the residual As fraction (F5) was apparently higher in the dump soils II (25–34%) than in the remaining soils and stream sediments (11–19%).

Figure 2. Speciation of As in 9 representative samples. The results of sequential extraction according to Wenzel [32].

Figure 3. Comparison of the amounts of As extracted with 1M ammonium nitrate and fraction F1 [32].
3.3. Mineralogical Analysis of Representative Samples

3.3.1. Microscopic Observations and X-ray Diffraction (XRD) Analyses

Microscopic observations revealed the presence of 0.02–2 mm large rock fragments (lithoclasts) in all the samples, both in soils and stream sediments. The shapes of rock fragments were irregular and highly differentiated. Mineralogical composition of lithoclasts was relatively homogeneous in dump samples (No. 2 and 3) and in soil samples No. 6 and 7. Quartz, K-feldspars and metamorphic slates (quartz-mica, muscovite, sericite and siliceous and graphite slates) were the predominant minerals, which was confirmed both by microscopic study and XRD analysis (Figure S1). Some amounts of phyllosilicates were also detected in the samples No. 1–3. Additionally, the grains of carbonaceous rocks, of mainly micritic or siliceous-carbonaceous structure, were found as lithoclasts in the samples No. 2 and 7 (Table S2). Some grains of lithoclasts were associated with or covered by (hydroxy)Fe-oxides (Figure 4a).

Sulfidic minerals were present as admixtures in almost all the samples, particularly in dump soils (No. 2 and 3). Among them, the most abundant were chalcopyrite (CuFeS₂), pyrrhotite (FeS), and pyrite (cubic FeS₂), while marcasite (rhombohedral FeS₂) was identified relatively rarely. A characteristic feature of the samples No. 1–3 was the presence of (hydroxy)Fe-oxides, usually associated with rocks fragments, in particular with sulfidic minerals, and also forming single grains. The microscopic images, confirmed by XRD analysis, showed the presence of numerous arsenic-bearing minerals, in particular the grains of arsenopyrite, which were further analyzed by SEM-EDS. Sparse grains of loelingite were also found in the dump samples No. 2 and 3.

The mineralogical compositions of soil samples No. 1, 6, and 9 and stream sediments No. 4(S) and 5(S), differed from that of dump soils and were even more heterogeneous. The lithoclasts of the sample No. 1 consisted mainly of finely crystallized mudstones and slates, with less visible metamorphic features, indicating most likely a different geological origin of soil parent rock in the group I of settings. A characteristic feature of stream sediments and all alluvial soils, revealed by microscopic images, was the presence of thick rims built of goethite that surrounded the grains of lithoclasts (Figure 4b). The samples of two alluvial soils (No. 6 and 7) and stream sediments contained much higher amounts of (hydroxy)Fe-oxides, mainly goethite (FeOOH), as well as hematite Fe₂O₃, that exhibited the intensive red or brownish-red color in reflected light. The presence of (hydroxy)Fe-oxides, mainly goethite, as well as schwertmannite (iron-oxyhydroxysulfate) was confirmed by XRD in the samples of sediments, i.e., 4(S) and 5(S), with their basal reflection lines 4.48 Å; 3.34 Å and 2.56 Å. A poorly crystalline scorodite (hydrated iron arsenate FeAsO₄·2H₂O) was found in the samples No. 6 and 5(S), which was indicated by weakly expressed reflection lines 4.48 Å, 3.06 Å, 3.00 Å and 2.50 Å (Figure S1). A particular feature of the samples No. 7 and 8 was the presence of relatively high amounts of organic components that formed fine black areas and microveins inside the grains, or the rims around the rock fragments.
In sample No. 7, the organic compounds occurred partly as associated with Mn-oxides. The latter were also present as separate, gray-colored, well crystallized grains (Table S1).

3.3.2. Scanning Electron Microscopy–Energy-Dispersive Spectroscopy (SEM-EDS) Analysis

Three samples, No. 2, 6 and 5(S), highly enriched in As, that represented the groups II, III and V, were subjected to a more detailed analysis by SEM-EDS that allowed us to compile the submicroscopic pictures of grains accompanied by information on their chemical composition. The Sample No. 2 represented non-acidic soils developed on the mine dumps. The important components of its fine fractions were various sulfidic minerals, usually well crystallized. They occurred usually separately and sometimes were overgrown by other components, mainly (hydroxy)Fe-oxides. Special attention was paid to the analysis of As-bearing phases. The main mineral that contained As, abundant in the sample No. 2, was arsenopyrite. It occurred mostly separately, in the forms individual grains that differed in their size (Figure 5). Its small grains were clean and undisturbed, while the large ones were often fractured and usually covered by the goethite rims. The data obtained from the SEM-EDS analysis of those grains indicated a relatively low content of As, 23.6–31.9% (Table 4), which was clearly lower than that calculated from the stoichiometry of arsenopyrite, which is 46% [34]. The As:Fe ratio, which in the light of the analyzes was 1:0.88–0.95, did not correspond to the typical composition of arenopyrite (1:0.74), while the As:S ratio (1:0.39–0.49) was close to stoichiometric. Such an effect was probably caused by the fact that the grains of arsenopyrite, even if seemingly undamaged, were partially covered with or encrusted with iron compounds, including goethite. A relatively low As content in the grains examined can also be partly explained by the presence of admixtures introduced probably into the sample during its preparation, which would explain the presence of C, Al and Si reflections (Table 4). The results did not confirm the presence of secondary As-bearing minerals, such as scorodite, on the surface of arsenopyrite, which was reported by numerous authors in similar studies [25,35–39].

![Figure 5](image-url). Backscattered scanning electron microscopy images with energy-dispersive spectroscopy (SEM-EDS) of soil No 2. Arrows indicate the mineral grains with the highest As concentrations. The numbers in brackets identify the subsamples of the soil No. 2. Detailed data on chemical composition of the sample in the points marked in the photos presented in the Table 4.
Table 4. The data on chemical composition of five subsamples of soil No. 2 in the points with the highest concentrations of As, as revealed by SEM-EDS analysis.

| Sample | Point | C   | O   | Al  | Si  | S   | K   | Ca  | Fe  | As  | Fe:S:As |
|--------|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|---------|
| 2/1    | 1     | 21.0| 6.7 | 0.7 | 1.6 | 12.9| 26.7| 30.5|     |     | 0.88:0.42:1 |
|        | 4     | 22.1| 7.5 | 0.8 | 1.7 | 12.2| 25.4| 30.2|     |     | 0.84:0.40:1 |
| 2/2    | 5     | 20.5| 6.6 | 0.6 | 1.3 | 13.4| 25.6| 31.9|     |     | 0.80:0.42:1 |
|        | 6     | 21.3| 8.5 | 0.6 | 1.3 | 12.0| 24.6| 30.5|     |     | 0.81:0.39:1 |
| 2/6    | 2     | 25.8| 11.9| 0.9 | 3.3 | 11.0| 1.8 | 21.7| 23.6|     | 0.92:0.47:1 |
| 2/12   | 2     | 26.7| 10.4| 1.7 | 3.2 | 11.9| 0.8 | 20.8| 24.4|     | 0.85:0.49:1 |
| 2/17   | 1     | 25.7| 9.5 | 1.2 | 2.9 | 11.9|     |     |     |     | 0.95:0.47:1 |

The presence of various heterogeneous phases, having a mixed chemical composition or forming very fine intergrowths, was a typical feature of sample No. 2. For instance, several large clusters of chalcopyrite intergrown by pyrrhotite were identified. Some structures identified as Fe and Fe-Cu sulfides contained the admixtures of arsenic.

The SEM-EDS image of the stream sediment sample 5(S) was utterly different from that obtained from the dump soil No. 2, while the soil No. 6 had several features similar to the soil No 2, and indicated high similarity to the sample 5(S).

The most characteristic feature of the sediment sample 5(S) was the presence of high amounts of goethite and other (hydroxy)Fe-oxides, mainly poorly crystalline or amorphous. They were identifiable macroscopically by the intensive yellow color of the sediments. The presence of goethite was also confirmed by XRD and SEM-EDS analyses. The SEM-EDS analysis indicated that goethite was present in sample No. 5 in very large amounts, and in various structural forms, mainly as the rims around rocks fragments, and as separate, small, poorly crystallized grains dispersed in the sample matrix. The mineralogical composition of this sample showed also the presence of siliceous minerals (quartz, feldspar) and single anthropogenic grains (most likely slag). Lithoclasts and the internal parts of mineral grains were not fractured and remained well preserved, as they were usually covered by thick goethite rims (Figure 6). No sulfidic minerals were found in the sample of No. 5, but there were sparse grains of a mineral identified by SEM-EDS as scorodite FeAsO$_4$·2H$_2$O that contained 32–34% As and 22–24% Fe, the shares consistent with the stoichiometric composition of this mineral. The rims on various grains, identified as goethite, contained usually small amounts of As, below 10%. Most likely, As was present there in the forms absorbed on Fe compounds, not converted into secondary crystalline minerals. The presence of sulfur in various proportions in relation to Fe was probably associated with the admixtures of fine crystalline grains of schwertmannite and amorphous minerals from the group of hydrous ferric arsenate sulfate [36,40–42].

Soil sample No. 6 with the exceptionally high As content, was collected in the stream valley, at the small distance from the collection of the sediment sample No. 5(S). Its morphological features indicated the abundance of yellow-colored goethite and blackish organic matter. SEM-EDS analysis of the grains and rims that were identified as goethite showed, similarly to the sample of stream sediment No. 5(S), a relatively low share of Fe (40–43% by weight), elevated amounts of oxygen (approximately 36%), and the presence of arsenic (that varied in various points in the range 2.3–11%). The content of As was clearly much lower than that in typical secondary arsenic-bearing minerals (such as scorodite or zykaite that contain over 29% As [34]. Chemical analysis of the grains identified as goethite, showed also the presence of small admixtures (below 1%) of Si, Al, Ca, Na, Cl, P and Pb.
and as separate, small, poorly crystallized grains dispersed in the sample matrix. The mineralogical composition of this sample showed also the presence of siliceous minerals and as separate, small, poorly crystallized grains dispersed in the sample matrix. The mineral composition of this sample showed also the presence of siliceous minerals and as separate, small, poorly crystallized grains dispersed in the sample matrix.

Figure 6. SEM-EDS image of the sample No. 5(S)—stream sediments. The grains are covered by rims built of goethite. Chemical analysis did not confirm the presence of considerable As concentrations in the sample. (a) the grain of goethite covered by a crushed rim built of goethite-like (hydroxy)Fe-oxides, (b) enlarged fragment of the grain a; (c) the grain of K-feldspar (darker grey) surrounded by a crushed rim built of goethite-like (hydroxy)Fe-oxides, (d) small, poorly crystallized grains of (hydroxy)Fe-oxides.

4. Discussion

The presented picture of soil properties and As speciation is undoubtedly fragmentary, and cannot be considered comprehensive, as the samples, both in its whole collection and within the groups, were highly differentiated. This research confirmed the previously reported observations [7,8,43,44], that the soils in the area under study contain very high concentrations of As, many times higher than the values considered safe according to the provisions of Polish law [45,46], set for forested lands at 50 mg/kg. However, the currently soluble forms of As, determined in extraction with 1M NH₄NO₃, constitute a very small fraction of the total content (<1.3%), with the median share of 0.02% in 52 tested samples. This confirms the low mobility of As in the environment [11–13]. However, in some samples, an actual solubility of As was significantly higher compared to median or mean values, which is undoubtedly related to the possible release from the solid phase, especially under reducing conditions, due to reductive dissolution of hydrous Fe and Mn oxides that constitute the main sinks of As in soils and sediments. A considerably high mobility of As occurs in periodically flooded soils, whereas some studies indicate that after a longer state of waterlogging, due to various microbiologically mediated mechanisms, the solubility of As in soils decreases [47]. Perhaps these mechanisms, together with a relatively low pH of soil No. 8, can explain a very low solubility of As in that soil (No. 8) that was collected from the valley, and indicated apparent gleyic (reducing) features. Low As solubility in that soil was documented both by the extraction with 1M NH₄NO and in the fraction F1 in sequential extraction according to Wenzel.

A valuable result is a high correlation between the results obtained from extractions performed with 1M NH₄NO₃ and 0.05 M (NH₄)₂SO₄ (F1). The latter reagent is believed to selectively extract a non-specifically bound fraction of As, i.e., the easily exchangeable ions and the species that form outer-sphere complexes [32]. The results of soil extraction with ammonium nitrate were, however, much lower that those obtained with ammonium sulfate, despite its lower concentrations in extracting solution. The question arises, therefore, if 1M NH₄NO₃ should be recommended for the extraction of easily soluble As for the assessment of actual environmental risk.
The comparison of the sum of fractions $F_1 + F_2$ with the results of simple extraction with $0.43 \text{ M HNO}_3$, recommended for the assessment of potential solubility of trace elements [30] indicates that the latter can solubilize both specifically-sorbed As (present in soils in the surface-bound forms, and those are potentially mobilizable due to changes in pH or P addition [32], as well as those that can be released from inner-sphere complexes of (hydroxy)Fe-oxides by their reductive dissolution.

Sequential extraction by Wenzel [32] confirmed that in all the studied soils As was associated mainly with the (hydroxy)Fe-oxides, particularly with their amorphous fraction. The share of As bound in this form turned out to be particularly high in bottom sediments and in alluvial soils of the valley, strongly enriched in As, while the dump soils contained a smaller share of As in these fractions in favor of the forms considered residual. Further examination should be carried out to show if the primary As, in particular arsenopyrite, and other minerals that contained the admixture of As compounds were included in the residual fraction.

Mineralogical examination revealed that the main mineral components of the soils formed on the dumps are lithoclasts of metamorphic rocks (quartzites, shales) and grains of minerals such as quartz, feldspar, barite, mica, as well as commonly occurring iron sulfides of Fe and Cu (pyrrhotite, pyrite, marcasite, chalcopyrite). The grains of arsenic minerals, mainly arsenopyrite and loellingite, were also present in the dump samples. Major grains of As-bearing minerals in the dump soil No. 2 were very well preserved, and, therefore, not subjected to rapid weathering. Similar observations were reported by various authors [36,48,49]. Arsenopyrite is relatively stable under moderately reducing conditions, but it can be mobilized under oxidising conditions by both $\text{O}_2$ and $\text{Fe}^{3+}$, this process being promoted by microorganisms, especially by acidophilic Fe- and S-oxidising bacteria [48–50]. It may also be favored by the presence of other minerals, e.g., carbonates, which locally influence the pH [51]. The presence of cracks and fractures in the grains, documented by micromorphological analysis, may additionally accelerate the weathering process.

According to Basu and Schreiber [35] who compared the mineralogy of dumps and local stream sediments, arsenopyrite is often abundant in the host rocks of mine soils and is often rimmed with scorodite or sulfur and scorodite, which also infill fractures. Scorodite can be easily identified by a characteristic green–yellowish color. The outside parts of rims were reported to contain a mixture of scorodite and iron hydroxide [35]. In our research, the rims surrounding the grains of arsenopyrite in the dump soil (No 2) were identified as goethite, and did not contain significant amounts of As. Locally, As was present in small amounts, most likely in the form of absorbed arsenate ions.

The presence of scorodite, a secondary As mineral, was, however, confirmed in our samples of sediments and alluvial soil (No. 5(S) and 6), similarly as it was reported by various authors from similar environmental conditions [34,35]. Scorodite is a relatively stable mineral in oxidized environment [34,36–38,49]. The presence of single scorodite grains in our research cannot in any way explain the high content of total As in the samples examined, in particular in the sample No. 6. SEM-EDS and XRD analysis proved that this mineral was present in the samples 5(S) and 6, but in almost all of the points examined, its concentrations were very low (<11%), i.e., much lower than its stoichiometric content in the scorodite. The occurrence of crystalline scorodite or other secondary As-bearing minerals was also not confirmed, however small amounts of As were present both in the grains and rims identified as goethite, as well as in the non-crystalline and highly heterogeneous matrix. The apparent discrepancies between the results of chemical analysis and the results from mineralogical and SEM-EDS studies performed on the samples 5(S) and 6 can partly be explained by high heterogeneity of those samples, which would mean that the material subjected to SEM-EDS analysis might not fully correspond to the composition of that chemically analyzed in the laboratory. Undoubtedly, however, the main form of As in the tested samples of sediments and alluvial soil was not the grains of crystallized secondary minerals, but highly dispersed species adsorbed in non-stoichiometric amounts.
by goethite and schwertmannite, as well as in the form of highly amorphous pitticite $\text{Fe}^{3+}_{x}(\text{AsO}_4)_{y}(\text{SO}_4)_{z}x\text{nH}_2\text{O}$. Similar results were also reported by Drahota et al. [36], who analyzed the weathering products of similar dump material and found that the main difficulty in determining As speciation comes from the fact that it is often at very low concentrations and occurs in a variety of chemical forms within the same sample, including different mineral phases and surface complexes. They inferred also that the amount of As bearing crystalline phases with relatively low levels of As ($\leq 2.7$ wt% $\text{As}_2\text{O}_3$) was also surprisingly low with respect to total As content in the soil, and As is was probably sequestered by phases that were missed by the standard mineralogical methods. Non-stoichiometric proportions among Fe, As and S can be explained by variations and multiples of the bonding patterns, the relatively open structures of some arsenate minerals and extensive substitution of cations and anions and water [34]. It can be concluded, however, that the results concerning the As forms described by SEM-EDS correspond quite well with the results of sequential extraction, which showed that the As associated with amorphous iron oxides is a predominating form of As in sediments and soils, especially in the alluvial ones (Figure 2). However, it cannot be ruled out that As also forms some associations with organic matter, as suggested in some reports [52,53]. According to Langner et al. [52] natural organic matter can completely sequester arsenic through the formation of covalent bonds between trivalent arsenic and organic sulfur groups, which plays a very important role in arsenic immobilization in sulfur-enriched, anoxic wetlands [52]. The analyses performed in our study were not capable to identify such As species, for instance in the soil No. 8.

The knowledge on speciation of As in soils is obviously crucial from the standpoint of its possible environmental fate. Arsenic present in the dump material can be considered as moderately stable, particularly because the grains of its main mineral, arsenopyrite turned out to be surrounded and encrusted with goethite.

However, a slow, microbiologically mediated, weathering of arsenopyrite definitely takes place in the dumps, particularly if its grains are fractured, resulting in the release of As, Fe and strong acidification (which probably determined the properties of the sample No. 3). The presence of As in the studied soils, especially in valleys in highly diversified mineralogical and chemical forms, makes it difficult to assess the risk of its mobilization. The main environmental risk, concerning both dump soils and alluvial soils, seems to be associated with the dominant As species, associated with (hydroxy)Fe-oxides, that are stable under aerobic conditions, at pH 4–6, and with a lack of competing oxyanions [51]. However, the burial of sediments over time or drop of redox potential due to temporal flooding could promote the release of As from sediments via reductive dissolution [15–18,32,51]. Although a field analysis of redox was not performed, the presence of hydromorphic features in soil samples 6 and 7 proves that those soils are subjected temporarily to reducing conditions that are particularly favorable for the release of As as a result of reductive dissolution of (hydroxy)Fe-oxides, although they do not cause the formation of secondary As-hosted sulfides reported from strongly anoxic conditions [21,47,54,55]. In our research, no sulfide As minerals As were identified in the sediment 5(S) or in the soil No. 6.

Also a crystalline secondary mineral, scorodite, proved to be stable under oxidizing conditions, particularly in an strongly acidic environment [51], can be transformed at pH $>1.5$ to yield Fe hydroxides and soluble arsenates [25,39,51,56]. It can also be decomposed under reducing conditions (below $\text{Eh}\sim 100$ mV), due to reductive dissolution of Fe and As, and this process can be accelerated by dissimilatory Fe(III)-reducing bacteria [34]. On the other hand, however, buffering pH at near-neutral values by dissolved carbonate and hydroxyapatite seeds can prevent solubilization of As by accelerating the oxidation of Fe(II), thus ensuring rapid coprecipitation of As as $\text{As(V)}$ in the ferric phases [57].

5. Conclusions

The material examined in this study was highly diverse, which is a typical feature of mine-affected soils. It contained varying amounts of As, which generally showed
very little actual solubility except in those soils that were likely to periodically undergo reducing conditions. Sequential extraction showed the dominance of As species bound to amorphous (hydroxy)Fe-oxides, particularly in the alluvial soils in the stream valley. Crystalline primary forms of As, arsenopyrite and loelingite were identified in the soils that developed on the mine dumps. In the stream sediments and alluvial soils, the only As-bearing crystalline mineral was scorodite present in single grains. Most of As was strongly dispersed there, apparently bound to amorphous Fe oxides, as well as to poorly crystallized goethite and schwertmannite. Those minerals contained significant amounts of As, highly differentiated and non-stoichiometric, which indicates that its immobilization in soils and sediments was caused by the mechanism of anion sorption rather than by formation and crystallization of secondary minerals. The key role of amorphous Fe oxides in As sorption in the studied soils, particularly in bottom sediments and alluvial soils, was also confirmed by sequential extraction.

Submicroscopic studies indicated that the dump material is subjected to various weathering processes that result in the release of poorly bound components, including arsenic, from the primary minerals, particularly those that are strongly fractured. Strong sorption of As by (hydroxy)Fe-oxides, both amorphous and those with various crystallinity, should be considered from the standpoint of environmental hazard as a highly beneficial mechanism, particularly under aerobic conditions. The risk of As mobilization in the area under study is associated mainly with periodical occurrence of reducing conditions in which As can be released. Therefore, more detailed research should be carried out to determine the conditions in which As mobilization from various soil components, including primary and secondary As minerals, and (hydroxy)Fe-oxides, and its possible secondary immobilization. These processes appear to be crucial for determining the environmental risk associated with soil enrichment in As in the area under study.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/min11050491/s1, Figure S1. Examples of representative XRD diffractograms that identify the main rock forming minerals in soil samples: (a) Quartz (black) and muscovite (blue) in the dump sample No. 2, (b) K-Feldspar (albite) in powdered subsample No. 2, (c) Quartz in the sample of stream sediments No. 4(S), (d) Quartz, goethite, clay minerals and poorly crystalline minerals in the sample of sediments No. 5(S). Possible occurrence of scorodite, Table S1. Procedure of sequential extraction according to Wenzel et al. (2001), Table S2. Mineralogical composition of samples, as determined by microscopic observations.

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