minerals

Article

Metal Mobility in a Mine-Affected Floodplain

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Received: 5 August 2020; Accepted: 11 September 2020; Published: 15 September 2020

Abstract: The study attempted to map and predict the remobilization of metals in a floodplain which had been heavily affected by long-term Zn–Pb mining. This research, based on Zn, Cd, Pb, Ca and Fe speciation, mineralogy and the stratigraphy of sediments which had accumulated over the distance of a dozen or so km from the mine, revealed variable potential for metal mobilization. The results suggest that a drop in the water table, something to be expected after the closure of a mine, would be accompanied by a decrease in the pH of the river water and can induce the remobilization of metals associated with carbonates and exchangeable cations over the short-reach downstream of the mine. However, the mobilization of contaminants may be impeded by the alkaline, impermeable stratum of loams, which play a pivotal role in maintaining anaerobic conditions and buffering the acidity resulting from the partial degradation of sulfides. Based on the findings of the study, it can be expected that the intrinsic attenuation will limit the need for remediation works, although monitoring river water quality is recommended to determine the need for any intervention in cases where permissible quality values have been exceeded over a longer period. Results of this research can be useful as a reference for remediation works planned in other contaminated river systems experiencing water table lowering, where the mobilization of contaminants as a consequence of sediment oxidization can be expected.

Keywords: mining; metals; mine closure; sediment; pollution; mine water; river

1. Introduction

Metal mining generates contamination at both mine sites, where waste materials are stored in tailings and spoil heaps, as well as over longer distances from mines, when leachates or processing waters reach river systems [1,2]. The transfer of metals and associated substances from mine sites to the fluvial environment is a complex process depending to a large extent on the ore mineralogy of the exposed rocks and wastes [3]. Sulfide ore minerals, which are among the most commonly mined throughout the world, oxidize in contact with aerated waters, resulting in pH lowering and raising the content of sulfates and dissolved metals in the draining waters [4]. In such circumstances, pyrite weathering, resulting in acid mine drainage (AMD), is mainly responsible for the high mineralization of the receiving waters [5,6], but, in regions where carbonate lithology prevails, discharged neutral or alkaline waters can also contain a high content of dissolved substances [7].

In rivers, contaminants are transported either in solution or as solid particles in suspension. Dissolved compounds can precipitate on bedrocks or alluvia forming extensive coatings, efflorescence and crusts of iron, manganese, aluminum or salts of the other elements [8–10], whereas sediment-associated contaminants can infiltrate into the bed to the depths of many meters or accumulate in quiescent conditions on the channel bed [11,12]. The fresh in-channel precipitates in alluvia and sediment-associated trace metals are relatively unstable and, during floods, they are easily eroded and mixed with parent rock material, eventually accumulating on river floodplains [3].

The stability of metal contaminants in floodplains is controlled chiefly by the fluctuation of the groundwater table in relation to changes in river discharge [13]. It has been shown that the frequency of water table fluctuations and their magnitude are important factors. The mobility of metals is higher in areas inundated more frequently whereas short-term flood episodes have a minor effect on metal migration [14]. Metal remobilization has particularly been observed in coarse-grained deposits which exhibit anomalous metal peaks at levels related to the depth of the most frequent water-table fluctuations [15]. Mobile metals can retain in clay-rich or organic-rich zones and in zones where there is an accumulation of Fe oxyhydroxides [15,16].

Generally, periods of high water stages or floodplain submergence are particularly associated with the exhaustion of oxygen and the lowering of redox potential. They favor the formation of ubiquitous iron sulfides and the reduction in mobility of many metals [17]. Periods of drought or seasonal drops in the groundwater table result in the desiccation of the floodplain sediment and the aeration of pores leading to a rise in redox values which have been found to favor the release of many metals [18]. The stability of metal contaminants in floodplains is controlled chiefly by redox and pH [19]. High pH values can cause metal adsorption and precipitation, while low pH may weaken metal bonding strength and hinder metal retention [20,21]. The decrease in pH resulting from the release of H^+ into the pore water causes a remobilization of metals [22]. In turn, increasing Eh will accelerate the sulfide oxidation rate and degradation of organic compounds of sediment, inducing the release of metals [22]. The drastic and prolonged changes of water table levels resulting in Eh changes can, in turn, affect pH values [23]. Other important processes and factors affecting metal mobility in floodplains are adsorption/desorption processes, salinity, the presence of organic matter, sulfur and carbonates, pH and plant growth [13].

The behavior of metals and their remobilization ability in soils and sediments depends on the chemical forms in which they occur [21]. Therefore, the recognition of the chemical forms of metals is essential for predicting their potential environmental impact [24]. Selective sequential extraction procedures are commonly used in order to recognize metal mobility in soils and sediments, whereby different reagents are used consecutively to extract operationally defined phases from the solid matrices [25]. A BCR–a scheme developed by the Community Bureau of Reference–is widely used to supply information on the number of elements that can be mobilized in the short term [26].

The presented investigations aim at predicting the potential danger to the aquatic environment from potential metal remobilization in floodplain sediments which have been heavily polluted by ore-bearing particles originating from a Zn–Pb mine in southern Poland. This is very important for a study site with a long period of intensive mine operation associated with river sediment pollution, as the closure of the mine will be followed by a cessation of mine water discharge and a lowering of the water table in the receiving rivers. The study exploits a rare opportunity to evaluate the possible effect of oxidation of metal-polluted sediments, possibly resulting in loading the downstream river system with metals and other chemical compounds. The article focuses on metal mobility in the floodplain of the Biała and Biała Przemsza rivers in southern Poland based on the metal speciation in sediment profiles sampled at characteristic locations along the river system. The outcomes of the investigations will contribute to the planned scheme of the mine reclamation, but they can be extrapolated to the other contaminated river systems experiencing water table lowering. In such systems or regions containing acid sulfate soils, drops in the water table due to discharge cessation or long-term drought can cause the desiccation of floodplains and, as a consequence, the oxidization and mobilization of sediment-associated contaminants.

2. Study Area

The Biała Przemsza River, with 8 m^3/s of discharge and over 60 km in length, is an average watercourse for southern Poland. Since the 1950s, it has received mine waters from one of the largest lead and zinc mines in Europe, namely the one at Bukowno. The mine exploits sulfide ores of the Mississippi valley-type which are present in karstified carbonate rocks. These rocks constitute an abundant aquifer and the mine discharges huge amounts of water into the river. The largest volume of water, 2.75 m^3/s on average, is discharged in the middle reach of the Biała Przemsza River via a small tributary–the Biała River channel. Discharge of much larger amounts of water than the natural channel capacity induces flooding and sediment deposition in the Biała River valley and infiltration of sulfate-rich waters into the hyporheic zone of the Biała Przemsza River [27,28]. The permanently high-water table favors the maintenance of reducing conditions in the floodplain and the preservation of sulfide minerals which accumulated with the sediments over its long river reach. To date, the mining of lead–zinc ores is coming to an end and the mine's closure is planned for the following year, with a concomitant cessation of mine water discharge. It has been estimated that the time needed for groundwater level recovery may be up to 100 years [29], although some visible effects may be discernible after 25 years. It is obvious that the cessation of mine water discharge will result in the long-term desiccation and oxidation of floodplain sediments. These processes favor the degradation of sulfides, as well as sediment acidification and the mobilization of trace metals.

The Biała Przemsza, with its tributary the Biała River, cuts through the fluvioglacial sandy deposits which fill the valley bottom. They are high sinuosity, lowland rivers with gradients varying over most of their investigated course between 0.1‰ and 6‰. The width of the valley floor of the Biała River varies between 100 m and 200 m, whereas the width of the Biała Przemsza River valley ranges from 300 to 500 m. The floodplain is overgrown with wetland plant communities in the Biała valley and in the lower gradient reaches of the Biała Przemsza. The backswamp zone of the floodplain along the Biała Przemsza is separated from the river by a levee about 0.5 m high, whereas along the Biała River no levee is present.

The natural river flow is not only affected by the discharge of the mine water, but also by the drainage of the river water flowing across the area of a depression cone [30]. The surface of the cone at present reaches 600 km^2, as over 4 m^3/s of groundwater has been discharged on average from the mine for over 60 years [29]. This long-lasting drainage has resulted in the water table lowering by 120 m and the development of an unsaturated, approximately 100-m-thick zone [31]. The dewatering of ore-bearing rocks, which originally occurred in anoxic conditions, induces the oxygenation of sulfide minerals, particularly of the widespread marcasite and galena. It results in significantly raised concentrations of some elements in the groundwater, particularly of sulfates, magnesium and calcium. The pH values are raised to alkaline due to the buffering process and the rapid neutralization of any acid solution [32]. Mine waters constitute almost the entire discharge of the Biała River (99%) and over 50% of the discharge of the Biała Przemsza River in its middle reach [33]. Therefore, the rivers receiving the contaminated groundwater have significantly modified chemistry [34]. Whereas the average content of sulfates varies in range 200–250 mg/L, of calcium 80–120 mg/L and magnesium 20–50 mg/L, Zn and Fe concentrations reach 1.00 and 0.77 mg/L, the conductivity changes between 700 μS/cm and 1000 μS/cm and pH is from 7.5 to 8.1 [35].

3. Materials and Methods

Floodplain sediments were sampled over the 17-km-long reach of the Biała (B) and the Biała Przemsza (BP) rivers (Figure 1). The research was divided into two stages; first to recognize the general distribution pattern of the metal contamination and second to estimate metal speciation.

3.1. Sediment Sampling

In the first stage, extensive sampling across the whole meander bend of the Biała Przemsza River was performed about 11 km downstream of the mouth of the Biała River. For this, sediment profiles BPI-BPV of 4.8–5.0 m deep were sampled using an auger at increasing distances from the channel (Figure 1). Three of these profiles were sampled across the levee, whereas the other two profiles represent the backswamp zone. These profiles were sampled every 25 cm, placed into polyethylene bags in an ice cooler and transported to the laboratory as soon as possible. Every sediment sample was wet-sieved through a 0.063-mm sieve. The silty-clay sediment fraction obtained was then digested with 10 cm^3 of

65% HNO_3 (p.a.) in Teflon vessels using microwave digestion system (MDS 2000, Milestone-Sorisole, Italy) according to the EPA 3051 method. Cd and Zn concentrations in the sediments were determined using atomic absorption spectrometry (F-AAS, iCE3000, Thermo Scientific-Waltham, MA, USA).

In the second stage, six cores of 5 cm in diameter and lengths of 1.25–1.75 m were sampled for metal speciation using a multisampler (Eijkelkamp-Giesbeek, The Netherlands). Three of the cores (BPI–BPIII) were located at the respective sites of the levee zone in the meander bend of the Biała Przemsza River. It was assumed that this sampling site represents the 20-km-long, meandering, low gradient reach of the Biała Przemsza River. The other three cores (BI–BIII) were located along the Biała River approximately 1 km apart and a few meters from the channel (Figure 1). These cores represent differences in sediment stratigraphy along the 4-km-long reach of the Biała River, downstream from the concrete culvert where the mine waters are discharged. All cores for metal speciation were sectioned at 25 cm intervals. Individual samples were divided into two parts in separated plastic bags and immediately placed in vacuum containers. In one part of each sample, the physicochemical properties of the sediments were assessed.

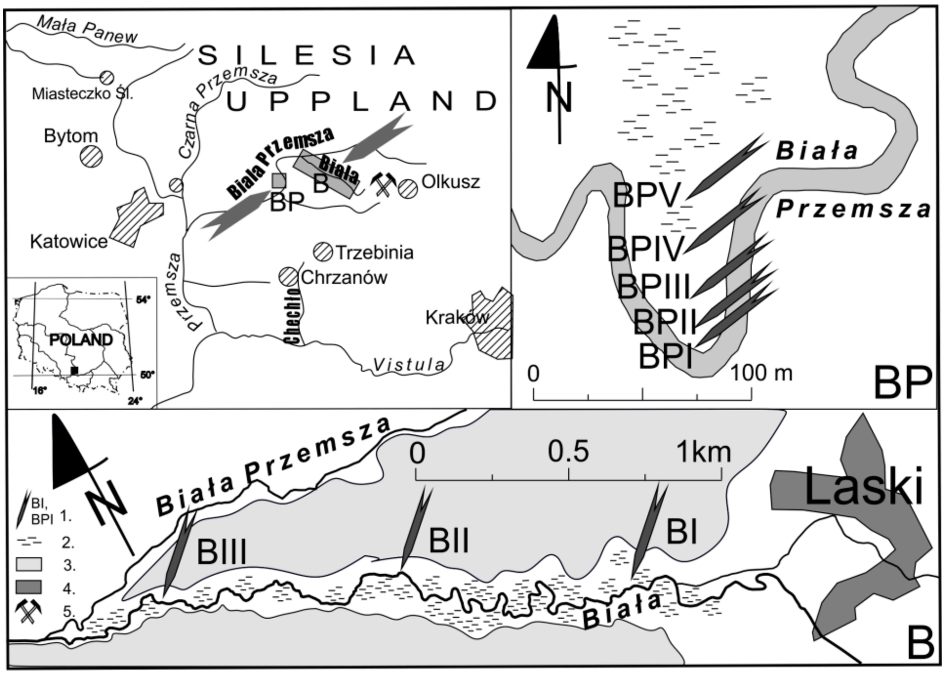

Figure 1. Location of research area and sampling sites; 1. Sampling site, 2. Wetlands, 3. Forests, 4. Buildup area, 5. Zn–Pb mine.

3.2. *Physicochemical Properties of the Sediments*

In the bulk sediment samples, the content of the organic matter was determined as losses on ignition (LOI) at 550 °C using a laboratory muffle furnace and carbonates by the volumetric method using a Scheibler apparatus (according to PN-EN ISO 10693 2014-06). The content of the silt–clay fraction was obtained by means of the sieve method (according to PN-B-02480 1998).

3.3. *Sequential Extraction of Metals*

The chemical forms of Cd, Ca, Fe, Pb and Zn were estimated after partitioning (3-step according to Community Bureau of Reference (BCR) method, [36]) of the other part of each sample in anoxic conditions (nitrogen atmosphere) in a glove box. In the first step, 40 mL of 0.11-M acetic acid was added to about 1 g of sediment and shaken for 16 h. The extract from the solid residue was separated by centrifugation (3500 rpm/rotation per minute for 20 min) and decantation. In the second step, 40 mL of 0.5-M hydroxylammonium chloride (pH = 2 with HNO_3) was added to residue from Step 1, shaken for 16 h and extract was separated as in Step 1. In the last step, 20 mL of 8.8-M solution of hydrogen peroxide acid-stabilized to pH in the range of 2–3 was added to residue from Step 2 and digested at 85 °C in a water bath until reduction of the volume to less than 1 mL. After this, 50 mL of 1-M ammonium acetate solution acid-stabilized to pH about 2 was poured and shaken for 16 h. The extract from the solid residue was separated by centrifugation and decantation as above.

The pseudo-total concentrations of these metals were obtained after extraction with 10 cm^3 of 65% nitric acid (p.a.) in a high-temperature digestion systems, SCP Science, Digi PREP HT-Champlain, NY, USA (120 °C, 2 h). In total, as a result of sequential extraction, four operationally defined fractions were obtained: acid-extractable, reducible, oxidizable and residual. Metal concentrations were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS, ELAN 6100, PerkinElmer-Waltham, MA, USA) in a certified hydrogeochemical laboratory (PCA certificate, no. AB 1050) at the AGH University of Science and Technology in Krakow, Poland, according to the standard certified analytical quality control procedures.

3.4. *Mineral Forms of Metal*

Scanning electron microscopy (SEM) was applied to selected, organic-rich samples where pyrite framboids were expected. Samples were dried in anoxic conditions to prevent oxidation of sulfide minerals. Samples were polished with diamond spray, using light oil as a lubricant. This enabled the preservation of water-soluble minerals in the polished sections. Polished sections were studied by reflected light microscopy on a microscope Hitachi S-4700-Tokyo, Japan with a Vantage EDS NORAN system analyzer with detection Si(Li) 135 eV at 20.0 kV at the Institute of Geological Sciences, Jagiellonian University, Krakow, Poland. This instrument allows effective magnification of 500,000 times with an excellent resolution of nanotextures. From the overall amount of over 20 microphotographs we selected a few of the most representative.

3.5. *Quality Assurance/Quality Control (QA/QC)*

The analyses were performed according to a standard certified analytical quality control procedure. All reagents used were of high purity and the people carrying out the analyses had adequate preparation and worked with compliance with the rules, which allowed them to minimize the occurrence of errors. Blanks and standard reference materials (Sediment River 1646) were analyzed at regular intervals, i.e., one blank and one standard for each set of ten samples, to assess the precision and accuracy of the measurements. For comparison, the dilution analyzed by the F-AAS was also measured by the ICP-MS method. Results for all analyzed metals were only slightly (<5%) different, which confirms very good analytical quality. Each spectrophotometric analysis was repeated three times. The RSD values for all analyzed metals were below 5%. Otherwise, the analysis was repeated.

4. Results and Discussion

The differences in the floodplain morphology of the Biała and the Biała Przemsza rivers result from the distinct deposition rate of waterborne sediment during the mining period in the second half of the 20th century. Over this period, the amount of mine water increased the discharge of the Biała River from less than 0.5 m^3/s to almost 3 m^3/s in the 1970s when the mine was extended significantly. Mine-originated suspended sediments were trapped over the 4-kilometer length of the Biała River, and the original surface of the floodplain was covered with a stratum of silty-clay sediment up to 1-meter-thick [34]. The bottom of the valley was transformed into a backswamp with no distinct levee along the river banks. In contrast to the Biała River floodplain, the levee remained the characteristic feature along the Biała Przemsza River where natural sedimentary processes did not alter. In the sampled meander of this river, the levee falls gently from the channel over a distance of 10–20 m. The rest of the floodplain is flat and lies a dozen or so centimeters above the average groundwater level. In recent decades, mine originated, fine-grained, contaminated sediments have contributed in small quantities to the levee material over this reach and were not present at larger distances from the river [37].

Based on previous sediment investigations in the Biała Przemsza valley [37], we studied the fine sediment fraction (<0.063 mm) to recognize the distribution of the metal contaminants on the example of Zn and Cd. The differences in the accumulation of mine-originating sediments were determined in five vertical profiles situated in the transect across the river meander (Figure 1). By separating the fine fraction from overbank samples, we could relate their contamination to that which has been transported as suspended matter [38]. As expected, sediments with the highest Zn and Cd concentrations occurred in profiles from the levee whereas, at larger distances from the channel, concentrations were on average two orders of magnitude lower (Figure 2). The highest metal content was in the upper ca. 1.5-m-thick sediment strata within a dozen meters wide zone from the channel which could contribute as the secondary water pollution source if water table lowering were to occur. For this reason, metal speciation was further studied in the Biała Przemsza floodplain in three 1.75-m-long cores sampled at the location of respective three profiles from the levee (BPI–BPIII). The selection of the three sampling sites for coring in the Biała River valley was based on the previous extensive research on sediment contamination by Wojcik [34]. The study proved that the highest Zn, Cd and Pb concentrations occur in the strata of loamy sediment which is up to 1-m-thick. Therefore, three sediment cores were collected to determine metal speciation. These were up to 1.25-m-long and represented the near-river bank locations, in its upper, middle and lower reaches (Figure 1).

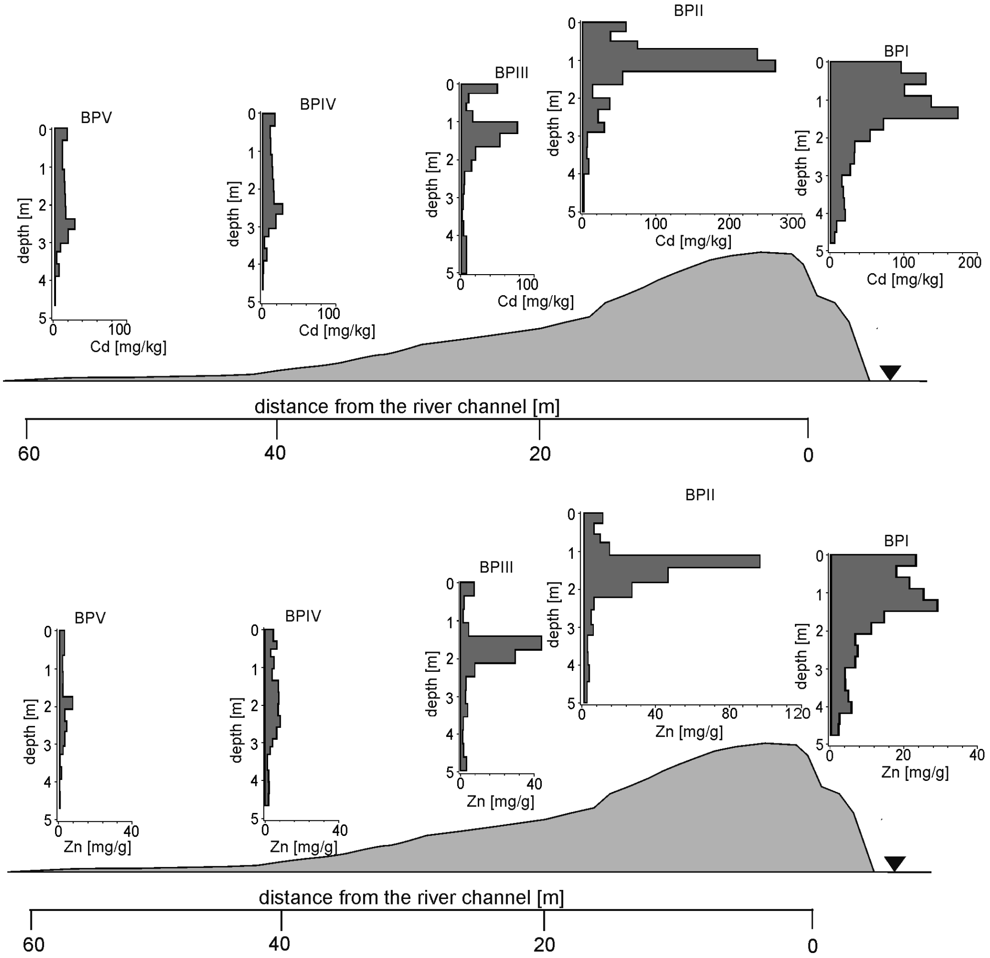

Figure 2. Distribution of Cd and Zn in <0.063 mm fraction of floodplain sediments of the Biała Przemsza River.

4.1. The Sediment Characteristics and Metal Speciation of the Biała River

Generally, two types of sediment, loams and sands were sampled in the Biała River valley for metal speciation. The loamy sediment was 1.2-m-thick in the upper profile (BI) and half a meter thinner in the other two profiles of the Biała River (BII, BIII) where it equaled 0.75 m. The loams in the BII and BIII profiles rest directly on sandy sediments which were identified as the natural material of the floodplain. The horizon separating these strata is clearly visible in both profiles, as well as at the depth of 1.2 m in the BI profile. It is also well reflected in the decrease of the content of the fine sediment fraction, carbonates, likewise LOI values (Figure 3). There is also a large difference in Ca concentrations between silt–clay sediments with 10–15% of Ca and the sandy sediments where Ca content is well below 1%. This difference is also clearly discernible in the mineral composition of the sediments (Table 1). Loams are composed of 60–70% of dolomites with 5–12% of calcite. These minerals are almost entirely absent in the fluvioglacial sands underlying the loamy strata and are characterized by the predominance of quartz grains (80–90%) with the admixture of orthoclase. There is also a noticeable difference in the content of metal-bearing minerals. Pyrite, marcasite, galena and sphalerite grains are associated almost solely with mine-originated loamy sediments while sulfides are present only in trace amounts in sands as Fe minerals. The mineral composition of loams in the river valley is very similar to the material of the mine tailings stored both in former open pits and in a 110 ha tailing pond, which was draining into the Biała River since 1957 [39]. It is also worth noting that almost 90% of the tailing material is comprised of a fine fraction ranging from 0.025 to 0.2 mm [40]. The almost pure quartz sand of the natural floodplain has a fluvioglacial origin. It fills the whole Biała Przemsza valley to a depth of up to several dozen meters [41].

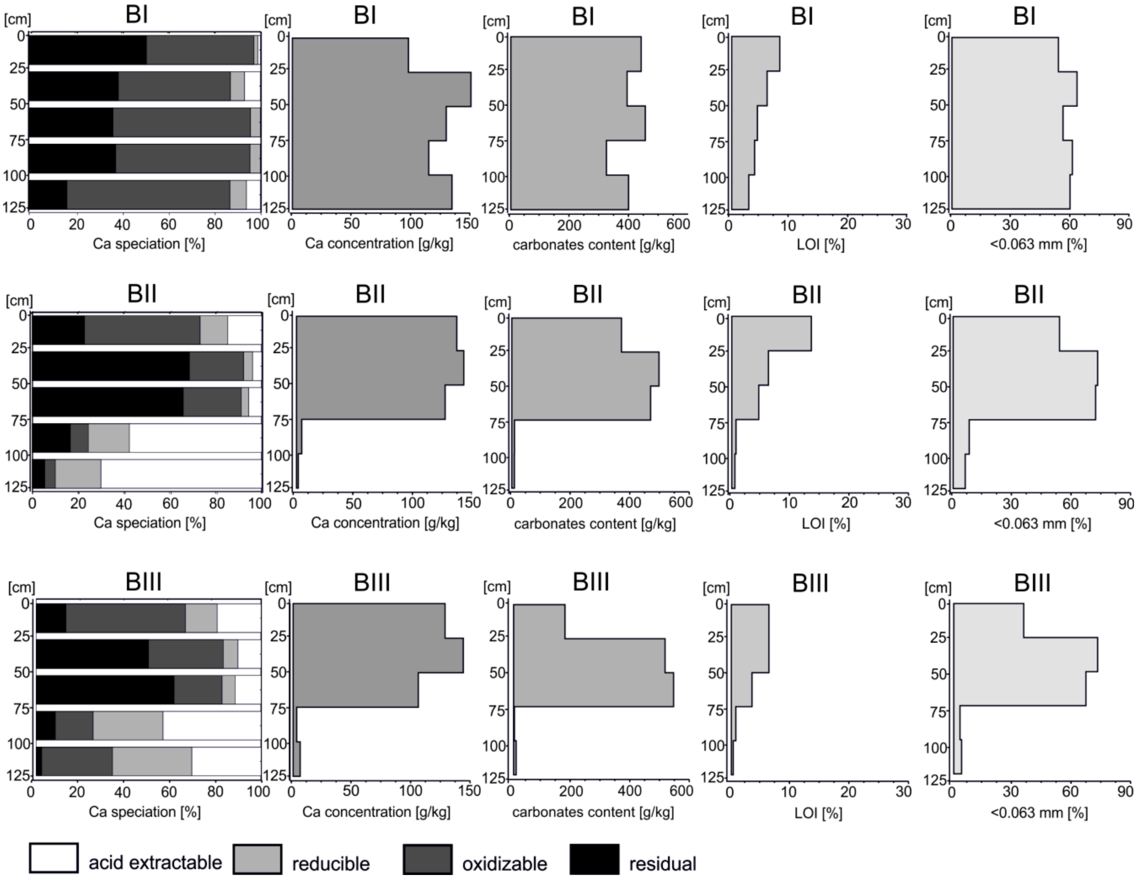

Figure 3. Carbonates, LOI, fine sediment and Ca content and speciation in the Biała River sediments.

Table 1. Minerals of fluvial sediments in the Biała River valley [%] (after [34]).

Mineral	**Sampling Depth [cm]**				
	0–30	**30–60**	**60–100**	**100–150**	**150–200**
Quartz	2.8–6.1	5.2–6.0	6.6–50.9	85.1–89.1	85.2–88.5
Orthoclase	0.0	0.0	0.0–7.4	4.1–11.0	5.7–8.4
Albite	0.0	0.0	0.0	0.6–1.2	0.7–1.5
Calcite	4.6–10.0	9.0–12.0	2.9–4.8	0.0–1.3	0.0–1.2
Dolomite	61.0–70.9	66.0–67.2	2.7–61.1	0.0	0.0
Pyrite	2.8–5.4	4.3–6.3	0.7–4.3	0.0–0.2	0.0–0.2
Marcasite	5.6–9.6	5.1–9.2	0.9–4.2	0.0–0.4	0.0–0.3
Sphalerite	0.4–1.0	0.5–1.0	0.0–0.4	0.0	0.0
Galena	0.3–0.6	0.6–0.7	0.0–0.5	0.0	0.0

The mine originated loam in the profiles has been modified by diagenetic processes. Its upper 25 cm sediment stratum became enriched with organic matter which is the product of the incomplete degradation of the abundant plant cover (dominated by *Carex gracilis*). It is usually black or dark in color and contains 7–13% of organic matter (expressed as LOI) with the content of silt–clay fraction 30–60% (Figure 3). Lower lying loams of all profiles are characterized by small ferruginous nodules dispersed in the gray, silty-clay sediments with smaller amounts of organics. Poorly degraded remnants of twigs or leaves are centers of ferric oxides precipitations. These strata are associated with lower, more uniform cyanic, silty-clays without rust-colored fragments. The cyanic color of the loams indicates the presence of permanent anoxic conditions favoring the reduction of Fe(III), whereas ferric nodules indicate the accessibility of oxygen from the surface along with roots or remnants of leaves. Loams in the profile BI are thicker by 50 cm. Interestingly, this lower ca. 0.5 m stratum of loams is yellow-the color of the excavated dolomites which, despite the anoxic conditions, have avoided diagenetic changes. This indicates that ca 0.75 cm of the overlying silt–clay stratum not only protects it against the access of oxygen, but also from the infiltration of anoxic groundwater resulting in the reduced appearance of Fe. This fact was confirmed to some extent by the earlier research of Wójcik [34] in which water did not appear in outcrops in the Biała valley despite digging 1.5 m below the groundwater level. A very important role of the sediment texture in maintaining reducing conditions was also emphasized by investigations in the Upper Colorado Basin [42], but in that river system it was recognized as a less important factor than the presence of organic carbon. In the Biała River, the influence of massive loams as a barrier to water and oxygen seems to be much more important, however the presence of organics contributes to maintaining anoxic conditions in the subsurface strata. This effect is well known from many sulfide-rich soil profiles, in which organic matter can retard pyrite oxidation through oxygen consumption by heterotrophic microbes and, overall, oxygen-limited soils hamper both the rate and amount of generated acids [43,44].

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The metal speciation differs between loams and sands of the Biała valley profiles. Generally, Zn, Cd and Pb in loams are associated with less mobile fractions than in the underlying sands (Figures 4 and 5). The highest residual metal concentrations there are in the yellow silts from the BI profile where the content of Zn exceeds 4%, Pb 3.5% and Cd values reach 300 mg/kg. This stratum, being the less diagenetically changed, could reflect the content of the original metals at the time of their accumulation. Concentrations of these metals are much higher than in overlying, diagenetically altered loams, suggesting that part of metals from the overlying loamy sediment was mobilized. This could only be explained to a limited extent by metal speciation shown on Figure 4, as differences in metal speciation between cyanic (25–75 cm) and yellow loams (75–125 cm) of the BI profile are relatively small, except Zn which is twice as abundant in the residual fraction in the yellow strata.

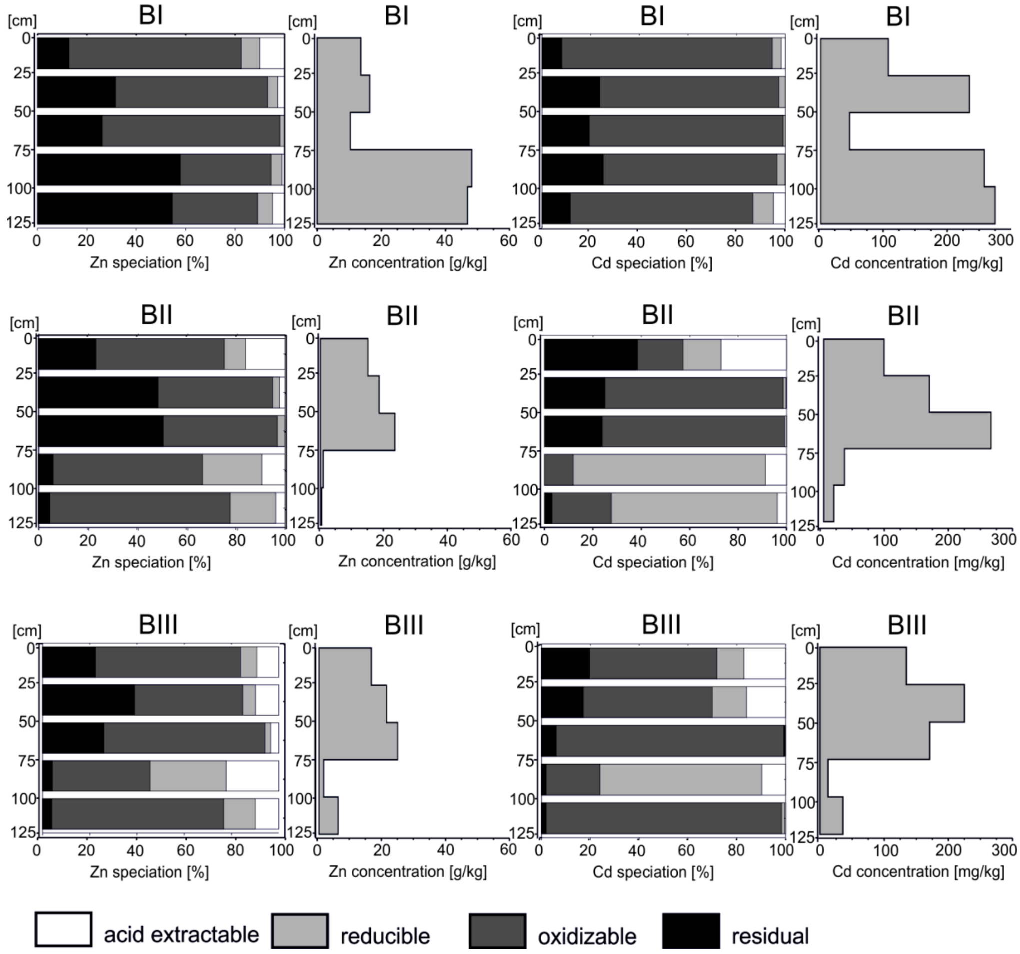


Figure 4. Zn and Cd content and speciation in the Biała River sediments.

These small differences within the loams perhaps result from the presence of a relatively high percentage of sulfide-associated Zn, Cd and Pb (sphalerite, galena) as indicated by the 40–60% average of these metals in the oxidizable fraction (Figures 4 and 5). Only up to 30% of Ca, Zn, Cd, Pb and Fe in the loams are associated with more mobile, reducible and acid-extractable fractions and their content increases downstream of the Biała River between the BI and BIII profiles. This change is clearly visible, particularly in the surface sediment strata for Ca, Zn and Cd which are known as elements that are relatively easily soluble under circum-neutral conditions [45]. These metals, particularly Ca, can be easily released from surface strata just above the water table due to the oxidation and decomposition of organic matter [13]. The oxidation reactions are known to induce the redistribution of immobile species to mobilizable species making their downward migration possible [46]. Moreover, a progressive increase of more mobile metals below the mine in some river systems as a result of the dissolution of mine-originating contaminants [47,48] seems to confirm the effect observed on the Biała River.

The lowest concentrations of Zn, Pb and Cd are present in the sandy sediments in the bottom 0.5 m of the BII and BIII profiles, where their respective values do not exceed 0.2 g/kg, 0.1 g/kg and 40 mg/kg (Figures 4 and 5). In these least contaminated samples, Zn and Pb are associated with the residual fraction of only less than 20% and with the oxidizable fraction in less than 60%. Cd, with up to 80% in the reducible fraction and a dozen or so per cent in the acid-extractable fraction, is the more mobile contaminant. Fe is also weakly bonded in the sandy stratum, particularly in the profile furthest downstream, BIII, where its residual fraction even drops to 20%. Concentrations of Fe in this stratum are also lower than in loams, even below 5 g/kg. Moreover, the Ca which occurs in sands at amounts two orders of magnitude lower than in loams, is associated in 60–90% with the two most mobile fractions, while not exceeding 1% in the residual fraction. The significant difference in the metal associations between sands and loams results from the secondary enrichment of sands. The loamy stratum can be a source of calcium and of the other metals, but these elements can also be transported with hyporheic water from the nearby river and retained within sediments because the Biała River water is abundant in calcium and has raised content of the other investigated metals [35]. The lateral metal transport outside the channel was found to be particularly effective in the enrichment of the sandy sediments of the Biała Przemsza River below the groundwater level, forming distinct, secondary peaks in the sediment profiles there [37].

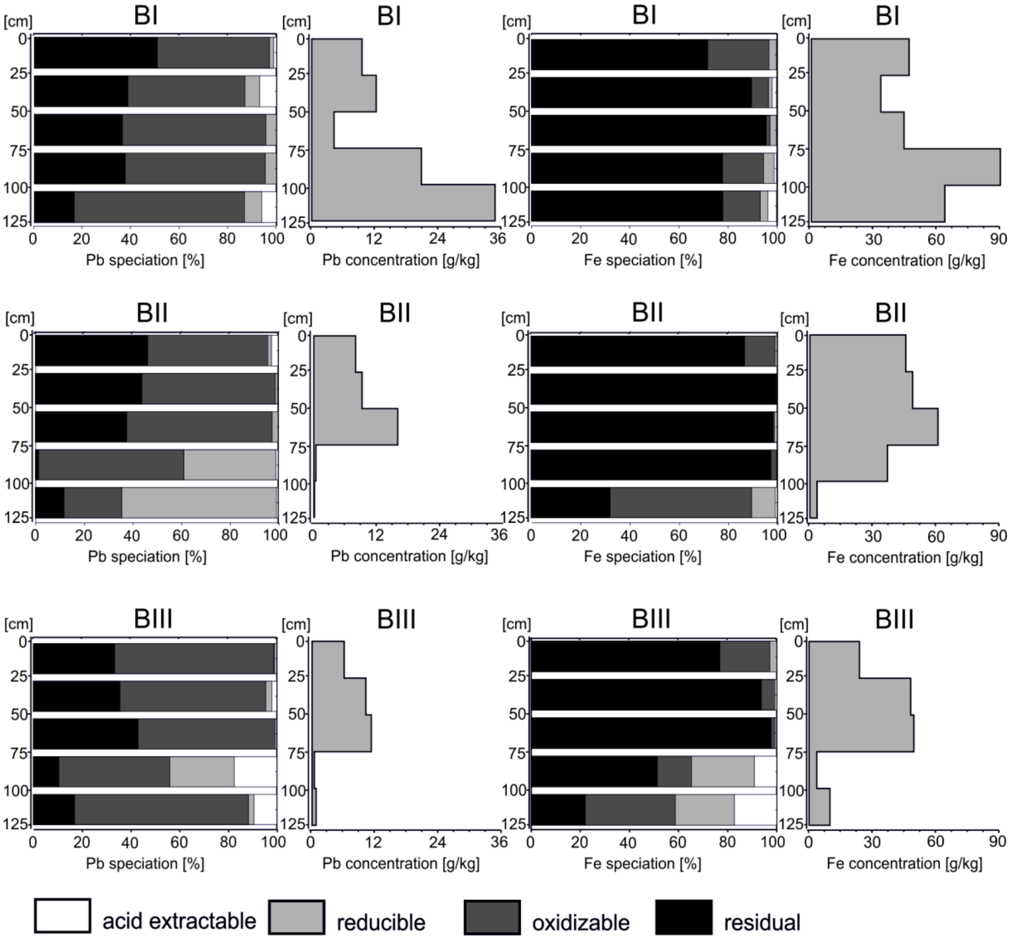


Figure 5. Pb and Fe content and speciation in the Biała River sediments.

4.2. The Sediment Characteristics and Metal Speciation of the Biała Przemsza River

Sediments in the BPI–BPIII profiles of the meander bend sampled on the Biała Przemsza floodplain are less differentiated than those of the Biała River floodplain. They are composed of almost homogeneous sands with the exception of the upper 25–50 cm, where the content of fine sediments increases to a dozen or so percent (Figure 6). These surface, mine-originating sediments make up the levee top which accumulated during the mining period. In the lower part of all the profiles, the content of the silt–clay fraction is lower than 1%, except for the profile BPI in which this content ranges between 1.0% and 2.5%. The stratification is poorly visible, but there are thin inserts of dark, more-organic, fine-grained sands. Generally, LOI values follow the distribution pattern described for the fine fraction. They are below 2%, but in the surface strata they increase to approximately 20%.

The content of the carbonates varies depending on the profile: the highest concentrations occur on the river bank and they decrease with distance from the river by one order of magnitude.

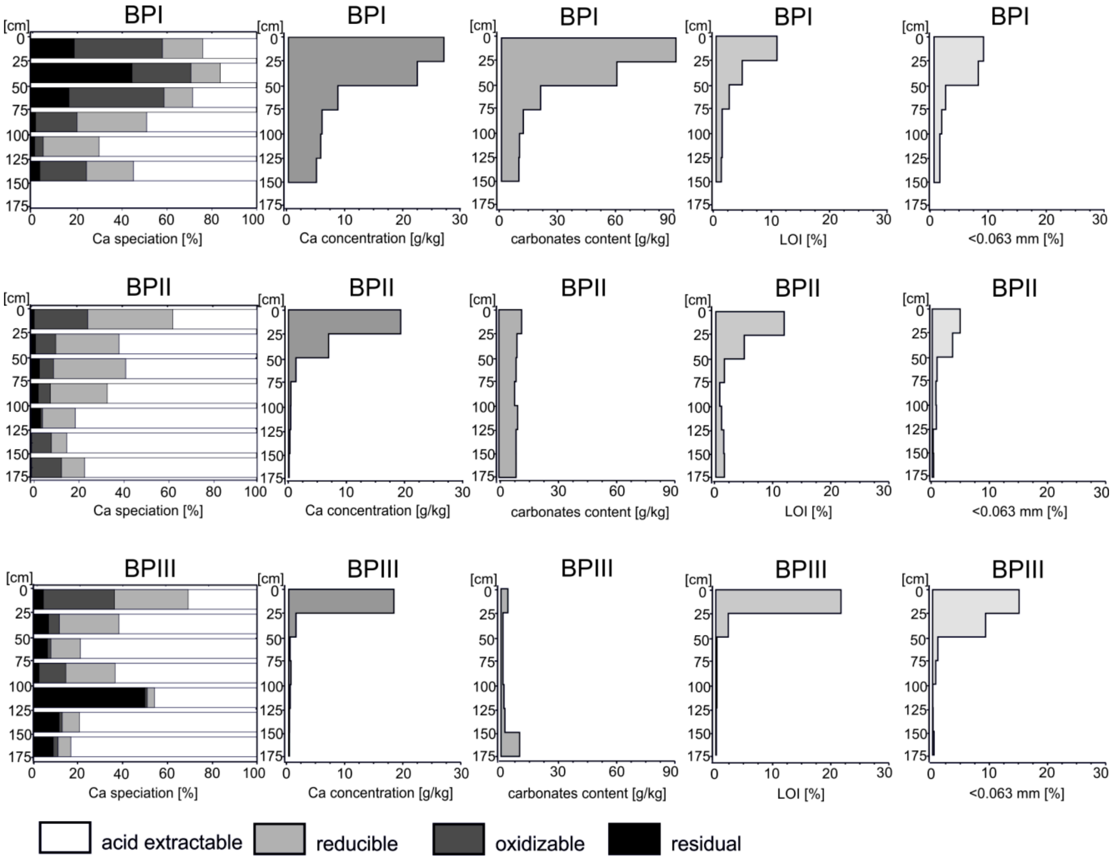


Figure 6. Carbonates, LOI, fine sediment and Ca content and speciation in the Biała Przemsza River sediments.

Maximum Zn, Pb and Cd concentrations are much lower than in the Biała River floodplain (Figures 7 and 8). In the top of the profiles they reach 8 g/kg, 2.4 g/kg and 50 mg/kg, respectively. Maximum concentrations of all these metals approximately halve between the channel and the outer part of the levee. The minimum contents of Zn, Pb and Cd there are at the lowest parts of all profiles and reach values close to the local background levels: 38 mg/kg, 7 mg/kg and 1.6 mg/kg, respectively. The speciation of Zn, Pb and Cd also differs from that in the Biała River profiles. Generally, these metals are associated with more mobile fractions than in the Biała floodplain, with only small amounts of the immobile residual fraction, which is lower than 20% for most of the samples. As a rule, these elements predominate in the oxidizable fraction with its highest values in the upper part of profiles and decrease progressively with depth, simultaneously to the decrease in metal concentrations. Moreover, the more mobile metals of the acid-extractable and reducible fractions predominate as one moves down each profile, reaching together in both fractions about 80% for Zn and Cd. Pb appears to be less mobile since in the acid-extractable and reducible fractions it only equals weakly contaminated bottom samples in 20% of cases. These results fit well with those obtained for the Biała Przemsza channel sediments [49] where Zn and Cd are equally associated in 50–60% with the most mobile acid-extractable fraction. It indicates that the prevailing part of these elements and 30–60% of Pb is adsorbed by the sediments or bound to carbonates which can be easily mobilized given even a small environmental change, such as a drop in pH value. Only about a dozen or so percent of these elements were associated with the two most resistant fractions, probably in particles originating from the mine. Even more mobile parts of Cd, Zn and Pb, reaching 90%, 60% and 80%, respectively, are to be found in the soils nearby the mine [50].

This was explained by the heavy contamination of the soil by the airborne deposition of dust from the post-flotation waste site.

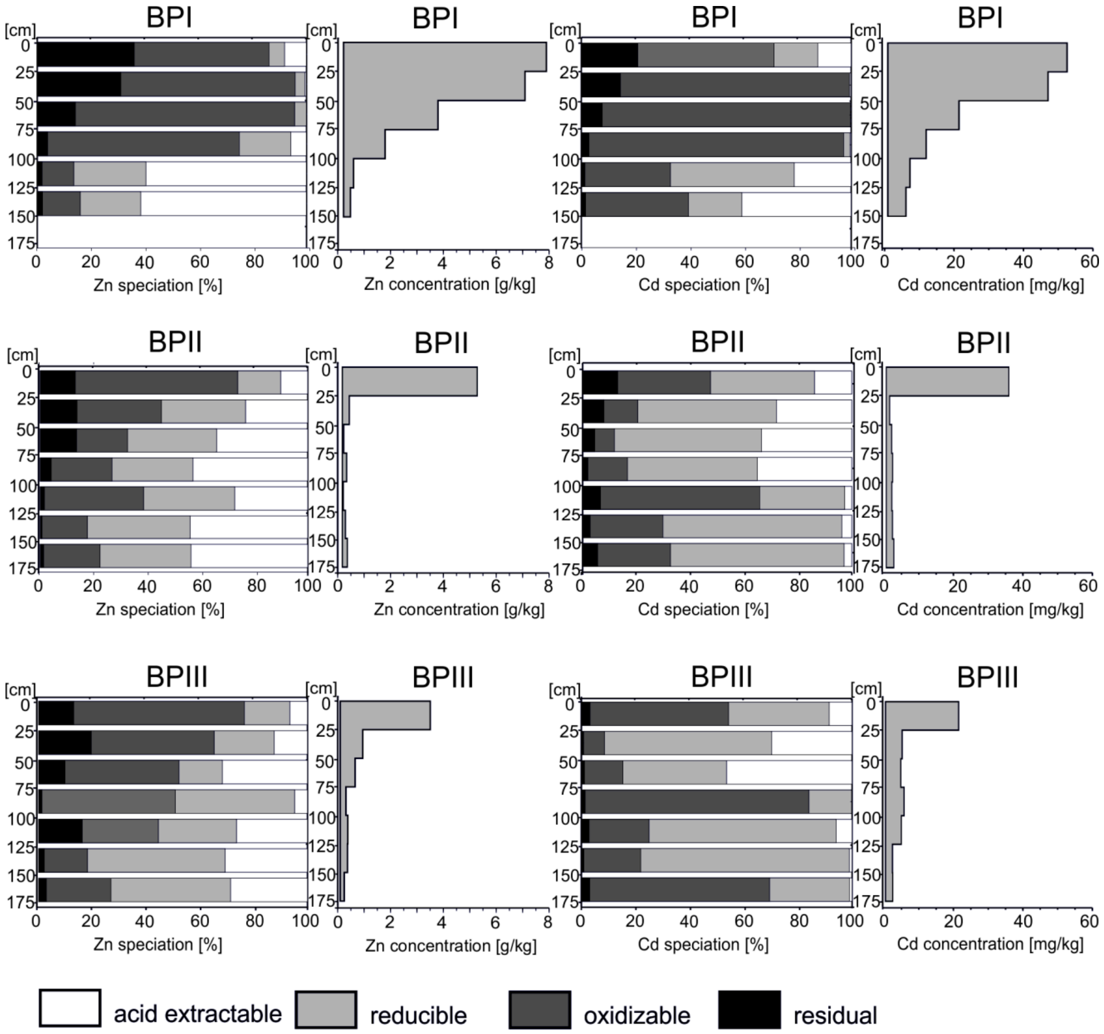


Figure 7. Zn and Cd content and speciation in the Biała Przemsza River sediments.

In general, the contents of Fe and Ca in the Biała Przemsza floodplain are also significantly lower than in the Biała floodplain (Figures 6 and 8). Their concentrations are the highest in the upper, approximately 75-cm-thick strata and decrease with depth. The maximum concentrations of Fe reach 24 g/kg, but most of them do not exceed 15 g/kg. Most of the Ca values do not exceed 10 g/kg, but its maximum content in the top of the profiles reaches 20–30 g/kg. Fe content of the mobile, acid-extractable and reducible fractions typically varies between 10% and 20% in each profile in the Biała Przemsza River valley. Nevertheless, 20–70% of Fe is present in the residual fraction and additional 10–80% of Fe constitutes the oxidizable, relatively immobile fraction of this metal. Ca speciation differs markedly from that observed for the Biała profiles in respect to potential mobility. On average, the total share of the relatively immobile residual and oxidizable fractions is even 2–3 times lower whereas the contribution of the most mobile acid-extractable and reducible fractions in most samples varies between 70% and 90%, particularly in the two profiles which are distant from the river.

The fluvial sands of the Biała Przemsza River have a mineralogy dominated by quartz grains. They are accompanied by up to a few percent of dolomite particles which originate from both the mine and, together with some orthoclase particles, the natural drainage of the rocks exposed in the catchment [51]. Besides these minerals, loosely dispersed clasts of hematite, anglesite and andesine and, in the surface strata, also mine-originating galena and sphalerite particles, could be found in the sediments [41]. In almost all of the sediment samples investigated microscopically, which were dark in color, framboidal pyrites were present. Sediments which were the most abundant in framboids were also rich in organic matter. A similar regularity has also been characteristic for the strata of the Biała River floodplain which are rich in organic matter, as well as for the sediments in the downstream reaches of the Biała Przemsza River [41]. Essentially, these particles are loosely dispersed among grains of sand or, in samples abundant in poorly degraded organic matter, they are organized in elongated structures filling the remnants of plant tissues. Most associations are smaller than 10 µm, but they can even reach 30 µm in diameter (Figure 9).

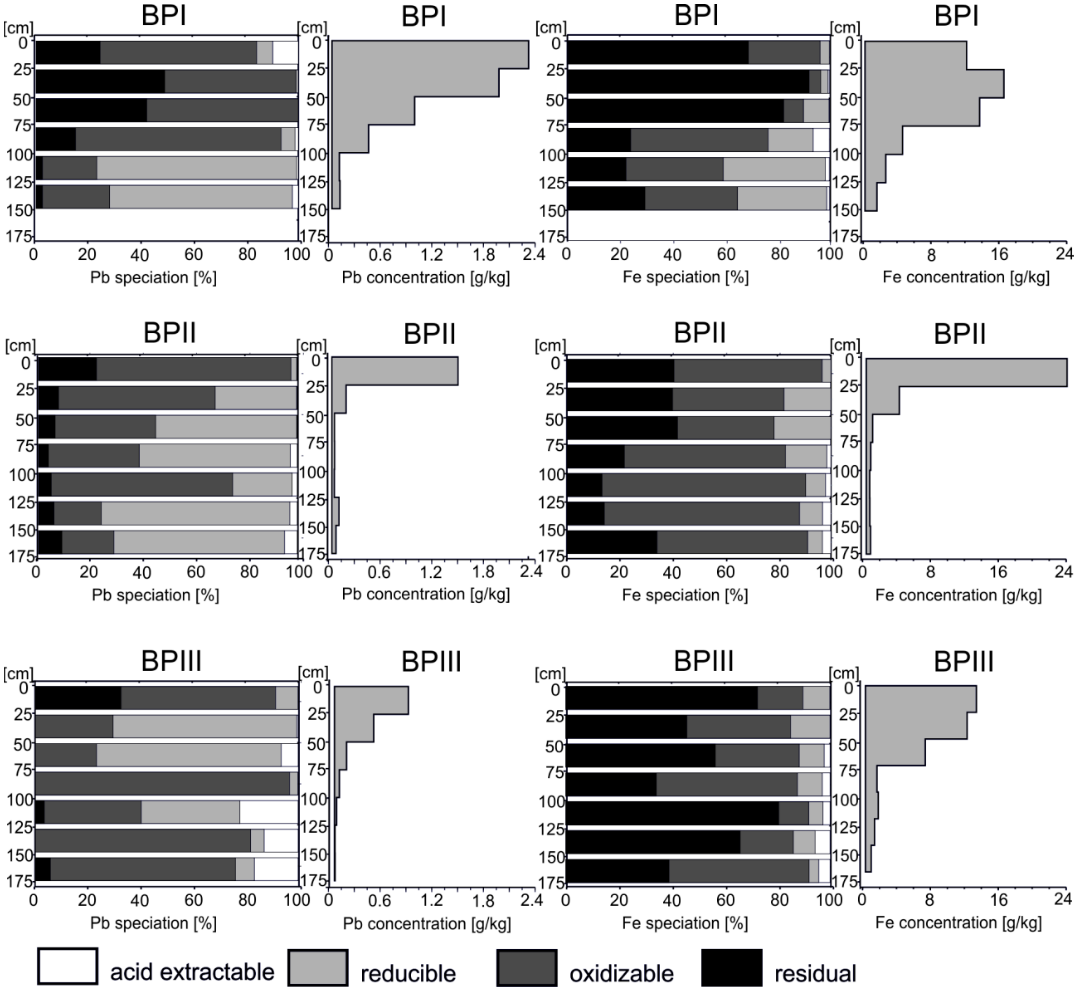
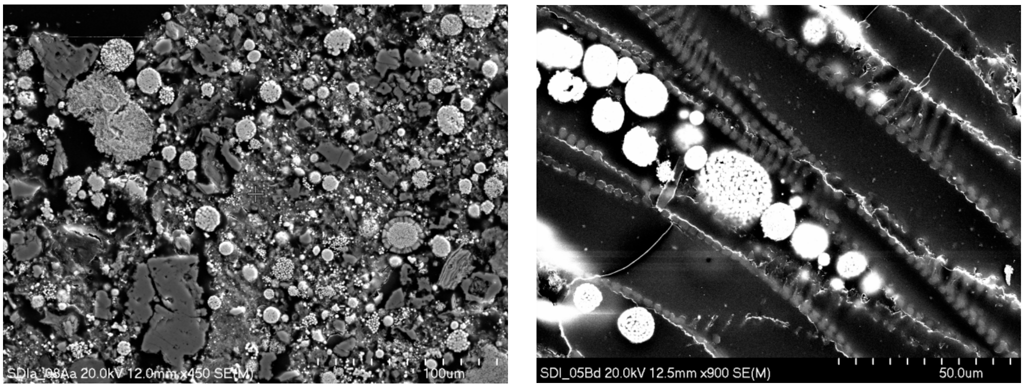


Figure 8. Pb and Fe content and speciation in the Biała Przemsza River sediments.

The formation of these raspberry-shaped spherical aggregates, which can be even several hundred micrometers in diameter, is characteristic for weakly reducing conditions in a low-temperature environment. They are considered a byproduct of the anaerobic oxidation of higher hydrocarbons with the contribution of sulfate-reducing bacteria [52]. Their presence in the investigated samples indicates the active diagenetic processes controlled by the presence of SO_4^{2-} and Fe^{2+} in ground water leading to the formation of Fe monosulfides [53]. Such conditions, with the surplus of free sulfate ions, occur in a marine environment where framboidal pyrites are widespread [54], whereas in the investigated floodplain sediments, sulfate ions are supplied with mine waters and trapped within the hyporheic zone from waters percolating through the meander bend [28]. Moreover, groundwater flows across the floodplain, probably accompanied by the decrease of redox potential, favor the progressive release of

Fe from sediments, leading to the increase of its content along the flow path, sometimes even by two orders of magnitude [37].



(**a**) (**b**)

Figure 9. SEM picture (samples from profiles BPI and BPII) of framboidal pyrites loosely dispersed in matrix of quartz, dolomite and organic material (**a**) and organized in elongated structures filling remnants of plant tissues (**b**).

4.3. Potential Metal Mobility

The results show that Zn, Cd and Pb are key contaminants of the Biała Przemsza River system. The sediment contamination by these metals and their potential mobility changes disproportionally with the distance downstream of the ore mine, but there is an abrupt change between the floodplains of the main river and its tributary. This is related to the distance from the mine and the difference in the flow magnitude of both rivers. The originally small dimensions of the Biała River channel favored the rapid entrapment of mine-originated sediments on the floodplain, including changes in the course of this short river. However, the more natural main river flow regime of the Biała Przemsza River favored the mixing of contaminants with natural fluvial sandy sediments and their dispersal over its longer distance. This change between river reaches can be termed the transition from the active channel transformation to the passive sediment transport [55].

The difference between the floodplain sediments of both rivers affects the potential metal mobility. Zn, Cd, and Pb speciation generally indicates that there is lower potential mobility in the Biała than the Biała Przemsza River. This general impression from the differences in metal speciation shown on Figures 3–8 can be confirmed by the mean contents of the mobile fractions [in%] which differs between the profiles of both rivers by 2–3 times for particular element (except Fe). The speciation, with large proportions of metals present in the residual and oxidizable fractions, reveals their bonding with mineral lattices or with sulfides or organic fractions [26]. It is a characteristic feature for sediments in mining areas with a large share of parent rocks and excavated minerals [24,25], but also for weakly polluted sediments where only a small portion of metals occur as being adsorbed or associated with carbonates, revealed by their presence in the acid-extractable fraction [26,56]. The high proportion of an immobile fraction of the three metals in the Biała River sediments is related to the deposition of mine-originating particles containing sulfides and dolomites. It differs markedly from the metal speciation in the sediment of the contaminated ponds of the investigated mining area supplied with waters seeping from the tailing. They are dominated (even to the tune of 85%) by the mobile, extractable part of metals and their speciation was found to be controlled by a high content of carbonates and only to the small extent by sulfides [57]. This suggests that when metals are mobilized from loams in the Biała floodplain and within the Biała Przemsza profiles, they are increasingly bonded to carbonates, as revealed by the percentage of the acid-extractable fraction which increases with depth. Such a degree of regularity in the speciation of the three metals is consistent with the increase in Ca mobility with depth, probably as a result of the dissolution of dolomite particles and the supply of slightly alkaline hyporheic waters containing 150–200 mg/L Ca [28]. Decalcification of hydric soils can be related both to an increased carbon dioxide pressure in the waterlogged soil combined with drainage of pore–water solutes as well as the oxidation of iron sulfides in the surface soil elevated over the water table [58].

The above observations indicate the high mobility of Ca which effectively reduces sediment acidity. This can be seen in the fact that the sandy sediments of the Biała Przemsza even have a neutral pH in the top of the profiles which are enriched with organic matter (Table 2). This phenomenon seems to be unique to the Biała Przemsza fluvial sediments which contain a Ca-rich top stratum rather than the other sandy soils in the river valley. This is because the arenosol of the mining area which are not impacted directly by dust deposition have a pH of 4–5 [59]. Nevertheless, the loamy sediments of the Biała River play a more important role as a buffer zone than the surface, Ca-rich stratum in the Biała Przemsza floodplain. The source of large amounts of Ca in the Biała valley is both the upper stratum of the loams raised over the water table, as well as its lower, hyporheic parts. This is evidenced by over 20 g/kg of mobile Ca and a pH reaching 8 (Table 2). Considering the extensiveness of the loams in the floodplain of the Biała River [34] and the overall high content of Ca, they evidently act as an important barrier preventing sulfide oxidation under current conditions. It also constitutes an important hydraulic barrier reducing metal mobility as indicated by the multifold difference of the Zn, Cd and Pb contents in the mobile fraction between the top of the loams and the bottom strata of the sandy sediment (Table 2). From one hand a sediment stratigraphy and a distribution of organic matter is known as a factor hampering metal mobilization from floodplain sediments [42], but from the other hand, in the case of prolonged drying, even massive silty-clays strata of a low porosity or sediments rich in organics, which favor maintaining reducing conditions, can be oxygenated, leading to the dissolution of sulfidic minerals [18]. In catchments where acid sulfate soils are widespread, the degradation of sulfides during droughts generates soil and water acidification and metal mobilization [43]. In these areas, post-drought floods can be heavily loaded with metals, but they can also contain raised amounts of sulfates and some major ions in concentrations which are dangerous for the aquatic environment [60,61].

Table 2. pH and potentially most mobile metals in the sediments of the Biała and Biała Przemsza rivers. Range and *median values* in mg/kg.

Biała River					
Sediment Depth	**Zn**	**Cd**	**Pb**	**Ca**	**pH**
Loams with organic > 0.25 m	1375–101,677 *1556*	2.0–76.0 *18.0*	62–227 *112*	20,597–27,735 *26,242*	6.8–7.2 *6.9*
Loams (altered)	1–14,455 *1495*	1.0–27.0 *1.0*	1–857 *10*	5860–17,140 *10,119*	7.1–7.6 *7.3*
Loams (unaltered)	506–2281 *1394*	1.0–13.0 *7.0*	9–2155 *1082*	4519–11,423 *7971*	7.9–8.0 *8.0*
Fluvial sands < 1.0 m	112–609 *442*	1.0–25.0 *6.0*	1–77 *38*	1–2578 *1643*	5.9–6.7 *6.2*
Biała Przemsza River					
Sands with organic > 0.25 m	12–634 *540*	1.3–2.5 *1.8*	1–228 *7*	59–6987 *6531*	6.3–7.1 *6.6*
Shallow fluvial sands	1–192 *64*	<1.0–2.0 *<1.0*	<1–10 *<1*	118–4090 *718*	6.1–7.2 *6.7*
Fluvial sands < 1.0 m	10–233 *55*	<1.0 *<1.0*	<1–6 2	74–3980 *204*	5.4–6.5 *6.3*

4.4. Metal Mobility—Perspectives

In the near future, the Zn–Pb ore mining on the site will come to an end and the following, several years-long process of the mine closure will be associated with a cessation of mine water discharge. Based on experiences from the closure of the nearby mine in 2010 [62] where the receiving stream became dry after the cessation of the mine water discharge, we may also expect drying of the Biała River channel for many years to come. This is also suggested by hydrogeological modeling [29]. Given the depth of the Biała River channel 1.0–1.3 m on average, the cessation of the mine water discharge can reduce the water level in the valley even by about one meter. Considering the experience of southern Australia, where a long-term drought had led to the desiccation of a floodplain which in turn resulted in bulk sulfide destruction [18] we should also consider at least partial desiccation of the subsurface soil horizons of the Biała River and its consequences. However, it is impossible to convert the valley bottom into a dry, bare soil area like in Australia, in the moderate climate conditions of Central Europe we would expect that a rapid terrestrialization of plant communities will result in continuous plant cover and a permanent supply of organic matter. Organic matter is a known factor which is crucial for maintaining reducing conditions at subsurface horizons and preventing the rapid oxidation of sulfides which would results in a drop of pH and a release of metals [17,53]. Beside the drop in water level, the pH of the water which will flow into the channel (drained from the shallow side valleys) and in the hyporheic zone is expected to decrease from 7.7–7.8 at present to natural, neutral values [28,35]. This decrease in water pH may be compensated by the loss of calcium from the loams due to leaching by rainwater, usually having a slightly acid reaction (pH = 5.4) [63], as suggested by the high content of this element in the surface sediment stratum. The leaching of Ca may be accompanied by an acceleration of metal mobilization and, after the exhaustion of the mobile part of metals from the surface strata, the process may be of a lower intensity, which will mainly be related to local rainfall, as observed in similar post-mining areas [64–66]. Overall, the processes of metal mobilization in the Biała valley seems to be hampered by the thick loams of low permeability strata covered by organic matter which is able to preclude access to oxygen by lower sediment strata [42].

It seems that, due to the much higher content of the mobile part of contaminants in the Biała than are to be found in the Biała Przemsza floodplain (Table 2), this short river reach can contribute more to river water pollution in the future than the dozen or so km-long reach of the Biała Przemsza. We suppose that the relatively smaller role of the Biała Przemsza floodplain in water pollution will also be associated with the much smaller change to its river discharge since it is continuously supplied by active springs outside the mining area. However, on the basis of the metal mobility, it is hard to predict the influence of the flow change along a significant reach of the Biała Przemsza River. Nevertheless, based on the existing literature, we may expect to see a tendency towards increasing amounts of metals in the most mobile, acid-extractable fraction, something which has been observed in the soil profiles of the investigated mining area over a 20 year period after the cessation of intensive dust accumulation [67]. Nevertheless, in the longer perspective of several decades, with the expected decrease in metal concentrations in the subsurface soil horizons, Zn, Cd and Pb in the region will tend to occur in more stable forms [60].

5. Conclusions

This research–based on Zn, Cd, Pb, Ca and Fe speciation, mineralogy and the stratigraphy of sediments which accumulated over the distance of a dozen or so km from the mine–revealed variable potential for metal mobilization. The results suggest that a drop in the water table, something to be expected after the closure of a mine, would be accompanied by a decrease in the pH of the river water and may induce the remobilization of metals associated with carbonates and exchangeable cations over the short-reach downstream of the mine. However, the mobilization of contaminants may be hampered by the alkaline, impermeable stratum of the loams, which play a pivotal role in maintaining anaerobic conditions and buffering acidity resulting from the partial degradation of sulfides. The loams, which are as much as several dozen cm thick over a significant part of the Biała valley, are expected to mitigate metal remobilization. As such, this is likely to be rather rapid than catastrophic after the cessation of mine water discharge. Despite the extreme metal content in the Biała River floodplain, it can be expected that the intrinsic attenuation will limit the need for remediation work, although the monitoring of river water quality is recommended to determine whether this may be the case in the future if permissible quality values are exceeded.

Author Contributions: Conceptualization, D.C.; methodology, D.C., U.A.-K.; validation, U.A.-K.; formal analysis, U.A.-K.; investigation, D.C., U.A.-K.; data curation, U.A.-K.; writing—original draft preparation, D.C.; writing—Review and editing, D.C., U.A.-K.; visualization, D.C.; supervision, D.C.; project administration, D.C. All authors have read and agreed to the published version of the manuscript.

Funding: The research was partially funded by the National Science Center, Poland grant no. 2014/15/B/ST10/03,862 and partially by statutory funds of the AGH University of Science and Technology no. 16.16.140.315.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses or interpretation of data; in the writing of the manuscript or in the decision to publish the results.

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