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Trace Metal Enrichment in the Colloidal Fraction in Soils Developing on Abandoned Mine Spoils

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Abstract: The release of colloid-bound trace metals from abandoned coal mine spoils can potentially be a significant source of contamination during weathering. We examined the size-dependent enrichment of trace metals in mine spoil samples using centrifugation and acid extraction to compare metal loading in the bulk and colloid fractions. A combination of X-ray diffraction (XRD), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), and focused ion beam (FIB) sectioning of selected colloids for transmission electron microscopy (TEM) analyses was used to determine the morphology and elemental and mineral composition at the micro- and nanoscales. In contrast to bulk soils, primary Fe-sulfides (up to 11%) and secondary Fe(III)-bearing phases (up to 5%) were a significant portion of the colloid mineralogy. Secondary Fe-(hydro)oxides and (hydroxy)sulfates were enriched with Mn, Ni, Cu, and Zn, and these metals showed stronger correlations with Fe in the colloid fraction (R^2 of 0.58, 0.77, 0.94, and 0.81, respectively) than in the bulk fraction (R^2 of 0.40, 0.09, 0.84, and 0.62, respectively), indicating that Fe-bearing colloids are likely major trace-metal-bearing phases. The results from this study will help to design better remediation projects for abandoned mine spoils to better account for a potentially underappreciated mode of contaminant transport.



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Keywords: colloids; mine spoil; soil

1. Introduction

Mine spoils are unavoidable byproducts of coal mining operations and include overburdened rocks and residual coal fragments and parent material. Before the passage of the Surface Mining Control and Reclamation Act of 1977, mine spoils had to be discarded untreated on landscapes, leaving them exposed to natural weathering [1]. Mine spoils often contain pyrite (FeS_2) and other metal sulfides, which form under reducing conditions. These minerals are unstable under oxic surface conditions and undergo rapid oxidative dissolution. Pyrite oxidation releases acidic runoff containing a high concentration of Fe (II) and S, known as acid mine drainage (AMD) [2,3]. When pyrite oxidation occurs in mine spoils, it acidifies the pore water and enhances the chemical weathering of the surrounding rocks [4]. Toxic trace metals such as Cr, Mn, Ni, Cu, and Zn are often present in pyrite and released during oxidation. As acidic pore water is transported, the dissolution of surrounding minerals, such as carbonates, can act as a buffer and increase the pore water pH. The more oxic and circumneutral pH conditions result in conditions favorable for the precipitation of secondary Fe(III)-(oxy)hydroxides (hereafter referred to as “Fe-oxides”) and Fe(III)-(oxy)hydroxysulfates (“Fe-sulfates”). For example, schwertmannite ($\text{Fe}^{3+}_{16}(\text{OH},\text{SO}_4)_{12-13}\text{O}_{16}\cdot 10-12\text{H}_2\text{O}$) and jarosite ($\text{KFe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$) are the first phases to precipitate from AMD-impacted pore water with high sulfate (up to 3 g L^{-1}) content at relatively low pH (2.5 to 4.5). Under slightly lower Eh conditions, jarosite is favored at pH ranging from 2.5 to 4.5, whereas schwertmannite is favored at pH 3 to 4.5 range [5–7]. Microbial activities at low pH can play a significant role in the formation of these phases [8]. Jarosite and schwertmannite are metastable and may dissolve or transform into more ordered structures at higher pH. As the concentration of sulfate in the

solution decreases (through Fe-sulfates precipitation), and pH increases (through carbonate dissolution), the precipitation of ferrihydrite (approximately $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ at pH 2–5) takes place. Poorly crystalline ferrihydrite further transforms into goethite at higher pH (~5). Goethite (FeOOH) can further transform into more crystalline hematite (Fe_2O_3) at higher pH (~7) and temperature.

The formation and precipitation of the secondary Fe-bearing deposits can play a significant role in sequestering trace metals (e.g., Cr, Mn, Cu, Ni, and Zn) released during pyrite oxidation [9–11]. It has been reported that the weathering of mine spoil can result in low trace metal concentrations in pore water with a subsequent enrichment in residual weathered material [12]. However, the potential for the mobilization of trace metals with colloids in these settings remains underexplored. Colloids represent a fraction of suspended particles below 10 μm and generally include clay minerals, metal oxides, and humic substances [13]. Studies have suggested that the chemical and mineralogical composition of colloidal composition depends on the parent material. Therefore, the mineral composition of colloids in an undisturbed soil profile is typically dominated by clay minerals, metal oxides, and humic substances. Colloids can play a significant role in contaminant sequestration and transport due to their high sorption capacity [14–16]. Natural soil colloids of humic-coated kaolinite grains have been reported to bond with the trace metals through bonds between the trace metals and humic substance (Pb, Cu) [17]. Adsorption and transport of toxic metals such as Mn, Cr, Cu, and Zn can be dominated by Fe-sulfates such as jarosite and schwertmannite [5,18]. Fe-oxides such as ferrihydrite and goethite have also been reported to adsorb Cu and Ni [19,20]. In other studies, Fe(III)-(oxy)hydroxides also have been reported to sequester and transport radionuclides (e.g., U and Ac) and metal(loid) (e.g., As) at long distances [21–25]. Thus, the sequestration of trace metals on colloids may have serious environmental consequences.

The objective of the current work was to: (1) determine the mineralogy and composition of phases in the colloidal fraction of soils developing on historic and abandoned coal mine spoil and (2) determine the size-dependent enrichment of trace metals in these materials. A combination of X-ray diffraction (XRD), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), and focused ion beam (FIB) sectioning of selected colloids for transmission electron microscopy (TEM) analyses was used to determine the morphology and elemental and mineral composition of the colloids at the micro- and nanoscales. In addition, acid extraction was used to compare the trace metal load in the bulk soil versus the colloidal fraction. It is anticipated that the results from this study will help to design better remediation projects for abandoned mine spoils by better accounting for a potentially underappreciated mode of contaminant transport.

2. Materials and Methods

2.1. Soil Sample Collection and Colloid Extraction

Eleven soil samples were collected from the Huff Run sub-watershed 25 located near Mineral city in northeastern Ohio, which covers part of Carroll County and Tuscarawas County (Figure 1). The early mines at the site started around 1853, and by 1936, most of the mines were abandoned, leaving un-reclaimed mine spoils, as it was not required by law before 1977 [26]. The soil samples were collected along a transect where spoil pile #1 was located near the bottom of a series of mine spoil hills, and spoil pile #11 was located at the top of the hill as a part of a previous study, and additional details regarding sample collection can be found in Smart (2021) [27]. In summary, it was presumed that spoil pile #1 was chronologically a part of the oldest mine spoil, and spoil pile #11 was from the youngest mine spoil due to a commonly practiced mining technique known as “shoot and shove”; although limited records were kept, it is estimated that the age difference between piles 1 and 11 are 50–75 years [27]. According to the “shoot and shove” technique, as the mining proceeds uphill, a trail of mine spoil is left behind that is chronologically separated by the time of their dumping [28,29]. After the organic O-horizon (approximately 2 cm) was removed, an 8.25 cm long cylinder pipe was inserted into the soil until the cylinder

was entirely in the soil. Samples were collected in triplicate from each location. Next, the soil material surrounding the cylinder was removed, and finally, the cylinder was extracted. The soil samples were oven-dried at 58 °C and sieved <1 mm before starting the soil colloid extraction experiment.

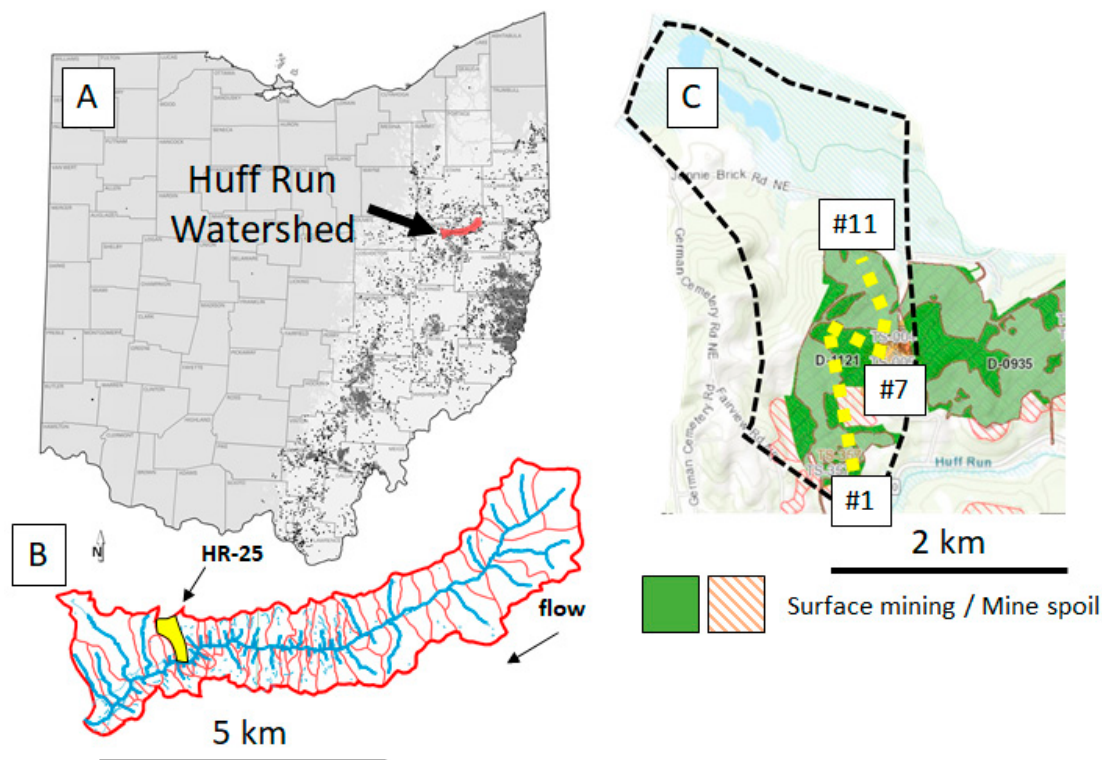


Figure 1. (A) Location of the Huff Run Watershed (in red), with Ohio coal counties shown in light gray and known abandoned coal mines in dark gray [30]; (B) watershed map [31] showing location of sub-watershed HR-25 (in yellow) and stream flow direction; (C) spatial extent of known surface area within HR-25 (the dashed outline) affected by coal surface mining (green) and mine spoil emplacement (hatched orange). The dashed yellow line indicates the transect along which the 11 surface soil samples were collected from abandoned mine spoil piles, with positions 1, 7, and 11 shown. Additional details on site topography and soil properties are available in Smart (2021) [27]. Coal mining data from: <https://gis.ohiodnr.gov> (accessed on 21 September 2022).

Soil colloids were separated from soil samples by two-step centrifugation. First, 25 g of soil was added into a 50 mL Falcon tube, followed by the addition of Milli-Q water, making the combined volume 50 mL. In order to allow water to penetrate through the soil, the Falcon tubes were shaken on a VWR Advanced Digital Shaker (model 10,000-2, VWR, Radnor, PA, USA) for 30 min at a speed of 75 rpm. After that, the Falcon tubes were centrifuged at 8000 rpm for 17 min to allow the larger soil particles to settle, while the finer colloids were still suspended in the solution (Supplementary Material Figure S1). After initial centrifugation, the supernatant (Sup-1 in Figure S1) with suspended colloids was carefully transferred into another 50 mL Falcon tube using a 10 mL pipette and further centrifuged at 10,000 rpm for 40 min to extract the colloidal sample. The colloids were deposited at the bottom of the Falcon tube, and clear supernatant was rendered (Sup-2 in Figure S1). The supernatant was removed from the colloids by using a 10 mL pipette. For further analyses, the separated colloids were oven-dried at 40 °C temperatures for 3–4 h.

2.2. Acid-Extractable Metal Concentrations in Bulk Soil and Extracted Colloids

Acid-extractable metal concentrations from bulk soil samples and soil colloids were achieved by following EPA 3050B soil and sludge digestion method [32]. Ultra-pure nitric acid (HNO_3) (10 mL for bulk samples; 1 mL for colloids) was added to the samples (1 g for bulk; 0.1 gm colloids), followed by addition of 5 mL HNO_3 at an interval of 30 min until the mixture was no longer generating any fume or bubbles. Then, 2 mL water and 3 mL 30% H_2O_2 solution was added to the mixture. The addition of 30% H_2O_2 solution continued in 1 mL aliquots until the effervescence generation was minimal or the sample appearance was unchanged. The mixture was heated at 95 °C temperature for 2 h or until the solution volume was reduced to 5 mL. The mixture was diluted to 100 mL by adding ultra-pure Milli-Q water. The particulates in the digestate were removed by allowing the samples to settle overnight on the counter. The supernatant was separated using a 10 mL pipette and further analyzed with a PerkinElmer 8000 inductively coupled plasma optical emission spectrometry (ICP-OES) (PerkinElmer, Waltham, MA, USA), which was used to determine extracted metal concentrations for the following elements, with their detection limits noted in parenthesis: Na (0.3 µg/L), Mg (0.3 µg/L), Al (5 µg/L), Si (0.3 µg/L), K (0.2 µg/L), Ca (0.2 µg/L), Mn (0.7 µg/L), Fe (0.3 µg/L), Cu (0.4 µg/L), and Zn (0.3 µg/L). Mixed standards (no. of standard = 10) were prepared for all the metal(loid)s (except Si), where Na, Mg, K, Ca, and Fe concentrations ranged from 10 µg/L to 2×10^5 µg/L; and Al, Mn, Cu, and Zn concentration ranged from 10 µg/L to 2×10^3 µg/L, respectively. Silicon was analyzed separately using eight standards ranging from 10 µg/L to 2.5×10^4 µg/L. If sample dilution was needed, 2% HNO_3 was used to dilute the samples. All reagents used were analytical grade, and solutions were prepared with distilled-deionized water (DDI- H_2O) (18.2 MΩ; Milli-Q Direct-Q 3UV-R).

2.3. Solid-Phase Characterization of Colloids Extracted from Bulk Soil

The extracted soil colloids were analyzed for mineralogical composition using a MiniFlex 6G Benchtop X-Ray Diffractometer (Rigaku, Tokyo, Japan) with D/teX Ultra2 detector, operated with a Cu X-ray tube ($\lambda = 1.5406$ Å) at 40 kV and 15 mA. A zero-background sample holder was used to analyze the colloid samples. Counts were collected from 2° to 90° with a step size of 0.02 and a speed of 0.2–0.3 °/min. Rigaku's PDXL software (version 2.8.4.0, Rigaku, Tokyo, Japan) was used to identify mineral phases, and quantifying relative abundance of mineral phases was performed using Rigaku's PDXL software, with the whole pattern powder fitting (WPPF) method, connected to the ICDD PDF-2 database. The shift axial displacement model of the peak shift correction function was applied. The fitting was performed using the split-pseudo Voigt function and the B-spline background model. The fitting quality of the experimental data was confirmed by using the following parameters: the goodness-of-fit term (S) that should be close to 1 for a good fit and two reliability factors R_p and R_{wp} (weighted differences between measured and calculated profile values) that should be close to or less than 10%. The bulk soil and soil colloids were characterized for grain size, texture, morphology, and metal(loid) composition using a Hitachi Benchtop TM3030 scanning electron microscope (Hitachi, Ibaraki, Japan) equipped with Quantax70 energy dispersive x-ray spectrometry (SEM-EDS). Nanoscale characterization of selected representative extracted colloids were prepared by focused ion beam (FIB) milling for transmission electron microscopy (TEM) (see details below). The FIB sections were extracted using a Helios Nanolab 600 dual beam (formally produced by FEI) using an in situ lift-out technique similar to the ones previously described [33]. The FIB sections were prepared by: (1) embedding the material of interest into epoxy to increase internal stability (by decreasing porosity and fractures) and subsequent sample preparation as a puck or petrographic-grade thin section; (2) deposition of a protective and unreactive strap of platinum over the area of interest, followed by a pair of ~15–20 µm long by ~10 µm wide and ~7 µm trenches milled around the area of interest with high energy (30 kV Ga+) heavy ions; and finally, (3) the lifting out and milling of 1000 nm thick electron-transparent samples for electron microscopy. Thermo scientific Apreo SEM (formally produced by

FEI) (Lausanne, Switzerland) was used to identify regions of interest for the FIB section. A Tecnai F20 TEM (formally produced by FEI) (Lausanne, Switzerland), operated at 200 kV, was used for EDS chemical analysis; crystalline phases were identified using selected area electron diffraction (SAED).

3. Results

3.1. Mineralogical Composition of Soil Colloids

The extracted colloids from 11 mine spoil samples were analyzed for mineralogical composition (Figure 2, Figures S2–S12) and compared to the mineralogical composition of the bulk soils they were extracted from [27]. The bulk soils were dominated by clays and quartz, with some micas and feldspars (Figure 2A). In contrast, the soil colloids were dominated by micas, with variable amounts of quartz, feldspars, and clays (Figure 2B). Further, non-silicate phases were detected in the colloid samples, including chalcopyrite and jarosite (Figure 2B). No discernible trend in mineralogical abundance across the spoil pile transect was observed in either the bulk soils or colloid extractions.

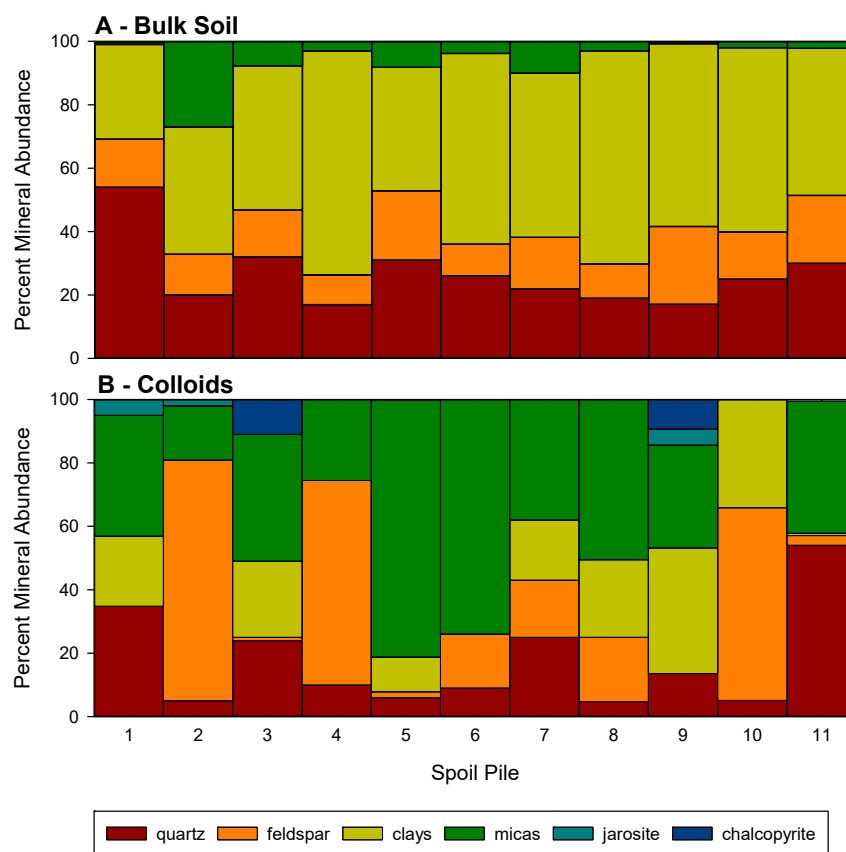


Figure 2. Mineralogical composition of (A) the bulk soil developing on abandoned mine spoil and (B) colloids extracted from bulk soil samples. Mineral group members are as follows: feldspar = orthoclase + albite; clays = kaolinite + chlorite + vermiculite; and micas = muscovite + biotite. Details on the XRD pattern fit results are presented in the SI document. Bulk soil XRD data are from Smart (2021) [27].

In the colloids, micas (primarily muscovite with some biotite) were most abundant when averaged across all sites. The average mica content was $40\% \pm 23.14\%$, with the highest contributions detected in spoil pile #5 (81%), followed by spoil pile #6 (74%) (Table S1). The average contribution of feldspars was $26.26\% \pm 29.39\%$, with the highest contributions detected in spoil pile #2 (~76%), spoil pile #4 (~65%), and spoil pile #10 (~61%). Kaolinite was also detected in the soil colloids, with an average contribution of $24\% \pm 9\%$. The highest kaolinite content was detected in spoil pile #9 (39%), followed by

spoil pile #11(30%). The average quartz content was relatively low ($17\% \pm 16\%$) and varied from ~5–54%, with the highest content detected in spoil pile #11 (54%), followed by spoil pile #1 (34%). Besides the common rock-forming minerals, chalcopyrite and jarosite were also detected in a number of samples. Chalcopyrite was detected in spoil pile #3 (11%) and spoil pile #9 (9.2%), whereas jarosite was identified in spoil pile #1 (5%), spoil pile #2 (~2%), and spoil pile #9 (5%).

3.2. Morphology, Texture, and Composition of Soil Colloids

The SEM images of the extracted soil colloids confirmed that the extraction process yielded particles less than 10 μm in diameter, with a relatively uniform size distribution from 5 to 10 μm (Figure S13). The colloid composition was dominated by grains consistent with micas and other (alumino)silicates (Figure S13) consistent with the XRD results. Further, Fe-bearing phases with varying sizes, shapes, and chemical composition were noticeably abundant (Figures 3 and 4). Colloids with high Fe and O content were observed in all colloidal samples and exhibited significant metal enrichments. The representative Fe-O-rich colloids ranged from ~3 to 10 μm , and EDS analyses identified the presence of Cr, Mn, Cu, and Ni associated with these phases (Figure 3). The (alumino)silicate minerals were observed as individual colloids and in aggregation with Fe-bearing phases. Colloids consistent with the composition and morphology of pyrite were also observed (Figure 3E). The framboidal pyrite exhibited high O along with trace metals such as Mn and Cu on the exterior of the grain. A significant portion of the observed Fe-O-rich colloids were also enriched in S content consistent with the composition and morphology of Fe-sulfates (Figure 4). These Fe-O-S phases could be differentiated from S-bearing Fe-O-dominant phases and Fe-S phases based on their composition as determined by EDS analyses (Table S2). The Fe-O-S phases consisted of individual particles <1 μm in diameter and in particle aggregates ranging from 4 to ~10 μm and were consistently associated with Mn, Cu, Ni, and Zn (Figure 4). We note that other metal(loid)s of interest (e.g., As) were not detected by SEM-EDS analyses in the soil colloids (or by acid extraction discussed below) and that As is present in both primary sulfides [34] and secondary Fe-oxides [35] in similar mine spoil materials at this field site but were not detected in colloids being transported in soil pore water [36].

3.3. Nanoscale Characterization of Extracted Colloids

Three representative extracted colloid particles were analyzed by coupled SEM-EDS and FIB-TEM analyses for nanoscale characterization (Figures 5–7). The first grain was dominated by Fe, Ni, and S in the colloid, with O around the exterior of the colloid surface based on preliminary SEM-EDS analysis (Figure 5A). The FIB-TEM analyses indicated that the grain was primarily dominated by an Fe-O-rich phase adjacent to a thin (<10 nm thick) Fe-S-rich phase, which was also enriched in Cu and Ni (Figure 5B). The Fe-O-rich phase did not yield an electron diffraction pattern and is likely poorly crystalline or amorphous and was spatially correlated with a grain identified as muscovite (Figure 5C), consistent with the morphology and texture of primary grains coated with secondary Fe-rich phases. The second grain had a diameter of ~3 μm and was also dominated by Fe and S, with some Ni, Ca, and Si present (Figure 6A). Similar to the grain described above, analysis of the extracted FIB section indicated that the grain included an Fe-O-rich portion that was enriched in Mn and Cu and adjacent to the Fe-S-rich portion enriched in Ni and Cu (Figure 6B). The underlying grain was identified as anorthite based on electron diffraction, and again, no crystalline Fe-bearing phases were detected. The third colloid had a diameter of ~3 μm and was dominated by Fe, S, and O along with trace amounts of Mn, Si, Al, K, Mg, and Ca in SEM-EDS analysis (Figure 7A). Further TEM analyses of the FIB foil extracted from the colloid showed that the core of the colloid mainly contained Fe and S, with trace amounts of Ni and Cu (Figure 7B). Due to the excess thickness of the FIB foil, the electron diffraction data were not conclusive for this colloid.

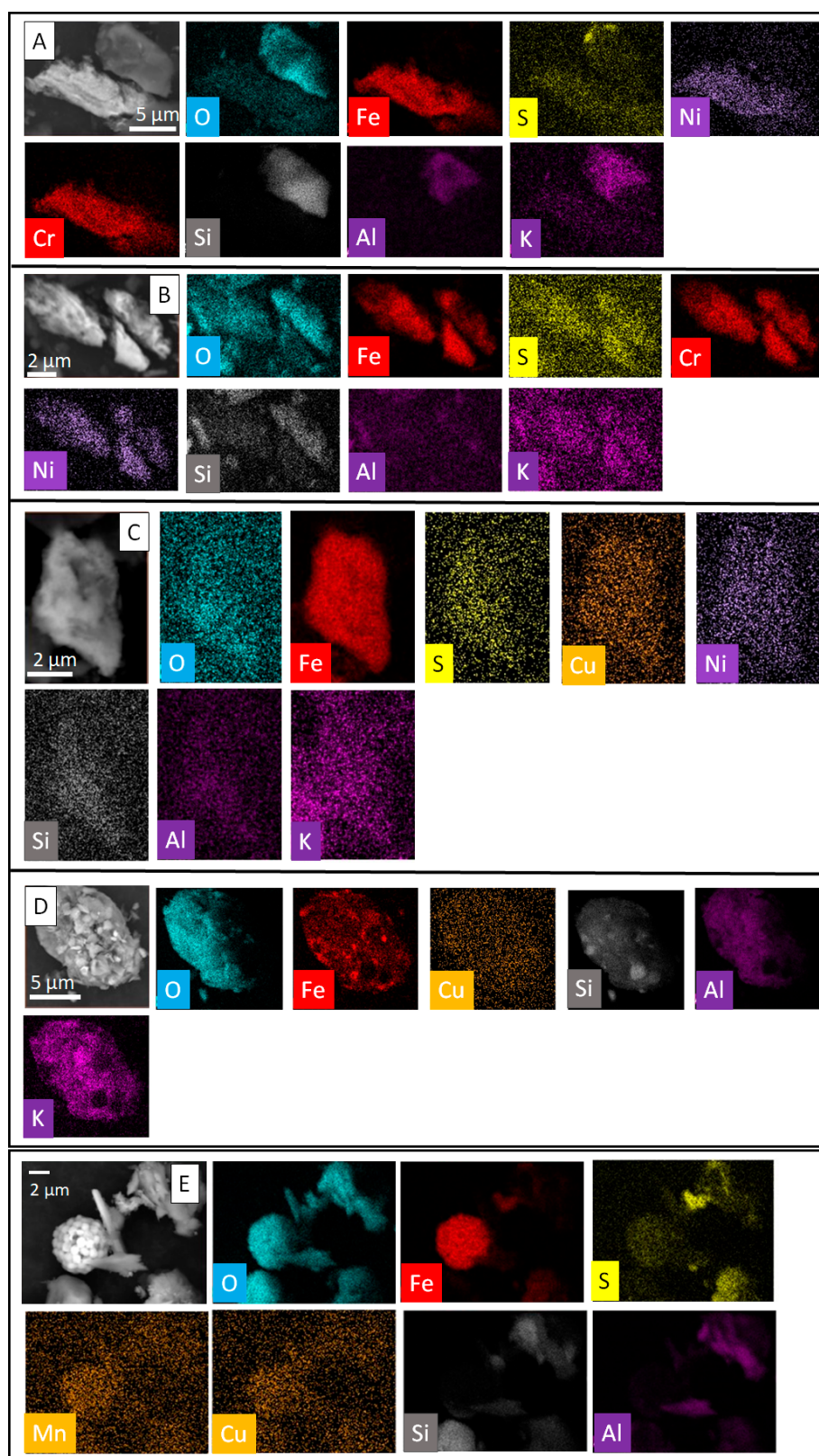


Figure 3. (A–D) Representative Fe(III)-(oxy)hydroxide and (E) pyritic colloids collected from bulk soils developing on historic coal mine spoil and collected from spoil piles 1 (A,B), 2 (E), 3 (C), and 9 (D).

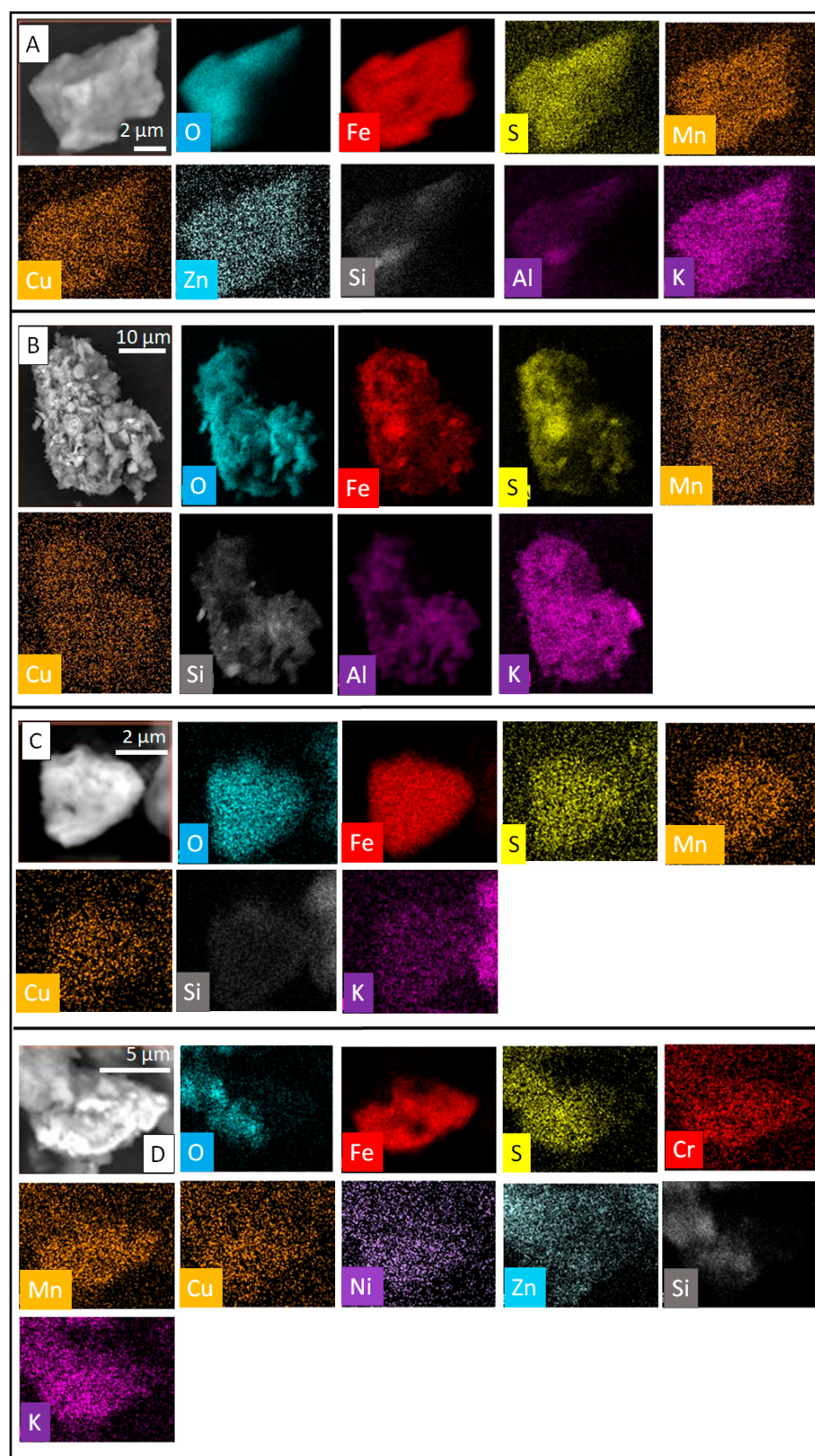


Figure 4. (A–D) Representative Fe(III)-oxyhydroxysulfates colloids collected from bulk soils developing on historic mine spoil and collected from spoil piles 2 (A,B), 9 (C), and 10 (D).

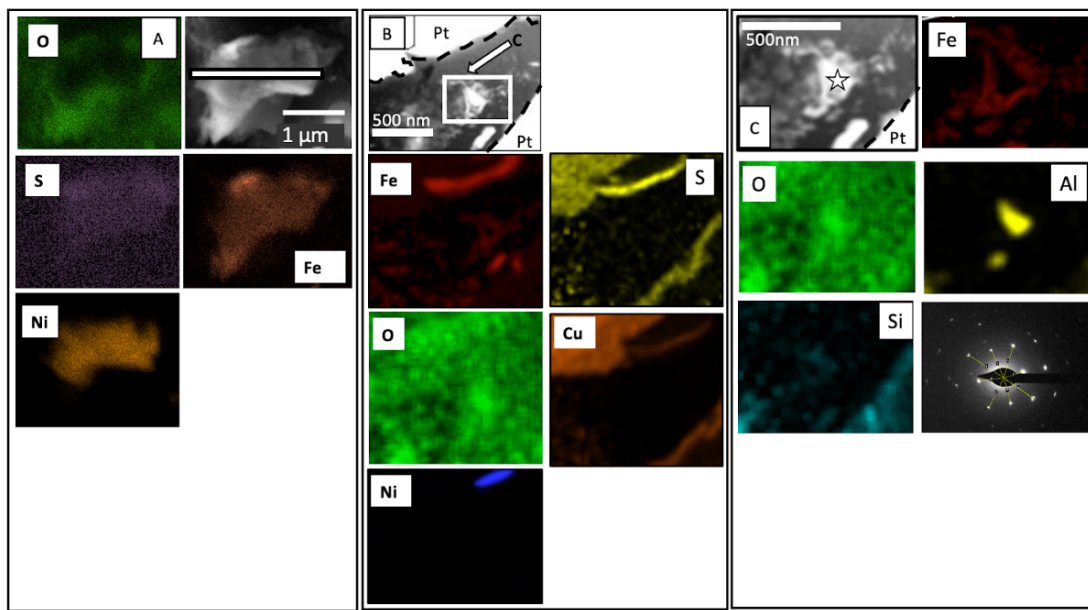


Figure 5. (A) SEM image and EDS element maps of a representative colloid soils developing on historic coal mine spoil; the white line represents the site of FIB section extraction. (B) TEM image of the extracted FIB section with EDS element maps; the dashed black line represents the boundary between the FIB section and the Pt mount, and the white box labeled C is shown in panel (C). (C) TEM image, EDS element maps, and electron diffraction image collected at the starred location; the grain was identified as muscovite based on the $(-1,1,4)$ reflection with a d-spacing of $3.4954 \text{ \AA}$.

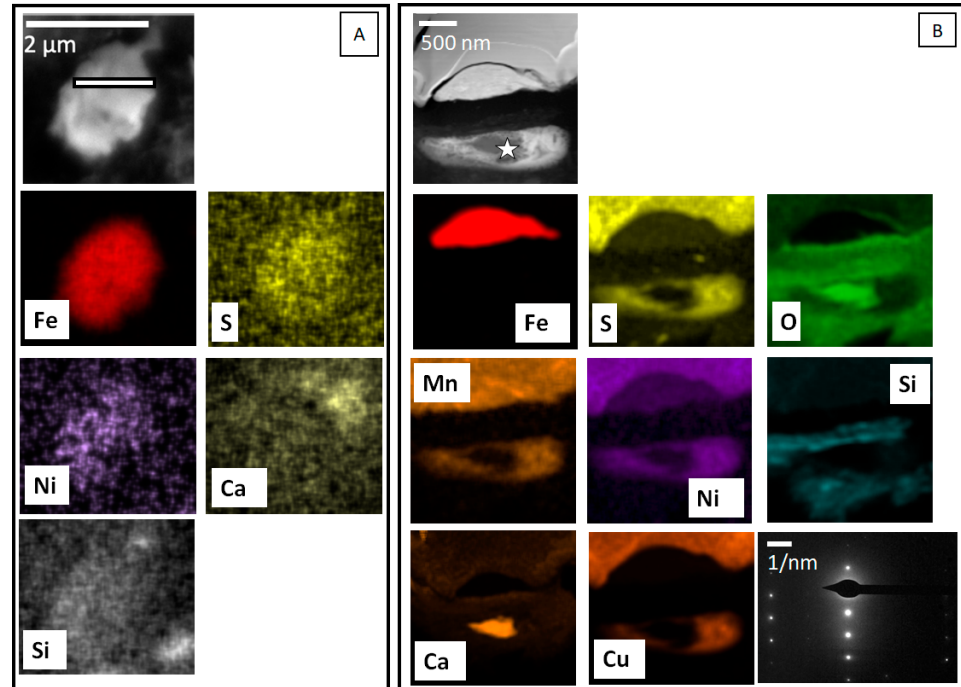


Figure 6. (A) SEM image and EDS element maps of a representative colloid soils developing on historic coal mine spoil; the white line represents the site of FIB section extraction; (B) TEM image of the extracted FIB section with EDS element maps. The dashed line represents the boundary between the FIB section and the Pt, and the white line represents the contact between targeted colloid and surrounding material. The grain was identified as anorthite based on the $(-1,-7,1)$ reflection with a d-spacing of $1.7813 \text{ \AA}$.

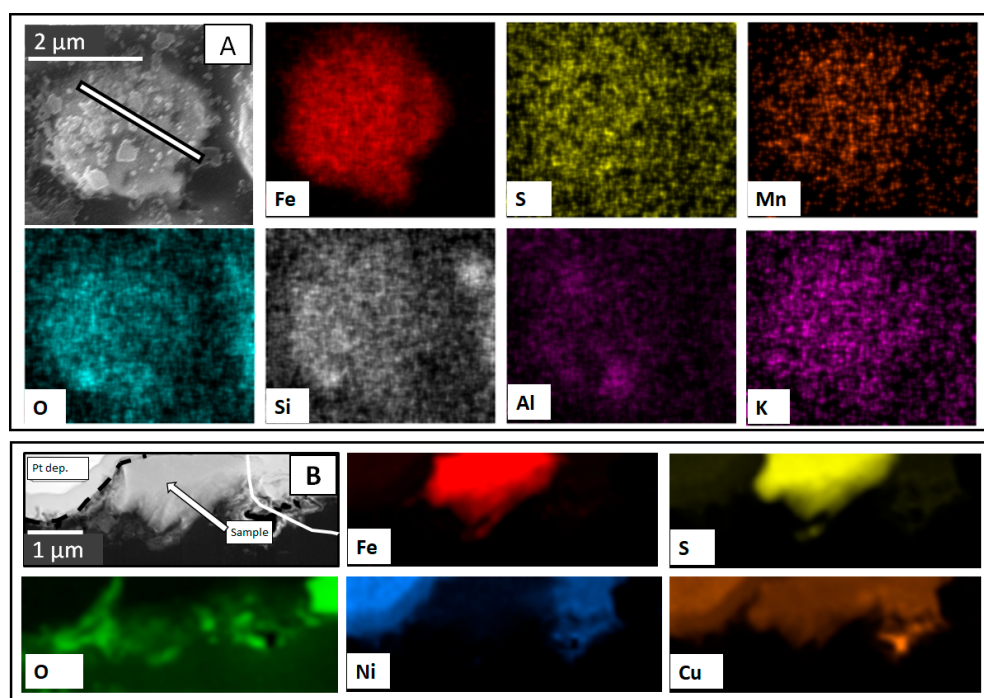


Figure 7. (A) SEM image and EDS element maps of a representative colloid soils developing on historic coal mine spoil; the white line represents the site of FIB section extraction; (B) TEM image of the extracted FIB section with EDS element maps. The dashed line represents the boundary between the FIB section and the Pt, and the white line represents the contact between targeted colloid and surrounding material.

3.4. Acid-Extractable Metal Distribution in the Bulk and Colloid Fractions

The acid-extractable metal concentrations for bulk soils and extracted colloids varied widely across the sampling transect (Figure 8). All sample values are reported in Table S3, and average values are shown in Figure S14. Metal-specific profiles are as follows:

The concentrations of extractable Na (Figure 8A) were consistently low in all samples (less than 10 mg/kg) except spoil pile #2, where Na concentrations were high in both bulk extract (17.47 mg/kg) and colloidal extracts (39.30 mg/kg). The concentrations of extractable Na in bulk and colloidal extract were similar and did not show an obvious difference. The concentrations of extractable Na in colloidal extracts from spoil piles #6 and 9 were below the detection limit.

The concentrations of extractable Al in the bulk extract were higher in spoil piles #4, 5, 6, 7, and 9 compared to that of colloid extract (Figure 8B). The concentrations of extractable Al in bulk extract and colloidal extract were very similar in spoil piles #2, 3, and 8. The concentration of extractable Al in the colloidal extract was only higher in spoil pile #1 compared to the bulk extract. The Al concentration in the colloidal extract from samples 6 and 9 were very low (for spoil pile #6 extract 1.07 in bulk vs. 0.08 g/kg in colloid extract and for spoil pile #9 extract 1.12 in bulk vs. 0.11 g/kg in colloid extract).

The concentrations of acid-extractable Si were consistent and did not show any noticeable variation (Figure 8C). The Si concentrations in the colloidal extract were consistently higher compared to that of bulk extracts.

The Ca concentration in bulk and colloidal extract from spoil piles #1, 2, 5, and 7 were comparatively higher than that of the rest of the samples, where the highest concentration was encountered in spoil pile #7 (265.3 in bulk vs. 313.4 mg/kg in colloid extract) (Figure 8D). Similar to Na and Al, the Ca concentrations in the bulk extract of spoil piles #6 and 9 were higher; however, the difference were within or close to the analytical margin of error.

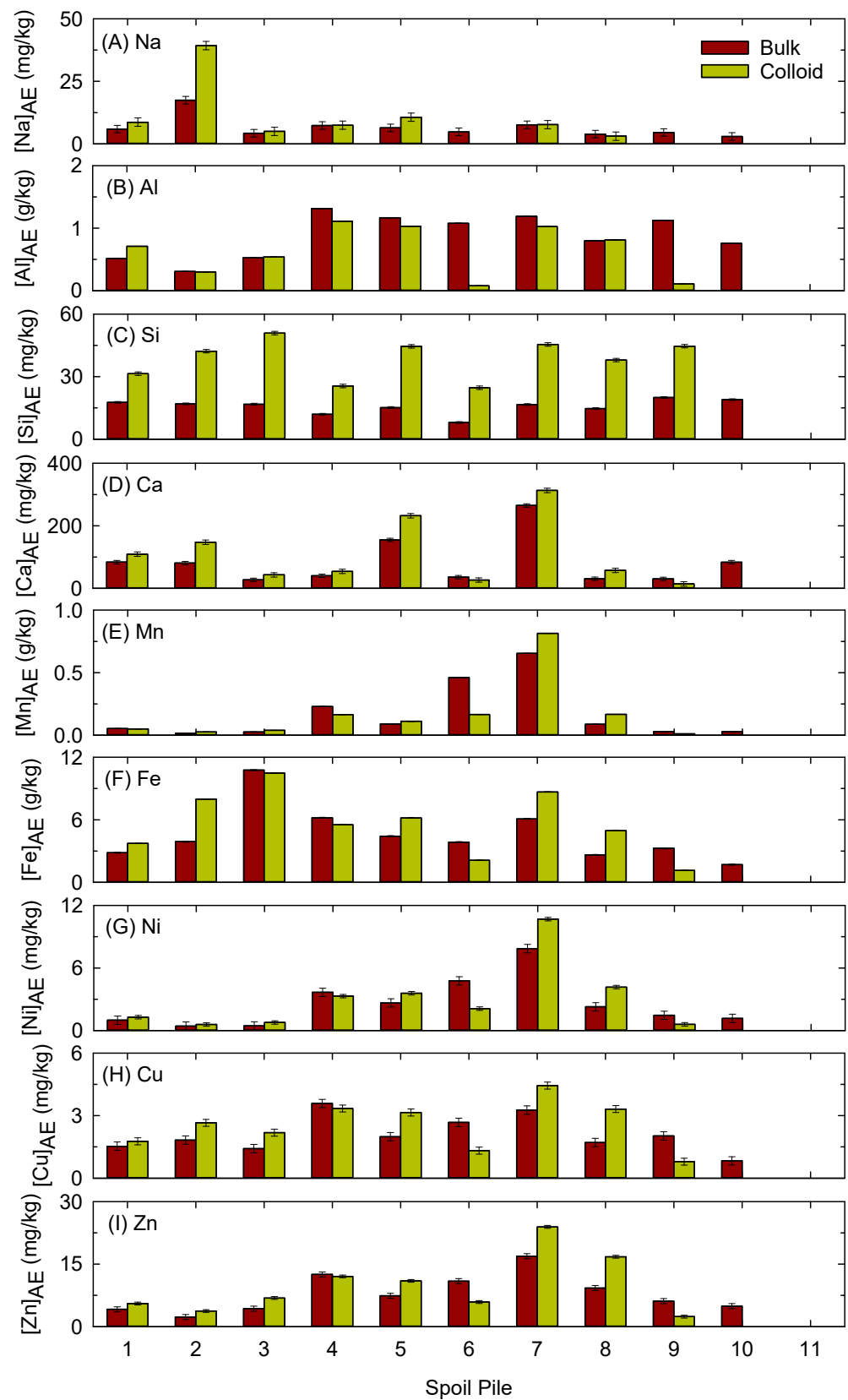


Figure 8. Acid-extractable Na (A), Al (B), Si (C), Ca (D), Mn (E), Fe (F), Ni (G), Cu (H), and Zn (I) concentrations of bulk mine spoil (red bars) and mine spoil colloids (yellow bars) with analytical errors (which are small enough in some cases to not be visualized). Values for Al, Mn, and Fe are reported as g/kg; the rest are reported as mg/kg. Bars not shown represent analytes below the detection limit.

The acid-extractable Mn concentrations were relatively low in spoil piles #1, 2, 3, 5, and 9 (less than 0.1 mg/kg) (Figure 8E). The extracts from spoil piles #4, 6, 7, and 8 exhibited relatively higher Mn concentrations. The highest Mn concentrations were detected in spoil pile #7 where Mn concentration in colloidal extract was higher compared to that of in bulk extract (0.65 in bulk vs. 0.81 mg/kg in colloid extract). The Mn concentration in spoil pile #7 was followed by that in spoil pile #5 where Mn concentration in bulk extract was higher compared to that in colloidal extract (0.46 in bulk vs. 0.16 mg/kg in colloid extract).

Iron was the most abundant element in the acid-extractable metals in both bulk and colloidal extracts (Figure 8F). The highest concentration of Fe in both bulk and the colloidal extract was present in spoil pile #3, followed by spoil piles #7, 2, 4, and 5. The rest of the samples exhibited relatively lower concentrations. More acid-extractable Fe was present in the bulk fraction of spoil piles #3, 4, 6, and 9, whereas more acid-extractable Fe was present in the colloidal fraction in spoil piles #1, 2, 5, 7, and 8. The highest concentrations of Fe in the bulk extract were determined in spoil pile #3 (10.75 mg/kg), followed by spoil pile #4 (6.2, 6, and 4.42 mg/kg, respectively), and the rest of the sample had less than 4 mg/kg. The highest concentrations of Fe in the colloid extract were determined in spoil pile #3 (10.5 mg/kg), followed by spoil piles #7, 2, 5, and 4 (8.66, 7.96, 6.1, and 5.5 mg/kg, respectively), and the rest of the sample had less than 5 mg/kg.

The acid-extractable Ni concentration for samples spoil piles #1, 2, 3, 5, 7, and 8 showed higher Ni concentration in colloidal extract compared to bulk extract (spoil piles #1, 2, and 3 within a margin of analytical error) (Figure 8G). Only spoil piles #4 (within the margin of analytical error), 6, and 9 exhibited higher concentrations in bulk extract compared to colloidal extract. The highest Ni concentration in bulk extract was determined in 7 (7.85 mg/kg), followed by spoil piles #6, 4, 5, and 8. The highest Ni concentration in colloidal extract was spoil pile #7 (10.7 mg/kg), followed by spoil piles #8, 5, 4 and 6.

The concentration of acid-extractable Cu was consistently present in greater amount in colloidal extract (Figure 8H). The highest acid-extractable Cu concentration in bulk extract was determined as 3.5 mg/kg in spoil pile #4, and the lowest was determined in spoil pile #3 as 1.4 mg/kg. The highest concentration of acid-extractable Cu in the colloidal extract was observed in spoil piles #4, 7, 6, and 2 (6, 5.4, 4.45, and 3 mg/kg, respectively).

The concentrations of acid-extractable Zn in spoil piles #1, 2, and 4 were very close (Figure 8I). In spoil piles #3, 5, 7, and 8, the acid-extractable Zn concentration was higher in the colloidal fraction compared to the bulk fraction. However, the acid-extractable Zn was higher in the bulk extract compared to the colloidal extract in spoil piles #5 and 9. The highest Zn concentration in bulk extract was determined in spoil pile #7 (16.9 mg/kg), followed by spoil piles #4, 6, 8, and 5 (12.5, 10.9, 9.2, 7.3 mg/kg, respectively). The highest Zn concentration in colloidal extract was determined in spoil pile #7 (23.9 mg/kg), followed by spoil piles #8, 4, 5, and 5 (16.75, 12, 10.96 mg/kg, respectively).

The average acid-extractable base metal concentrations (Na, Al, Si, and Ca) were relatively low compared to the acid-extractable trace metal concentrations (Table S3 and Figure S14). Except Al and Mn, all metals analyzed displayed higher concentrations in colloidal extract than bulk extracts. For acid-extractable Al, the concentration in bulk extract was higher than that in the colloidal extract. For acid-extractable Mn, the concentration in bulk extract was almost equal to that in the colloidal extract. The average acid-extractable concentration of Na, Al, Si, and Ca in bulk extracts were 6.53 ± 4.13 mg/kg, 0.88 ± 0.34 g/kg, 15.73 ± 3.51 mg/kg, and 83.14 ± 75.27 mg/kg, respectively. On the other hand, the concentration of extractable acids Na, Al, Si, and Ca in the colloidal extract were 11.72 ± 12.41 mg/kg, 0.64 ± 0.4 mg/kg, 38.63 ± 9.33 mg/kg, and 111.05 ± 102.5 mg/kg, respectively. The average acid-extractable Mn and Fe concentrations in bulk extracts were 167.36 ± 219.91 mg/kg and 4558.92 ± 2604.83 mg/kg compared to their concentrations in the colloidal extract, which were 171.77 ± 249.31 mg/kg and 5638.7 ± 3067 mg/kg. The average acid-extractable Ni, Cu, and Zn concentrations in bulk extract were 2.57 ± 2.33 mg/kg, 2.08 ± 0.85 mg/kg, and 7.87 ± 4.52 mg/kg, respectively, compared to 3.00 ± 3.19 mg/kg, 3.71 ± 1.29 mg/kg, and 9.79 ± 6.69 mg/kg in colloidal extract, respectively.

Given the prevalence of trace metals associated with Fe-bearing phases based on the SEM-EDS and TEM analyses (Figures 3–7), element correlation regressions were analyzed to compare metal distributions in bulk versus colloidal fraction. When the Fe concentration in spoil piles #2 and 3 was considered, trace metals showed little to no correlation with Fe (Figures S15 and S16), and the Fe concentration in spoil piles #2 and 3 was considered an outlier. Acid-extractable Na did not show any correlation with Fe in bulk extract ($R^2 = 0.02$, Figure S15B); however, Na concentration was moderately correlated with Fe in the colloidal extract ($R^2 = 0.76$, Figure S16B). The extractable Al showed moderate correlation with Fe concentrations in both bulk and colloidal fraction ($R^2 = 0.77$ and 0.58 , respectively, Figures S15D and S16D). Silicon did not show any correlation with acid-extractable Fe in either bulk or colloidal fraction (Figures S15F and S16F). The extractable Ca exhibited moderate positive correlation with Fe only in bulk phase ($R^2 = 0.72$, Figures S15H and S16H). Manganese showed low-to-moderate positive correlation with Fe in bulk and colloidal extract, respectively ($R^2 = 0.4$ and 0.58). The acid-extractable Ni showed moderate-to-high positive correlation with Fe in bulk and colloidal extract, respectively ($R^2 = 0.53$ and 0.76 , respectively), whereas Cu showed high positive correlation with extractable Fe in both bulk and colloidal fraction ($R^2 = 0.84$ and 0.94 , respectively). Zinc also exhibited moderate-to-high positive correlation with Fe ($R^2 = 0.62$ and 0.81 , respectively).

4. Discussion

4.1. The Relationship between Bulk and Colloid Mineralogical Composition

The transport of trace metals at mine sites with abundant abandoned spoil can have a serious environmental impact resulting in the contamination of local watersheds. Metal transport is typically focused on aqueous speciation; however, metal-bearing colloids have more recently been recognized as a potentially major vector of contaminant transport in these settings [37,38]. These colloids can form from the chemical precipitation of Fe-bearing colloids due to supersaturation. However, at a mine spoil site, the physical breakdown of the rocks also can be an important source of colloid generation due to the excavation, destruction of the soil matrix, loss of aggregability, and enhancement of oxidation [39,40]. Primary pyrite and other metal sulfides can potentially go through physical weathering, resulting in the generation of colloidal pyrite [12]. The transport of these pyrite colloids can further act as a vector for contaminant transport and eventually oxidize to form AMD [41], and it is therefore critical to determine the mineralogical phases they are associated with.

In this study, we observed the enrichment of Fe and the trace metals in the colloidal phase with a positive correlation between acid-extractable Fe and extractable trace metal concentrations. The formation and mobilization of these trace metal-bearing Fe colloids may play an important role in trace metal transport at an AMD site. The SEM-EDS analyses of the pore water colloids collected from the study site revealed the presence of Fe-bearing colloids in pore water, similar to what was observed in the soil (Figures 4–6). In addition, trace metals such as Ni and Mn were observed in association with the Fe-bearing colloids.

Further analysis of the colloids with FIB-TEM revealed the presence of Cu as well in the pore water colloids (Figures 4–6). The formation of the secondary mineral surface coating of Fe-oxide was also observed around a feldspar grain (Figure 6). These findings are in line with previous studies that reported trace metal association of Fe-bearing colloids in the pore water. Possible pyritic colloid was also identified in the pore water where Fe was associated with S. The selected area electron diffraction (SAED) identified feldspar in the colloid; however, no crystalline Fe-bearing phase was identified, which indicates that the Fe-bearing minerals in the colloids are Fe minerals with low crystallinity (possibly jarosite, schwertmannite, or ferrihydrite).

The mineralogy of colloids typically resembles that of the bulk soil from which the colloids are derived through physical and chemical weathering [39,40,42]. Previous studies have reported that while bulk mineral composition can be dominated by quartz and feldspar, the colloidal fraction can be dominated by micas, clays, and secondary oxides, especially Fe-bearing phases [36,43,44]. Previous work has also shown that mobile colloids

can be enriched with kaolinite and secondary metal (e.g., Fe and Al) oxides relative to the bulk originating soil [45]. We observed similar behavior in soils developing on historic coal mine spoil: the previously reported bulk mineralogy of the spoil piles is dominated by quartz, feldspars, and kaolinite [27], whereas the colloids exhibit a much strong contribution from muscovite. More significantly, primary Fe-sulfide and secondary Fe-oxides were detected by bulk XRD in the colloidal fraction.

The quartz content in the colloidal phase of the soil exhibited a decreasing trend as the elevation increased from spoil pile #1 to spoil pile #11 except in spoil pile #7 and 11. The enrichment of quartz in sediments has been regarded as a result of weathering, where more soluble minerals are weathered away. Over time, sediments tends to enrich in quartz more; thus, quartz enrichment has also been used as a proxy for residence time. The mineralogical data observed suggest a possible trend of decreasing age from spoil pile #1 to spoil pile #11. This observation conforms the traditional understanding that the age of the mine spoils increases with increasing elevation, and it is also in line with the industry practice known as shoot and shove to dump these mine spoils. A general decreasing trend in quartz content in the bulk mine spoils was also reported by Smart (2021). Besides the common rock-forming minerals mentioned above, the presence of chalcopyrite (spoil pile #3) and Fe-oxide (spoil pile #1 and 2) minerals such as jarosite were also detected in the colloidal fraction. This finding contrasts with the previously reported bulk mineralogy that did not show any presence of pyritic or Fe-oxide minerals in bulk mine spoil. This may be due to the low content of pyritic minerals in the bulk soil. The chemical and morphological analyses using SEM-EDS further confirmed the presence of pyritic colloids and Fe oxide in mine spoil.

The SEM-EDS analyses revealed the presence of colloids with chemical composition consistent with Fe(III)-(oxy)hydroxide (high Fe and O content) and Fe(III)-oxyhydroxysulfates (high Fe, S, and O content) (Figure 3). The possible Fe(III)-(oxy)hydroxide colloids were commonly associated with Cr, Ni, and Cu, whereas Mn and Cu, along with Cr, Ni, and Zn (Figure 3), were most commonly associated with possible Fe(III)-oxyhydroxysulfates. The adsorption of trace metals into the Fe-bearing deposits is a well-studied and -known fact; however, the adsorption capacity may vary based on the crystallinity of the Fe-bearing deposits [19]. The possible oxidation of pyrite in the mine spoil may be attributed as the source of the trace metals, as pyrite may contain trace metals as an impurity in the structure [4]. Besides Fe-oxides, framboidal pyrite was also observed among soil colloids (Figure 3). The significant presence of O in association with the pyrite may indicate the presence of a Fe-oxide secondary mineral coating on the pyrite [46,47]. The presence of Fe-oxide MSCs has been reported to sequester trace metals such as As, Ni, Cu, and Zn [47,48]. The SEM-EDS images of the framboidal pyrite exhibited the association of Mn and Cu with the pyrite grain, and no sign of oxidation was observed, which may indicate that the Mn and Cu were incorporated into the pyrite. It has also been reported that trace metals such as Cu can also be adsorbed onto the pyrite surface and form secondary sulfide minerals at the surface by replacing Fe [46]. Identifying Fe-bearing reactive phases in soil colloids and their close association with trace metals such as Cr, Mn, Ni, Cu, and Zn exhibit their importance in trace metal transport.

4.2. Relationship between Extractable Metals and Soil Composition

The acid extraction of metals from sediments and soils can identify and quantify specific metal contaminant risks as a function of particle size. However, the relationship between colloid mobility and specific metal migration may be dependent on site-specific conditions. For example, colloids have been shown to preferentially mobilize Zn over Cu [49] and preferentially mobilize Cu over Zn [50]. The acid extraction of bulk mine spoil and the mine spoil colloids exhibited a lower average concentration of Na, Si, and Ca in both bulk and colloidal extracts compared to Al, Mn, Fe, Ni, Cu, and Zn (Figure S14). The lower Na, Si, and Ca concentration can be attributed to the extraction method used, which targets elements that can easily become available in the environment (e.g., elements associated

with oxides, oxyhydroxide, and sulfides) and not suitable to digest silicate minerals (quartz and feldspars), and the lack of calcium carbonate minerals. The source of the Na, Si, and Ca concentration observed in both bulk and colloidal is likely the exchangeable cations present in clay minerals.

Except for Al and Mn, all the metals (Na, Si, Ca, Fe, Ni, Cu, and Zn) showed higher concentrations in the colloidal extract than in the bulk extract. The average Al concentration was higher in bulk extract compared to colloidal extract. In contrast, the average Mn concentration in both bulk and colloidal extracts were similar (0.16 mg/kg in bulk vs. 0.17 mg/kg in colloid, Figure S14). The current data suggest an enrichment of the trace metals in the colloidal portion, including secondary oxides and phyllosilicates. This observation aligns with previous studies that reported trace metal Cu, Ni, and Zn enrichment in clay size fraction (less than 2 µm) at a mine spoil site [51]. Among the trace metals, Ni was the most enriched trace metal in the clay fraction (14 times) compared to the bulk fraction [51]. Manganese was reported to be enriched in the bulk portion more than the colloidal fraction [51]. Other studies also reported the trace metal enrichment in secondary minerals such as clay minerals, Fe, Mn, and Al oxides; hydroxide; and hydrosulfates in the finer fraction [52]. In this study, we observed that the trace metal concentration closely followed Fe concentration in bulk and colloidal extract. In this work, we observed a correlation between the trace metal concentration and the concentration of extractable Fe and Mn (Figure S15). The extractable Mn exhibited a positive correlation with extractable Fe for most of the sample in bulk (except spoil pile #3) and colloidal extract (except spoil pile #2 and 3) (Figure S15). Similarly, extractable Ni, Cu, and Zn were also positively correlated with extractable Fe concentrations in both bulk (except spoil pile #2) and colloidal extract (except spoil pile #2 and 3) (Figure S15). The concentrations of Ni, Cu, and Zn were also positively correlated with extractable Mn concentrations in bulk and colloidal extract (Figure S16). Such a positive correlation across all the trace metals with the extractable Fe concentration suggests that the trace metals were likely associated with Fe phases, similar to what was observed with SEM-EDS and XRD analyses of the colloids. Both possible Fe(III)-(oxy)hydroxide and Fe(III)-oxyhydroxysulfates have been studied and reported to exhibit high adsorption capacity for trace metals, whereas pyrite is a well-known source of trace metals at an AMD site [18,53,54].

5. Conclusions

The extractable trace metal (Mn, Cu, Ni, and Zn) concentrations in bulk and colloidal samples collected from soils developing on abandoned mine spoils were directly associated with extractable Fe. Further, there was significant enrichment of trace metals in the colloidal fraction compared to the bulk fraction, and these were associated with the Fe species in the colloidal phase, including Fe(oxy)hydroxides, Fe(oxy)hydroxy sulfates, and Fe-sulfides. The presence of pyritic minerals in the colloidal fraction of soils at similar sites has not been reported previously and may have a serious impact on trace metal uptake and/or transport. This study further enhances our understanding of trace metal transport and sequestration at sites with legacy coal mine waste. Environmental conditions that result in colloid mobilization (e.g., rainfall) may enhance the risk of trace metal transport via Fe-bearing colloids. On the other hand, conditions that promote anoxic conditions (rain or snow and subsequent porewater saturation) in the mine spoil may result in an aqueous transport of trace metals following reductive dissolution of Fe-oxides. These results indicate that watershed managers may need to consider metal transport under conditions besides aqueous transport.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min12101290/s1>, Figure S1: Colloid extraction protocol; Figures S2–S12: XRD patterns and fits of extracted colloids; Figure S13: Representative SEM-EDS data of non-Fe-dominant colloids; Figure S14: Average extractable metal concentrations; Figures S15 and S16: Correlations between acid-extractable metals in bulk and colloid samples; Table S1: Mineralogical abundance data; Table S2: Representative EDS analyses of colloids; Table S3: Metal acid-extraction data.

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