



## Research Article

# Sedimentological and geochemical traces of metallurgical activity in the Świślina River valley (central Poland) at the Doły Biskupie site

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### Abstract

Prehistoric and historic iron metallurgy in the Holy Cross Mountains in central Poland developed along with human Przeworsk Culture activity (during the Roman period) and within the boundaries of the Old-Polish Industrial District (OPID) during the Middle Ages and during recent centuries. At the Świślina catchment, there are many archaeological sites showing intense prehistoric metallurgical activity. The later medieval and modern iron industry was significantly smaller. At the Doły Biskupie site, slags and microscopic iron spherules (hammerscales) were found in alluvia. The microscopic spherules separation method (MSS) enabled analysis of these small artefacts created during iron ore smelting and forging. Iron spherules were detected in floodplain sediments, which are characterized by increased content of trace elements. The presence of these artefacts in shallow sediment layers in the confluence section of the river may be an indicator of archaeologically confirmed prehistoric metallurgical activity in the catchment area. Study of these residues enabled an attempt to reconstruct the river valley environment during the prehistoric and historical period. The MSS method can be used to detect iron spherules in alluvia in other river catchments, confirming the presence of yet-undiscovered bloomery sites.

**Keywords:** Micro- and macroslags, Hammerscales, Old-Polish Industrial District, Bloomeries, Prehistoric and historical metallurgy, Świślina River valley, Holy Cross Mountains

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### INTRODUCTION

Research on the occurrence of traces of human activity in landforms and sediments has been undertaken for many years. Soil erosion products were carried to the main river valleys, forming so-called cultural sediment (Natermann, 1941), flood, bottom, anthropogenic muds (e.g., Klimaszewski, 1948; Poser and Tricard, 1950; Mensching, 1951a, 1951b, 1957; Reichelt, 1953; Zandstra, 1954; Hempel, 1956, 1976; Klatka, 1958; Lüttig, 1960; Jäger, 1962; Mäckel, 1969; Huckriede, 1971; Schirmer, 1973; Linke, 1976; Ložek, 1976; Modderman, 1976), or agricultural muds (Rutkowski et al., 1988; Rutkowski, 1991), a sediment typical for the Subboreal and especially for the Subatlantic. Further research results from various areas proved, however, that these muds were deposited throughout the late glacial and Holocene, although at a different rate (Kalicki, 2006). Many authors, however, still closely associate the appearance and sedimentation of these muds with an anthropogenic factor (e.g., Klimek, 1988, 2003; Lipps, 1988; Hiller et al., 1991; Pastre et al., 1991; Litt, 1992; Brown, Keough, 1992a, 1992b; Alexandrowicz, 1996), which undoubtedly had a strong influence from the Middle Ages (e.g., Schirmer, 1995; Klimek, 1996; Houben, 2003) and

initiated such deposition in small mountain catchments in the last few centuries (e.g., Hong, 1995; Mäckel and Zollinger, 1995; Klimek et al., 2003; Houbrechts et al., 2004; Kukulak, 2004).

Research in the Doły Biskupie area has shown that this type of anthropogenic sediment formed a terrace (11–9 m above river level [m arl]) and a floodplain (5.5–4.5 m arl) that accumulated during the smelting activity period, which is confirmed by slag remnants found in alluvia (Klatka, 1958). These slags can be connected with the prehistoric (Roman period) (Radwan, 1963; Bielenin, 1992; Orzechowski, 2007) or even the medieval metallurgy activity operating within the Old-Polish Industrial District (OPID) area. These remnants are mostly bloomery slags that were discovered throughout the entire catchment area. Intensive archaeological research aimed at analysing these artefacts was carried out in the second half of the twentieth century. However, there is a lack of any wider analysis of the human–environment context within this subject. Using mainly aerial photography and environmental intelligence, more bloomery sites were found. The prehistoric iron ore excavation source theory has not been fully explained. It is suggested that the shallow iron ore was obtained from limonite, which was found in karst depressions or in other lowlands (Janiec and Kardyś, 2021).

Studies of the river valley bottom sediments have confirmed the presence of slags of different ages, mostly where archaeological work did not reach, like at the Doły Biskupie site (Klatka, 1958), or in other rivers in the Holy Cross Mountains, like Czarna Nida (Przychodni, 2002, 2006; Krupa, 2013, 2015).

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Further research in the Świślina River using new methods revealed changes in sediments, indicating new possibilities of interpreting the results obtained (Kalicki et al. 2021a, 2021b), and attempted to relate them to prehistoric or contemporary anthropogenic factors. These studies could be used as comparative material from other sites, where similar analyses in the OPID area have already been carried out (Przepióra et al. 2019, 2021, 2022a, 2022b; Kalicki et al. 2021c, 2023) and will continue in the future.

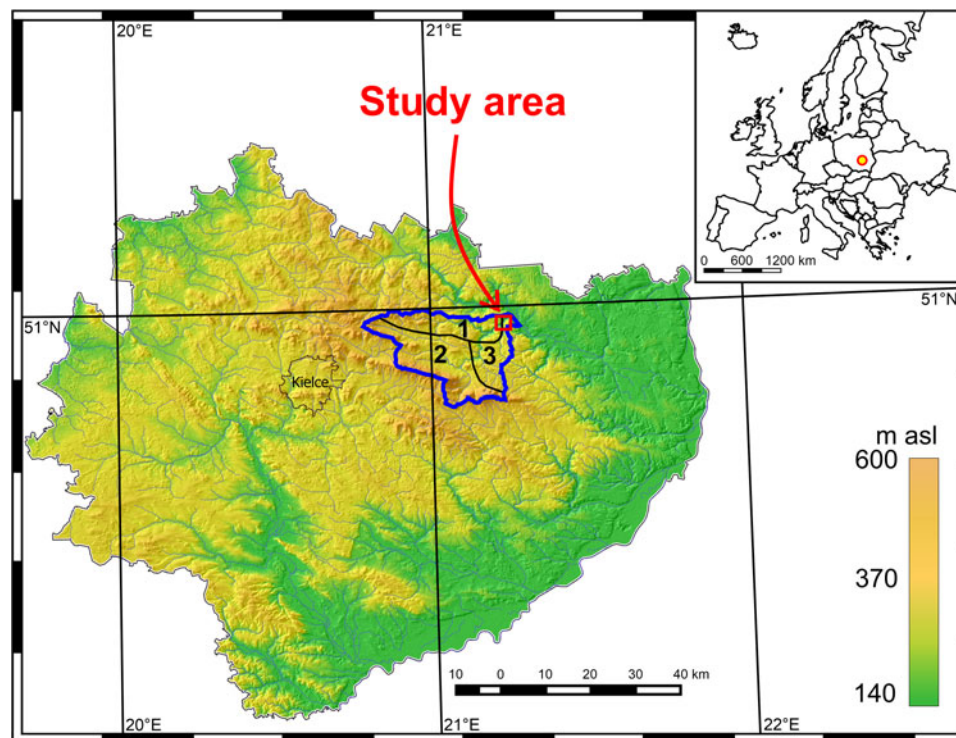
## STUDY AREA

The research area is located in the northeastern part of the Świętokrzyskie Voivodeship in the western part of the Kunów commune near the village of Doły Biskupie in the lower reach of the Świślina River (Fig. 1). The Świślina River, a 36-km-long right tributary of the Kamienna River, belongs to the middle Vistula River basin. Its sources are located at an altitude of 343.9 m near the village of Siekierno and the confluence at 177.3 m above sea level (m asl) (Bado, 2012). The average slope of the river is approximately 4.6‰ (from its sources to the confluence of Pokrzywianka River is 6‰ and 1.5‰ in the lower course) (Śliwa, 2007). The riverbed is meandering. The sinuosity index is 1.51 for the entire river length and 1.56 downstream of the Wióry Reservoir. In its middle section, the riverbed is approximately 3.5–4.0 m wide and 6–7 m downstream of the Wióry Reservoir (Bado, 2012). The Świślina River and its tributaries have a pluvial–nival regime characterized by high variability and a significant amplitude of extreme daily and seasonal flows. There are two peaks in the outflow: in March and April (caused by snow supply) and in May and June (caused by rain supply). There are three extreme

flows in the lower (Nietulisko Duże village) section: February/March, July, and October (Kupczyk et al., 1994; Koślacz et al., 2006; Suligowski et al., 2009; Bado, 2012).

The Świślina's 414 km<sup>2</sup> catchment area is located in the Kielce Upland and is extremely asymmetric, with almost no left-side tributaries. It covers fragments of three physiogeographic mesoregions: Suchedniów Plateau (the upper and middle course of the Świślina basin), the Holy Cross Mountains, and the Sandomierz Upland (Fig. 1) (Kondracki, 1977, 2002; Solon et al., 2018; Richling et al. 2021). The catchment is located in the eastern forelands of the Holy Cross Mountains, in the geomorphological macroregion of the Kielce Upland subprovince (Klimaszewski, 1978). The Świślina River valley marks the border between two mesoregions: the Opatów (Sandomierz) Upland (to the SE), and the Suchedniów Plateau (to the NW).

The study area is located in the northeastern part of the Mesozoic margin of the Holy Cross Mountains, north of the Łysogóry main range (Wróblewski and Wróblewska, 1996). In this monocline, there is a predominant NW–SE strike and a NE dip of the layers. Among the Mesozoic rocks, there are two basic lithological complexes: the lower one, dominated by clastic rocks (mainly sandstone, mudstone, conglomerates, and clays from the Lower Triassic to the Middle Jurassic) and the upper one, which consists of chemical–zoogenic rocks (various types of limestone, marl, and oolite from the Upper Jurassic to the Upper Cretaceous) (Kosmowska-Suffczyńska, 2000). The Świślina River valley near the village of Doły Biskupie is crossed transversely SE–NW by the Godów–Mnichów fold, containing the oldest rocks (from the Lower Triassic) in the whole basin (Filonowicz, 1966, 1968).



**Figure 1.** Location of the study area within a sketch map of the Europe (inset). The Świślina drainage basin (blue limit) and research area (red box) are shown on the Świętokrzyskie Voivodeship Digital Elevation Model (DEM; created by M. Frączek on the basis of data obtained from CODGIk, MGGP Aero, no. GI-FOTO.703.44.2014) with physiogeographic mesoregions (1–3) of Poland in the catchment area (Kondracki, 1977, 2002): 1, Suchedniów Plateau (342.36); 2, Holy Cross Mountains (342.34–35); 3, Sandomierz Upland (342.36).

A characteristic feature of this relief area is the vast, monotonous surfaces of the Palaeogene peneplain, which cut both the fold structure of the Palaeozoic core and the large radial undulations of the Mesozoic bedrock. The basement in most of the catchment area is covered with Pleistocene loess. Locally in the valleys, there are also fluvioglacial sands and gravels of the South-Polish (San) glaciations and Vistulian sandy-gravel alluvia (Fig. 2). Their thickness ranges from 3 to 6 m and builds an erosive–accumulative terrace up to 1.5 m above the Holocene floodplain (Filonowicz, 1968; Bado, 2012). The Holocene fine alluvium (mainly overbank facies) is made of redeposited loess (Klatka, 1958) and weathered Silurian clay slates and flood rhythmites near Nietulisko (Filonowicz, 1968). The Pleistocene loess is cut by a dense network of many young erosive forms—gullies, arroyos, and sunken lanes, which are also intensively modelled today. Headward erosion can withdraw the source funnel of such a form up to 20 m/yr (Klatka, 1958).

**AIM OF THE STUDY AND METHODS**

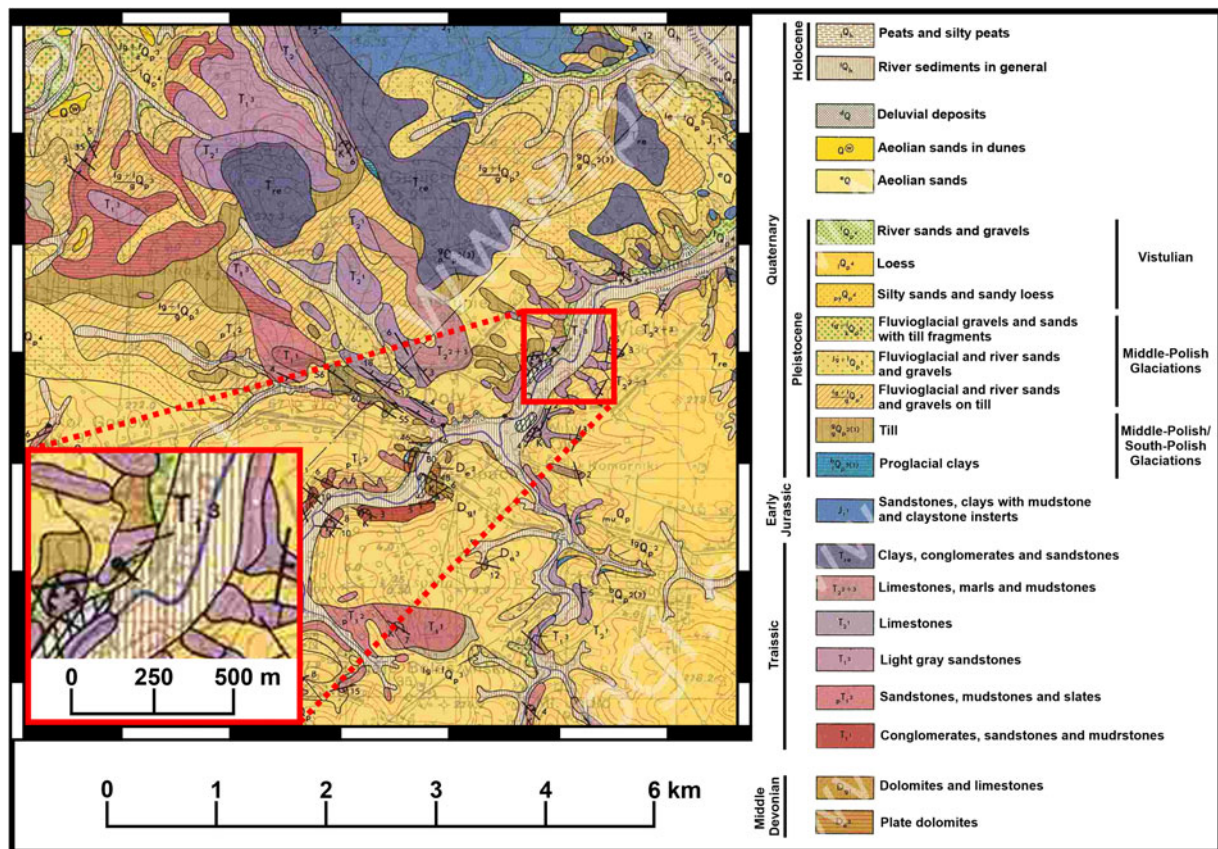
The study aims to identify the structure, especially the anthropogenic factor, of the Świślina River valley bottom in the Doły Biskupie village vicinity and to confirm and refine the results of valley sediment studies from the 1950s (Klatka, 1958) with an emphasis on prehistoric and medieval metallurgical activity impact using new research methods. Results were compared with archaeological data to verify the impact of the anthropogenic factor and the period when it occurred. This is pioneering research in the Holy Cross Mountains, based on microscopic

residue from the iron smelting found in the analysis of the alluvia. The results may be used to reinterpret the accumulation processes of other river valleys in the OPID area (Fig. 3).

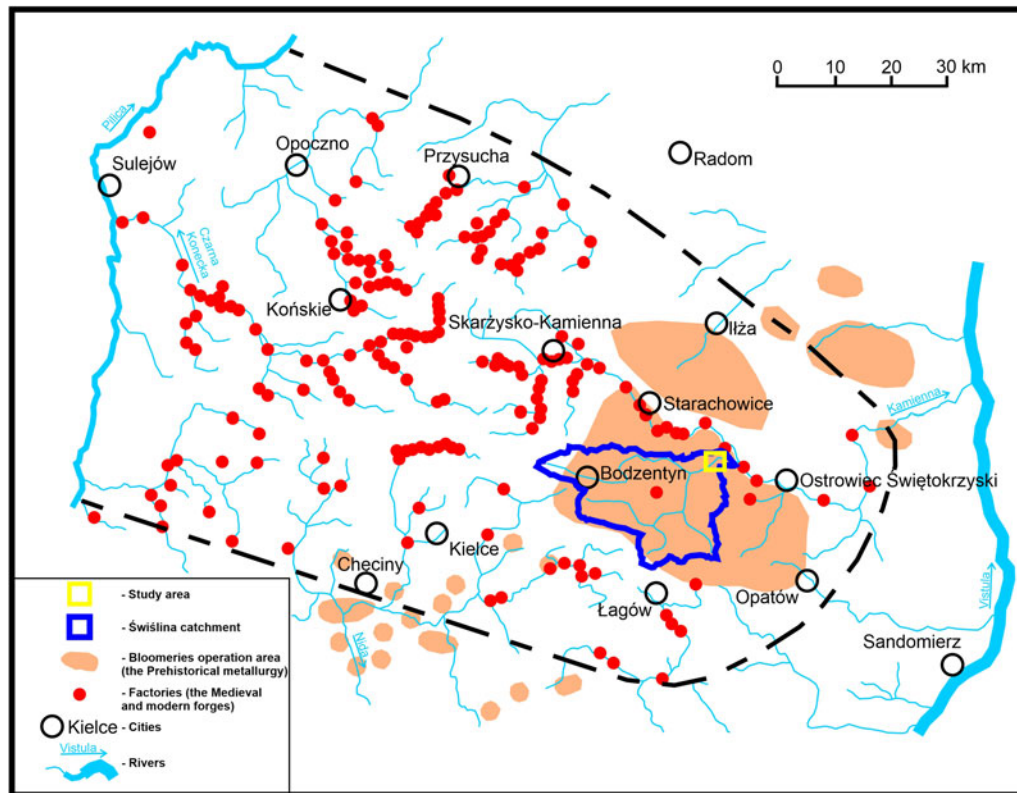
During field research, the DB1 profile was made on the left accumulative bank, and samples were taken for laboratory analysis. This profile represents the structure of the floodplain. About 40 m NW from the DB1 on the terrace, two other profiles (K1 and 2) were made earlier by Klatka (1958). Presently, the edge is completely overgrown with bushes and covered with turf, making it impossible to uncover these profiles again. For this reason, the archival profiles described in the 1950s were used in this paper.

Seven samples were taken from the profile and dried to prepare them for analysis. The grain-size analysis was carried out using a set of sieves measuring from 2800 to 63 μm (DIN ISO 3310/1) and the Retsch-Rahmen at the Geomorphological and Hydrological Laboratory of the Department of Geomorphology and Geoarchaeology at the Institute of Geography and Environmental Sciences at the Jan Kochanowski University in Kielce (Poland). All sandy samples were identical in weight (100 g) to obtain meaningful and comparable results. The finer deposit (<1 mm) measurements were made in the Mastersizer 3000 particle size analyser (Malvern Instruments Ltd). The GRANULOM program was used to graphically process the results. This program enables the calculation of Folk and Ward (1957) grain size–distribution parameters.

Geochemical analyses included pH determination using the potentiometric method with the ELMETRON CP-411 pH meter, made by suspension of samples in distilled water in a 1:2.5 ratio. The CaCO<sub>3</sub> content was determined using



**Figure 2.** Geological structure of the Świślina catchment near the study site (red box) based on Detailed Geological Map of Poland 1:50,000, sheet Stupia Nowa (Filonowicz, 1966; www.pgi.gov.pl).



**Figure 3.** The Old-Polish Industrial District (OPID) border based on M. Radwan's map (Bielenin, 1992), with updated bloomer activity areas based on A. Przychodni (2002). Study site location is in the Świślina catchment area (adapted by P. Przepióra).

Scheibler's method. The selected heavy metal element contents in the sediments were analysed with the help of Jan Horák (University of Hradec Králové). An XRF-type BAS Delta HHXRF analyser spectrometer from the Delta Professional series was used. The X-ray fluorescence spectrometry (XRF) method is based on measuring the fluorescent radiation that begins to be emitted from the sample when it is bombarded with high-energy X-rays. This method enables the identification of elements and determines their concentration. The spectrometer automatically measured each sample three to five times, and the results were averaged. The concentrations of five elements were measured (Cu, Zn, Pb, Mn, and Fe), and the values are presented in milligrams per kilogram. For the device used in this study, the following limits of quantification were determined for each of the elements: Cu = 5–7 mg/kg, Zn = 3–5 mg/kg, Pb = 2–4 mg/kg, Mn = 10 mg/kg, and Fe = 10 mg/kg (0.001%) (Klusakiewicz, 2019).

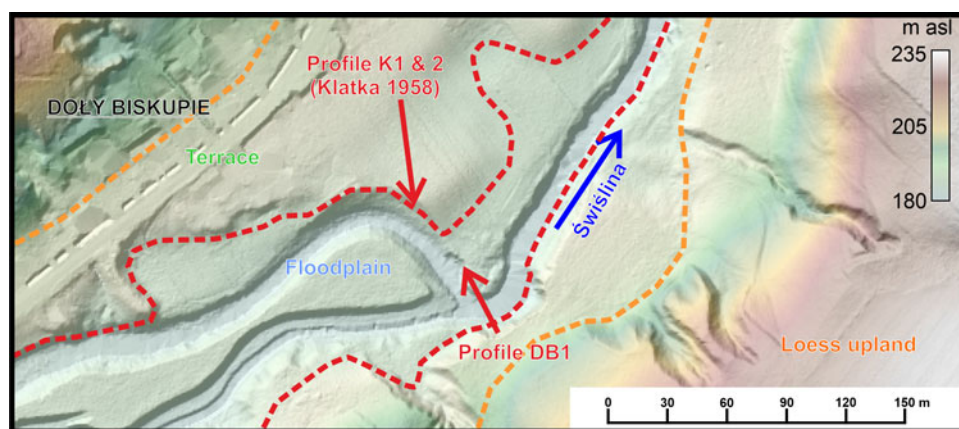
The magnetic spherule separation (MSS) method was also applied. This method has so far been used mainly by researchers in the Ardennes area (Belgium) (Richardeau, 1977; Houbrechts et al., 2020). The MSS method, slightly modified, consists of sifting the dry sample through a set of sieves to obtain a material with a 200–63 µm size range. Depending on the ferromagnetic particle, from 1 to 10 g of material was used, which facilitates further conversion of the concentration of iron spherules in the sediments (in special cases, the weight may change). The material from the compartment obtained is spread on a tray or a piece of white paper. The sample is spread over the surface by sliding a precision magnetic gripper to separate the ferromagnetic particles from the rest of the sediment. These particles are transferred from the

gripper to a microscope slide with a piece of self-adhesive double-sided tape. The material is carefully spread over the tape to keep it firmly attached. The characteristic microscopic iron balls (number of magnetic spherules per gram of material, ms/g) are counted manually under the microscope. Data were standardized and presented as magnetic spherules per 10 g in order to highlight the results obtained.

The camera research consisted of an historical and archaeological materials query, including previous publications about the study area. Graphical processing of the laboratory results obtained was also done with CorelDraw.

## RESULTS

A river gap section with steep valley slopes near Doły Biskupie, cut in the soft Lower Triassic and the Pliocene–Pleistocene rocks, separates two flat plateaus. There are remnants of the Palaeogene planation surface cutting the monoclonal Triassic inclines, which descend with steep edges 50–60 m high into the Świślina River valley. The edges of the main valley are cut by many smaller dry erosion valleys created in different ages. In the right valley slope, there is a clear levelling (plain), which could be interpreted as a rock or erosive–accumulative terrace, but the thick layer of loess masks the deeper geologic structure and the original morphology. The study site is located in this section at the estuary of the former paper mill canal (Fig. 4). Two levels can be distinguished in the valley bottom: a terrace (11–9 m arl) represented by the K1 and K2 profiles (Klatka, 1958; Fig. 5) and a floodplain (5.5–4.5 m arl) represented by the DB1 profile (Fig. 6).



**Figure 4.** Study area on the Digital Elevation Model (DEM) showing profile locations (red arrows), borders of the terrace and floodplain levels (red dotted line), and loess upland (orange dotted line) ([www.geoportal.gov.pl](http://www.geoportal.gov.pl)).

### *K1 and K2 profiles (Klatka 1958)*

Both outcrops were recorded and analysed by Klatka (1958) on the edge of the terrace. In its upper part, it is built up by overbank sediments consisting of silt and sandy silt. A large fragment of slag and iron was found in the silt intercalation of fine sand at a depth of 5 m. Charcoal occurs above 3.5 m and below 6.5 m (K1). At K2, slag and charcoal were deposited more shallowly at a depth of 2.5–1.0 m (Fig. 5). Slag and charcoal are traces of the prehistoric and medieval metallurgy (Klatka, 1958). There are channel sediments in the lower part of each profile. These are indicated by their structure and texture—medium- and fine-grained sand, bedded with the subfossil trunks.

### *Profile DB1*

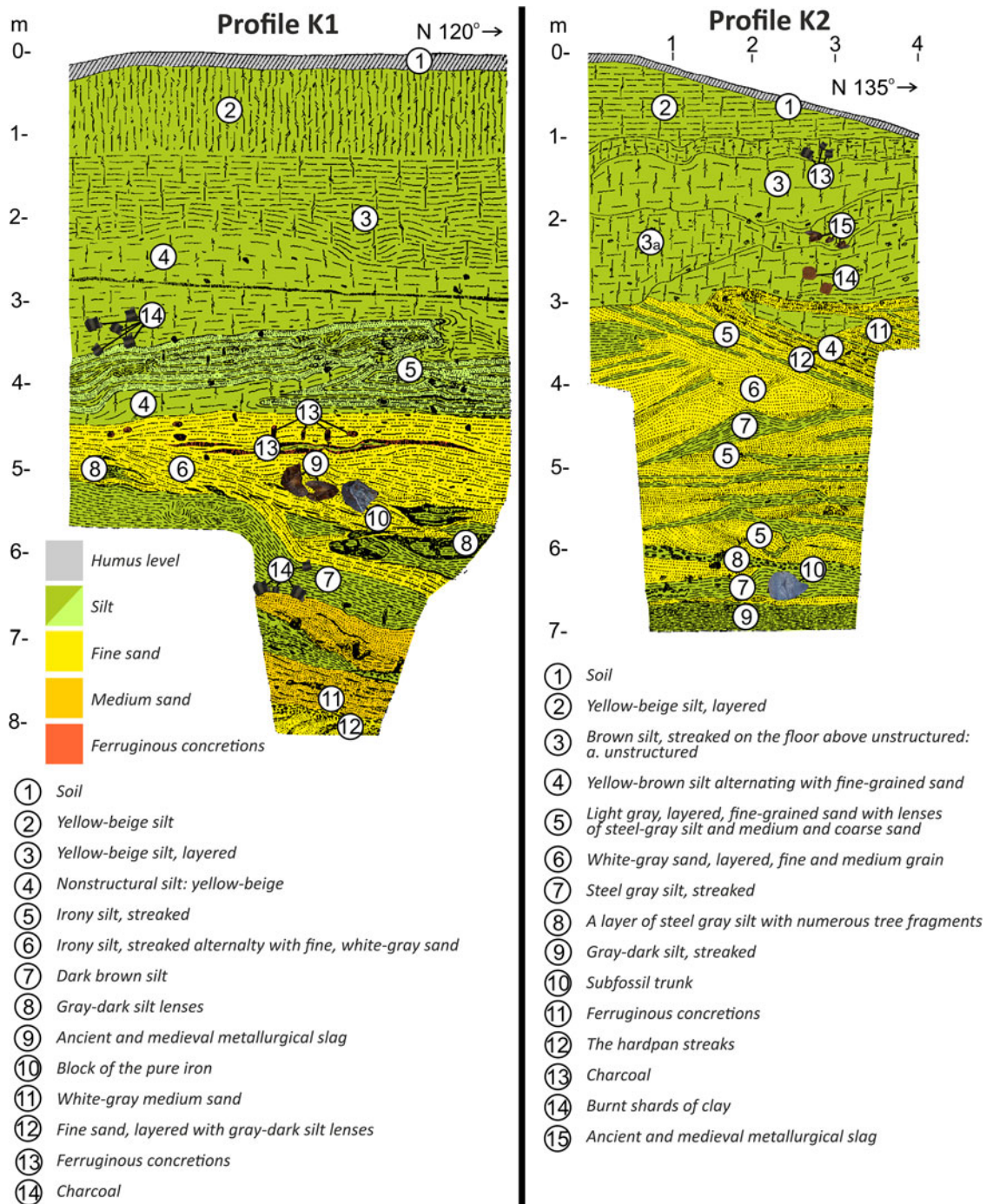
There is channel sediment in the lower part—sand with gravel (mean size [Mz] approx. 1.2 $\phi$ ), moderately well sorted (approx. standard deviation [ $\sigma_1$ ]=0.7), containing carbonate (approx. 14% CaCO<sub>3</sub> content). It is covered by overbank sediment more than 2 m thick that is composed of silt-sandy sediment (with a portion of fine sand up to 25–40%; Mz = 4–5 $\phi$ ) with a poorly expressed fining upward tendency, poorly sorted ( $\sigma_1$  from 1.1 to 1.7). In the alluvium there are two distinct sandy intercalations at depths of 1.6 m and approximately 1.0 m. The CaCO<sub>3</sub> content drops upward from approximately 14 to 2%, which causes the pH to change from neutral to slightly acidic. Geochemical analysis of selected elements (Cu, Zn, Pb, Mn, Fe) also shows an increase in their content upward of the profile, especially Cu and Pb. This tendency is visible throughout the profile but becomes clearest above the sandy layer from a depth of approximately 1.6 m (Fig. 7).

Macroscopic traces of the occurrence of larger slag fragments on the macro- (centimetres) and microscale (millimetres) were not detected anywhere in the profile. However, the separation of magnetic spherules (microslags) showed their occurrence. They were detected above the sandy layer at a depth of 1.6 m, from about 10 to 25 pieces/10 g of sediment. Their maximum is at depth of 1.0–0.3 m (in and above the second sandy layer). This maximum coincides with the abrupt increase in all five measured metals in the profile content: Fe (from approx. 3000 to 120,000 mg/kg), Mn (from approx. 100 to 300 mg/kg), Zn (from approx. 5 to 50 mg/kg), Cu (from 0 to 22 mg/kg), and Pb (from 3 to 20 mg/kg) (Fig. 7).

## DISCUSSION

Klatka (1958) discovered charcoal and slag in sediment connected with the prehistoric and medieval metallurgical activity in this region on the left bank of Świsłina River in the 1950s. The Świsłina River basin is located in the eastern part of the OPID, where ancient metallurgy dominated (Fig. 3). Slag from the prehistoric bloomeries was detected in almost the entire Świsłina catchment area (Radwan, 1963; Bielenin, 1992). Metallurgy was most likely still active here in the Middle Ages, but there is no information about forges along the river on archival maps, even from the modern period. Also, examining historical materials did not reveal the presence of metallurgical furnaces in the vicinity (Zieliński, 1965; Bielenin, 1992). The ruins of a modern rolling mill (a sheet metal works) at Nietulisko Duże near the estuary connecting the Świsłina to the Kamienna River (Suliga, 1995), dating from the nineteenth century, are the only remnants of modern metallurgical activity close to the study site. Also, a former paper mill 400 m upstream from the study site was previously in operation until the 1980s.

The traces of the metallurgical industry are mainly macroscopic slag fragments and iron spherules (Dungworth and Wilkes, 2007). Their absence in the sediment, however, does not mean that there was no metallurgical activity in the immediate vicinity. Slag can be redeposited during high river discharges or floods. The last large flood took place when the embankment built during the construction of the Wióry Reservoir in 2001 was destroyed after heavy rain (Biernat and Ciupa, 2007; Ciupa, 2012). Very similar catastrophic events on rivers in the Holy Cross Mountains have occurred quite often in the past. Historical materials show, for example, in the Czarna Konecka and Kamionka Rivers (Kalicki et al., 2019a, 2019b; Przepióra, 2021), many flash flood events taking place in the twentieth century or even the nineteenth century after anthropogenic small-scale water-retention system hydrotechnical structure failure (Kalicki et al., 2019c, 2020). The presence of magnetic iron spherules in sediments should also be interpreted in terms of their redeposition during catastrophic floods from this period. Usually, this material is transported by the wind (aeolian transport) up to 10 km from the source (e.g., bloomeries) and only later redeposited by fluvial processes (Houbrechts et al. 2020). The occurrence of macro- and microslags in the sediments of the Świsłina floodplain can therefore be interpreted as traces of prehistoric (Roman period) and probably medieval metallurgy



**Figure 5.** The K1 and K2 profiles of the Świślina terrace at Doty Biskupie (Klatka, 1958; adapted by Ł. Podrzycki and P. Przepióra).

in the catchment area of the OPID (Radwan, 1963; Bielenin, 1992; Orzechowski, 2007).

The Świślina floodplain in the study area is composed mainly of sandy silts (Figs. 6 and 7). There is a distinct sand and gravel layer on the bottom (lag deposits), and at a depth of 1.6 m there is a thin layer of sandy overbank sediment. The  $\text{CaCO}_3$  content increases with depth and reaches its highest value (about 14%) at the depth of the lag deposits. It is most likely related to the geologic structure, where the lag level consists of (among others) limestone, but the  $\text{CaCO}_3$  content may also be influenced by the remains of malacofauna. There is also a visible pH increase in

the profile ranging from slightly acidic to neutral, and even alkaline.

Geochemical analysis also showed a clear increase in the content of selected heavy metal elements in the sediments where iron spherules were detected (Fig. 7). The increase in the Fe, Mn, Zn, Cu, and Pb content perfectly reflects the appearance of metallurgical residues in floodplain sediments at the same depths. A similar situation was described in the Kamionka River valley, where a significant increase in Fe content was noted in sediment with metallurgical slag (Przepióra, 2021). Near the study area there is a lack of major roads, rail tracks, or industrial facilities as potential

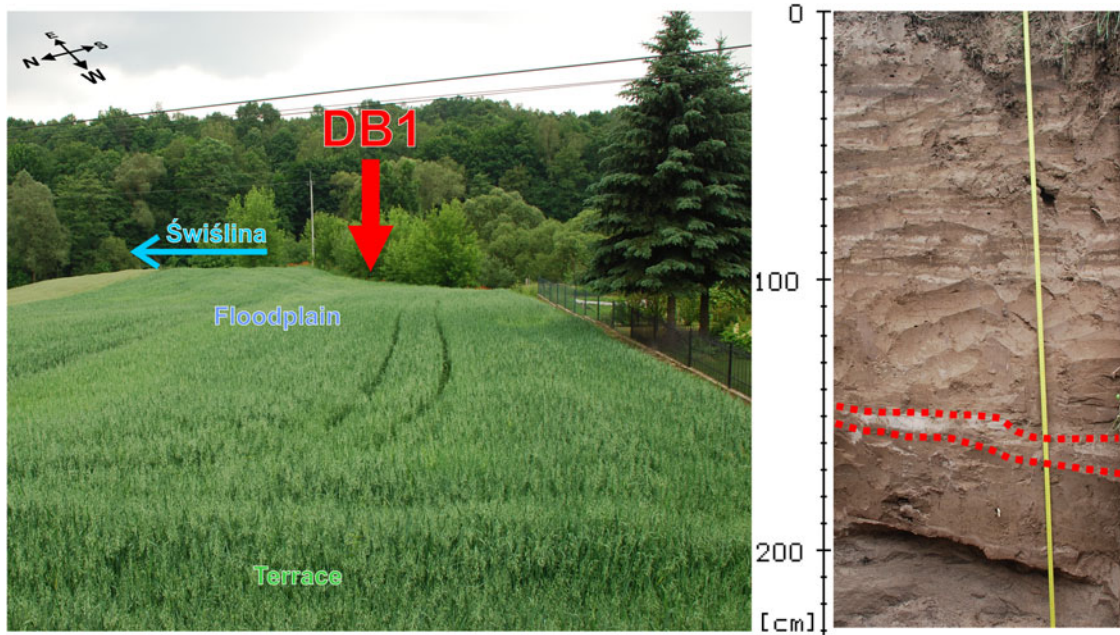


Figure 6. View of the study site towards the river (left) and the location of the DB1 profile (photo by T. Kalicki 2014).

sources of trace metals. Agricultural processes, however, could provide an alternate explanation for such pollutants in the soil.

The report from the years 1995–2015 (Kiczor, 2017) shows the geochemical background (samples from the Doły Biskupie site were collected and analysed in 2014). The nearest soil

measurement stations in terms of contamination with selected trace elements are in Wąchock (approx. 20 km NW) and Ćmielów (approx. 24 km E). Acidic soils with a pH from 4.6 to 5.0 predominate in the study area. None of the trace elements in the study area exceeded the norms during the study period.

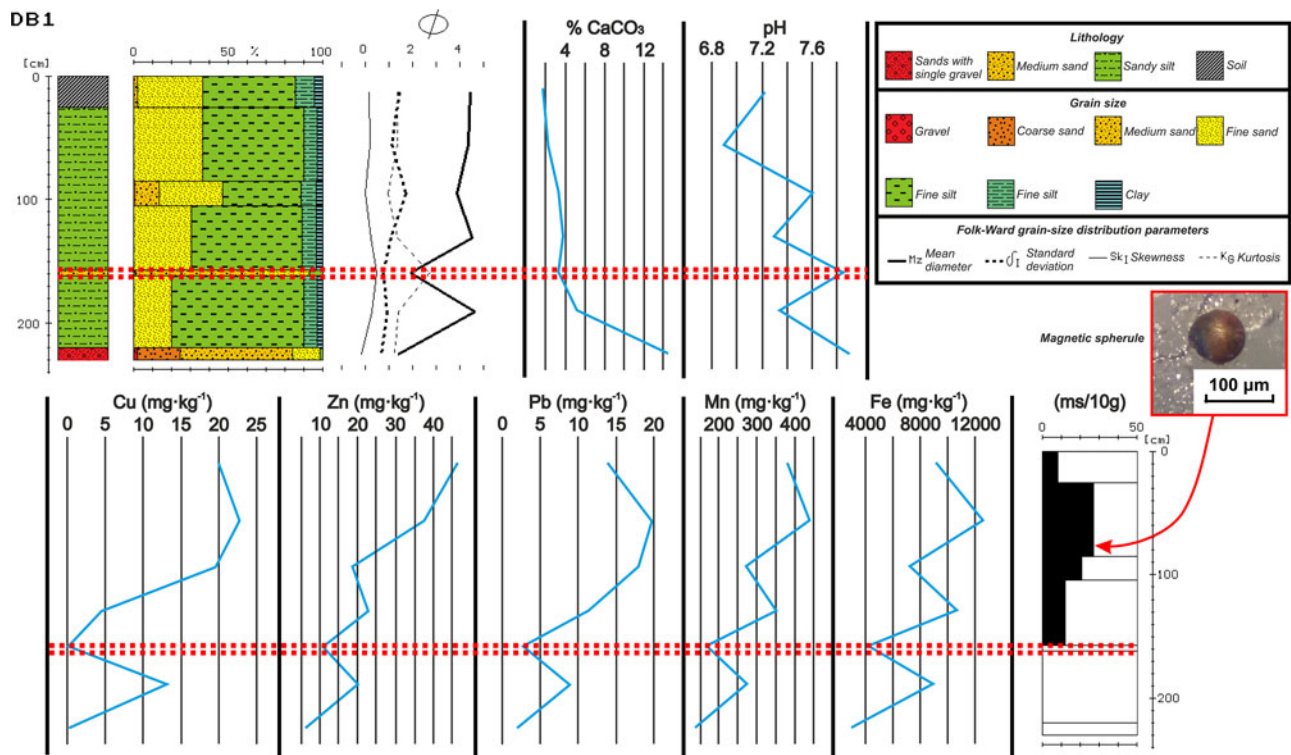


Figure 7. DB1 grain-size profile with Folk and Ward (1957) grain size-distribution parameters; CaCO<sub>3</sub> content; sediment pH; concentrations of selected elements (Cu, Zn, Pb, Mn, Fe); and the microslag content in magnetic spherules per 10 g of matter (ms/10 g) with the probable level where sediment accumulation began after the period of metallurgical activity (red, dashed line).

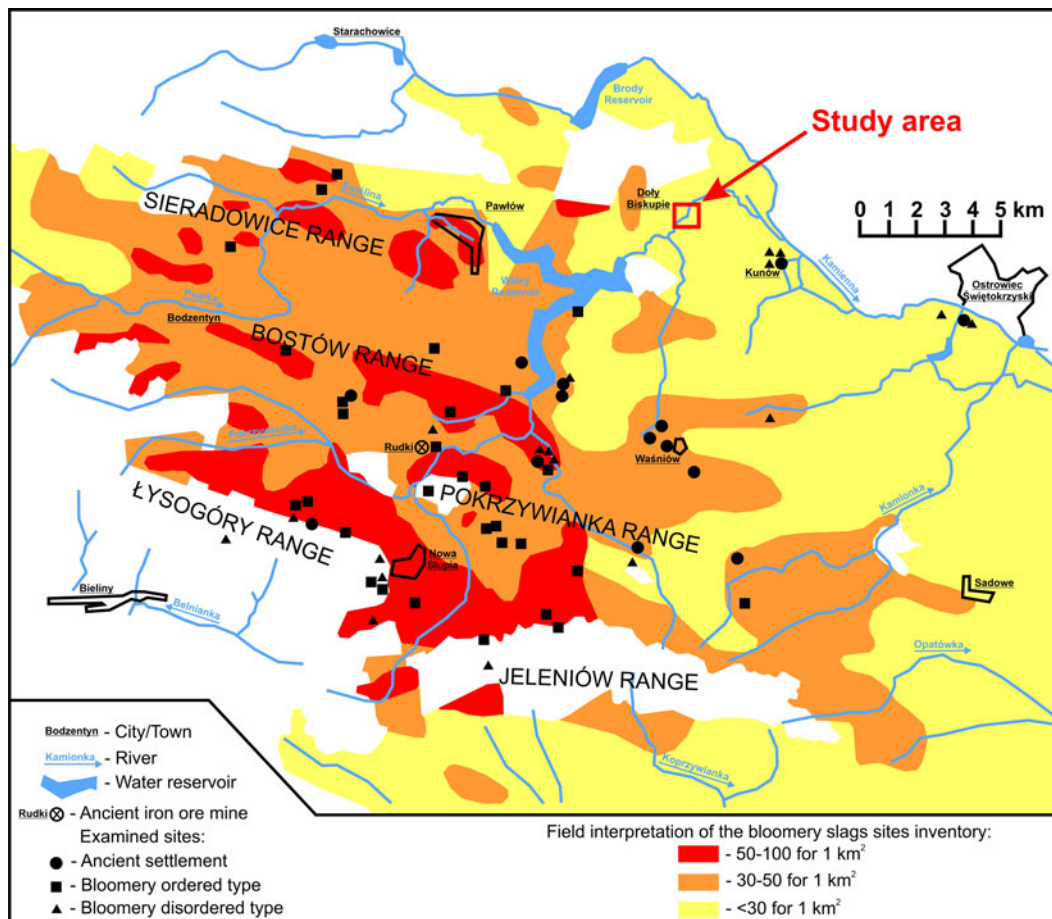
Only in Ćmielów was a higher Pb content detected, at approximately 70 mg/kg in 2015. However, the soil was still classified as slightly contaminated. The concentration of Cu was only 8 mg/kg, and Zn about 35 mg/kg. The values at the measurement point in Wąchock were very similar. Only Cu exceeded 30 mg/kg during the measurement period, and this value dropped to 3 mg/kg in 2015. The soils in the study area have a natural content of specific chemical components. The lack of major changes in the concentration of the measured substances or elements indicates a slight anthropogenic impact (Kiczor, 2017). These data confirm that the geochemical results from Doły Biskupie are within the limits of trace material contents shown in the report.

Many iron spherules were detected in the sediment above the flood layer at 1.6 m. These are most likely traces of the prehistoric (Roman period) or medieval metallurgical activity that Klatka (1958) wrote about. It has been experimentally confirmed that microscopic artefacts are of anthropogenic origin and can act as tracers for metallurgical activity (Dungworth and Wilkes, 2007). Iron spherules occur only above the flood layer, which may suggest that the younger sediments of the floodplain were deposited by the river during the period of metallurgical activity in the Świślina basin. However, there are no data about larger metallurgical plants from the last few centuries operating on the Świślina River, apart from the nineteenth-century sheet metal works in the confluence at Nietulisko Duże, downstream of the study site. The detection of microspherules in alluvia redeposited by the river

excludes the possibility that they are product of activity of later forges in the nearby Kamienna valley. However, there is only one known historical iron factory in the central part of Świślina catchment (Fig. 3). A single instance of metallurgical activity at a great distance would not contribute microspherules to the Doły Biskupie study site.

Of greater importance are traces of the largest concentration of prehistoric metallurgical activity in this part of Europe that have been preserved in this area (e.g., Orzechowski, 2007). Microspherules were most likely redeposited by the river from Świślina catchment area, especially the upper section of the river, where prehistoric metallurgy was more intense. There is a much larger number of bloomery sites, the density of which is estimated to be up to 50–100 for 1 km<sup>2</sup>. In the immediate vicinity of Doły Biskupie, there are far fewer of these sites, but the estimated density based on the inventory is up to 30 for 1 km<sup>2</sup> (Fig. 8). As Klatka (1958) suggested, large fragments of slag detected in the K1 and K2 profiles, due to their size and location, could rather be of local smelting origin (in situ). Because they are in fluvial cut and fill, however, this slag was most likely also redeposited from a site at a much shorter distance. Unfortunately, it is impossible to accurately determine the age of slag found in the sediments based only on the Klatka (1958) work.

The study site in Doły Biskupie is located in the gap section of the river and lack of historical metallurgy activity in its basin confirms that iron spherules found here may be an indicator of the



**Figure 8.** The main area of ancient iron metallurgy in the Holy Cross Mountains based on the 1950–1990 inventory results of K. Bielenin, Sz. Orzechowski, and T. Wichman (adapted by Rubinowski [1992], and later by P. Przepióra).



prehistoric metallurgical activity from the entire Świślina catchment area (Fig. 8). Relatively few iron spherules were present in the Świślina River alluvia (less than 30 in 10 g of material) compared with other research results, for example, from the Ardennes rivers (Belgium) (more than 100 in 1 g of material) (Houbrechts et al., 2020) or from the Kamionka River (Poland) (more than 25 in 1 g of material) (Przepióra et al., 2022a, 2022b), representing medieval and modern metallurgical activity study sites located near remnants of historical forges.

It should therefore be considered that the microscopic iron spherules preserved in the floodplain sediment are not in situ. This is confirmed by their location in the middle and upper part of the profile, above the clear flood sandy layer, which may signal fluvial events and changes in the Świślina basin. The re-deposition process of microscopic artefacts in Świślina could be similar to those at the Czarna Konecka River (Przepióra et al., 2021), where only a few spherules were found in young delta sediments (i.e., washing out the spherules from alluvia and river incision in older sediments without microartefacts). A large water reservoir built upstream from the study site at the beginning of the twenty-first century may currently restrict the delivery of the material, so iron spherules found in profile may have been deposited later during the catastrophic floods, for example, rupture of a dam in 2001 (cf. Biernat and Ciupa, 2007; Ciupa, 2012).

Very comparable results were obtained in studies from river valleys of a similar mining and metallurgical district in Wallonia (Belgium), where the method of searching for macro- and microscopic slag as well as for magnetic iron spherules was applied (Houbrechts, 2007; Houbrechts et al., 2003, 2004, 2020; Houbrechts and Petit, 2003, 2004, 2006). However, these results concerned only medieval and post-medieval metallurgical activities, as confirmed by historical materials. This research was mostly done near a former forge. The MSS method has also recently been successfully used on other rivers of the Holy Cross Mountains, including the Kamionka River (Kalicki and Przepióra, 2019; Przepióra et al., 2019, 2022a, 2022b; Kalicki et al., 2021c), where the medieval and modern metallurgical activity also predominated. A distinct postindustrial layer was also found, consisting of an accumulation of iron spherules within the floodplain, but this time from modern forges.

## CONCLUSIONS

The Świślina River valley is a diverse area in terms of geology and relief due to the thicker loess deposits, which occur especially in its lower section. Many dry valleys and gullies indicate intense erosive processes. Transport of material by fluvial processes filled the valley bottom with silty and sandy sediments. Detailed analysis of sediment lying at the Świślina Valley bottom near Doły Biskupie show it is younger alluvium of the floodplain, with many macro- and microscopic artefacts related to the smelting of iron ore.

In the mid- twentieth century, traces of the prehistoric (Roman period) and medieval metallurgy (slags) were discovered in the terrace sediments. Modern research methods confirm the presence of a sediment layer that most probably accumulated during the period of bloomery activity, which was widespread in the Świślina basin in the OPID. Historical and cartographic materials, on the other hand, exclude the possibility that the slags were from the medieval or modern metallurgy period. They were deposited directly in the vicinity of the former metallurgical furnace or redeposited from the upper sections of the basin (e.g., during a flood),

where the remains of bloomeries in the Holy Cross Mountains were discovered in great numbers.

The cause of geochemical changes in the study profile may be caused by natural (geologic structure) and anthropogenic factors (road transport and agriculture); however, iron spherules detected in the alluvium indicate the most likely source of these pollutants. The presence of microscopic artefacts in sediment with an increased content of trace elements may have been caused by an anthropogenic factor related to the prehistoric metallurgical activity. The Wióry Reservoir dam, built at the beginning of the twenty-first century, can effectively capture pollutants from the upper part of the catchment area. The iron spherules could have been redeposited from the upper catchment from before the dam construction during the flood of 2001, or they may also indicate the close presence of an additional bloomery site. Results obtained from the Świślina River valley, including the analysis of archaeological and historical data, might indicate that iron spherules from the prehistoric metallurgical activity (bloomery) period were detected for the first time using the MSS method.

MSS, combined with other methods, could be extremely useful in further research of other OPID catchments to study the human–environment relationship and could also contribute to detection of further bloomery sites in other river catchments of the Holy Cross Mountains region.

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