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RECONSTRUCTION OF POST-MINING ATTENUATION OF HEAVY METAL POLLUTION IN SEDIMENT OF THE ZLATÝ POTOK, EASTERN SUDETY MTS

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Abstract: The article presents investigations of heavy metal pollution in overbank and river bed sediments of the Zlatý Potok (Golden Brook) in Eastern Sudety Mts. northern slope and foreland. The region of former gold mining in Zlaté Hory (part of Eastern Sudetes), situated at the Czech-Polish border, was well known as one of the largest gold producers in the Czech lands since at least early medieval times. In the 20th century production was extended to polymetallic ores. In 1965-1993 about 6.5 mln tons of Cu ores were extracted with average content of Cu of about 0.5 %. The region is drained by Zlatý Potok and its tributaries, which cross the Czech-Polish border. Estimation of the former sediment pollution and their post mining changes were attempted by analyses of heavy metals concentration in a series of 5 vertical profiles outcropped in the upper reach of this river and in 7 profiles of the meander bend in its lower reach as well as by analysis of channel bed sediments along the entire 40 km river course. Despite considerable efforts in restoration of the area of spoil heaps and a former settling pond, an increase in Zn pollution of the most recent overbank deposits in the upper reach was observed. A peak of these metals is preceded by lower lying peaks of Cu and Pb. Peaks are related to the largest extraction of Cu in 1960s and 1970s and its decline, which was accompanied by the increase in Zn production at the very end of the mine activity. High pollution of the river bed sediments in Zlatý Potok and its tributaries was identified as the main source of contemporary overbank Zn and Cd pollution in this channel reach. However, this pollution source is small considering the load of pollutants stored, because recently it has not affected lower channel reaches, where peaks of Cu, Zn and Cd decrease simultaneously toward the surface in most of the vertical profiles investigated there. This effect is confirmed by generally low pollution level of the channel bed sediments along the entire middle and lower reach of the Zlatý Potok.

Keywords: sediment, river, heavy metals, pollution, mining, mine restoration

1. INTRODUCTION

It is well recognized that metal mining and processing is the most important source of heavy metals in fluvial systems. The number of active and historical metal mines, which are unevenly dispersed throughout the world, reaches several tens of thousands. Mining areas, even if drained by small streams, may also affect large river systems and impair aquatic habitat over distances exceeding hundreds of kilometers (Byrne et al., 2012). Pollution of rivers arises from erosion or leaching of mine waste dumps, flotation ponds, discharge of mine waters or breaching of tailing dams. Whereas modern mines often apply techniques which reduce penetration of river systems by metal pollutants, previous and historical mines worked without particular care about environment. For this reason, sediments accumulated downstream the metal mines can be a virtual archive of history of environmental impact and the changes of metal pollution in vertical sedimentary sequences may reflect, to some extent, changes in metal production (Ciszewski & Turner, 2009). These reconstructions may also be used as a valuable tool to assess efficiency of post-mining remedial activities at mine sites (Ciszewski et al., 2012).

Accuracy of the reconstruction of pollution history in a river system depends on the sampling density and the average thickness of annually deposited layers in the sediment vertical profile. Fine grained deposits of the slow and constant accretion rate over a long period of time are considered to be the most suitable for such a reconstruction and recently there have been some successful high-resolution reconstructions of the industrial impact in lake sediments (Schindler & Kamber, 2013), oxbow lake (Nguyen et al., 2009), river water reservoir (Grygar et al., 2012), and river estuary (de Mahiques et al., 2013). Fluvial overbank deposits as such are more difficult for such reconstructions because of lateral reworking and mixing with parent catchment material and extremely diverse thickness of sediment deposited across the river floodplain, which is specific for a particular flood and floodplain morphology (Wyzga & Ciszewski, 2010). Additionally, metal variability in overbank profiles may by affected by post-depositional remobilization processes (Ciszewski et al., 2008). Nevertheless, there are several historical floodplain pollution histories deciphered from vertical profiles of fluvial deposits which are based solely on historical records of metal production or are supported by ^{210}Pb and ^{137}Cs dating and careful selection of the sampling site, fraction of the analyzed sediments and sampling density (Lokas et al., 2010, Grosbois et al., 2012).

Post-communistic period of the end of the 20th century in all central European countries was characterized by the decrease of industrial production. Numerous plants were forced to obey more strict environmental law and introduce more efficient production technologies. The least effective plants including metal mines were closed, leaving the problems related to expensive remediation of mine sites. In some of them in the Czech Republic, remediation of mine sites with long extraction history was carried through. Nevertheless, some recent investigations downstream the mines indicate large pollution of the river sediments, which constitute important secondary source of river water pollution (Žak et al., 2009). In no case the influence of these sources on time related pollutants attenuation and downstream river sediment pollution was considered. The mine in Zlaté Hory Mts. in the northern Czech Republic is an example of such a plant (closed in 1993) and of its successful remediation. Despite the extensive mining in Zlaté Hory Mts. in the 20th century, the pollution of the Zlatý Potok (Golden Brook) which received mine waters was not recognized because most of the river course crosses the state border and flows onto Polish territory. Moreover, no predictions of time related changes in river sediment pollution and influence of mine remediation on river pollution were performed. The aim of the presented studies is to reconstruct the 20th century history and the contemporary state of the Zlatý Potok sediment pollution and focus them on changes in the post-mining period.

2. MATERIALS AND METHODS

2.1. Study area

The Zlaté Hory ore district, about 25 km^2 in area, is situated in the northern part of Eastern Sudety Mts., called Zlatohorská Highland. It is the mid-mountain ridge (500-900 m a.s.l.) descent northward down 500 m high, steep slope towards the undulated loess Głubczyce Plateau (350-250m a.s.l.). Main ridge of the Zlatohorská Highland is build up mostly of metamorphic rocks. Eastward they penetrate under the Devonian and Carboniferous sandstone-schist complexes. The northern foreland of this ridge is covered with silty-sandy tertiary deposits, capped by Quaternary glacigenic deposits related to two advancements of Scandinavian ice-shield. The loess cover is the uppermost complex, related to the last Pleistocene cooling. The valleys dissecting this territory are filled with sandy-silty alluvia overlaying the coarse sands or gravels.

The Eastern Sudety Mts. and its NE foreland is situated within the temperate climatic zone of Central Europe, between 50° 00' Nφ - 50° 15' and 17°00' - 18° 20' Eλ. It receives up to 1000 mm of precipitation per year, and its foreland between 650 to 750 mm/year, mostly during the vegetation season (Quitt vide Safar, 2003). During vegetation period heavy short rainstorms occur here up to for 145 days/year (Bielec-Bąkowska, 2002). Also during the winter/spring break seasons, the snow melting events cause moderate but frequent floods. They result in flooding of the lower valley floor steps or vegetated gravel bars in the channel and a build-up of fine alluvia.

Mountains of the ore district are composed of Devonian epimetamorphic volcano-sedimentary complex forming a complicated anticlinorium. Lensoidal and high-angle ore bodies contain mineralization with Pb-Zn and Cu. Moreover, the zone with disseminated, tectonically controlled mineralization structures is enriched with Cu-Zn (Au, Ag, Pb). The Zlaté Hory Mts. mining district contains five ore deposits: two Cu deposits containing sulphides, mainly pyrites with chalcopyrites, and three polymetallic ones containing sphalerite, galena and native gold (Jirasek & Hrabalek, 2007).

Placer Au deposits in the piedmont area in the Zlaté Hory district were mined probably by Celts as early as the Iron Age. Documented gold mining of Quaterary alluvia and of periglacial slope covers started in the Middle Ages when mines were built to the depth of about 60 m and drained by dewatering mine galleries of several km in length. The ore mining peaked in the 16th century reaching primary lodes containing 33 mg$\cdot$kg^{-1} of gold, 19 mg$\cdot$kg^{-1} of Ag and about 3% of Pb. The depth of mines exceeded 250 m but the exploitation was interrupted many times by flooding, wars, and progressive ore exhaustion. Since then the exploitation declined and in the 18th and 19th century the mining focused on vitriol, pyrite and chalcopyrite used for the production of sulphuric acid (Večeřa & Večeřova, 2010).

Ore mining in the 20th century started in 1965 and almost 6.5 mil. tons of Cu ore with 0.5% of Cu were extracted until 1990. The length of the galleries drifted in the mine amounted to 100 kilometers. Ores were reworked through the flotation technique and waste was placed on settling ponds and on heaps at the bank of the Zlatý Potok. Copper concentrate of $CuFeS_2$ with Cu content about 20-23% were filtered and transported to smelter plants in Krompachy (Bernatik, 2004). Nevertheless, waste was neutralized with 5-7 $kg \cdot m^{-2}$ of lime and isolated with 0.5 m of loams and 0.2 m of organic soil. Mine waters were clarified with a mixture of lime and bentonite and after partial reduction of Zn, Cu and Fe compounds were discharged to the Zlatý Potok (Tisnovska, 2004). Production of Cu concentrate rose from 260 kt in 1965 to 280 kt in 1975 and 320 kt in 1980. Later the production of Cu decreased and since 1988 a new technology of selective flotation enabled higher Zn production from ores exploited from eastern and western ore bodies. For example in 1990 about 80 kt of ore containing 1.2% of Zn was obtained, in 1991 - 240 kt of Zn ore, in 1992 – 211 kt and in 1993 - 131 kt of the ore containing also several to dozen g/kg of Au. The Zn ore extracted between 1988 and 1994 amounted to 750 kt (Bernatik, 2004).

2.2. Sediment sampling

Samples of overbank sediments were collected in the upper and lower reach of the Zlatý Potok (Fig. 1). The upper site was located seven kilometers downstream the former mine on the right bank of the river. The lower site was located in the meander bend about 30 km downstream the first site. On the first site three vertical profiles were located in the terraced floodplain with edges which mark former channel banks of different heights. The ZPGI profile was located in a bank outcrop to the average water level in the river channel at the depth of 1.2 m (Fig. 2). Here, the floodplain is up to 50 m wide and falls gently outward the present channel bank.

The ZPGII profile was situated at the terrace edge about 1.6 m high, separated from the floodplain by remnants of the paleochannel, filled partially with fine deposits. The ZPGIII profile represents a higher terrace level which raises about 1.2 m over the depression of the former river channel and about 1.7 m over the mean water table. The profile was exposed with a spade to the depth of 0.9 m in fine grained sediments which cover older gravels at the bottom. The other profiles: ZPGIV and ZPGV represent outcrops of the contemporary and former channel bank (Fig. 2). Both are about 1.3 m high over the water level. In the lower valley reach, six profiles were exposed along the meander axis on the left river bank. The surface of the meander is uneven with remnants of active and fossil chutes. The older, inner part of the meander is overgrown with trees of Salix sp (Fig. 3).

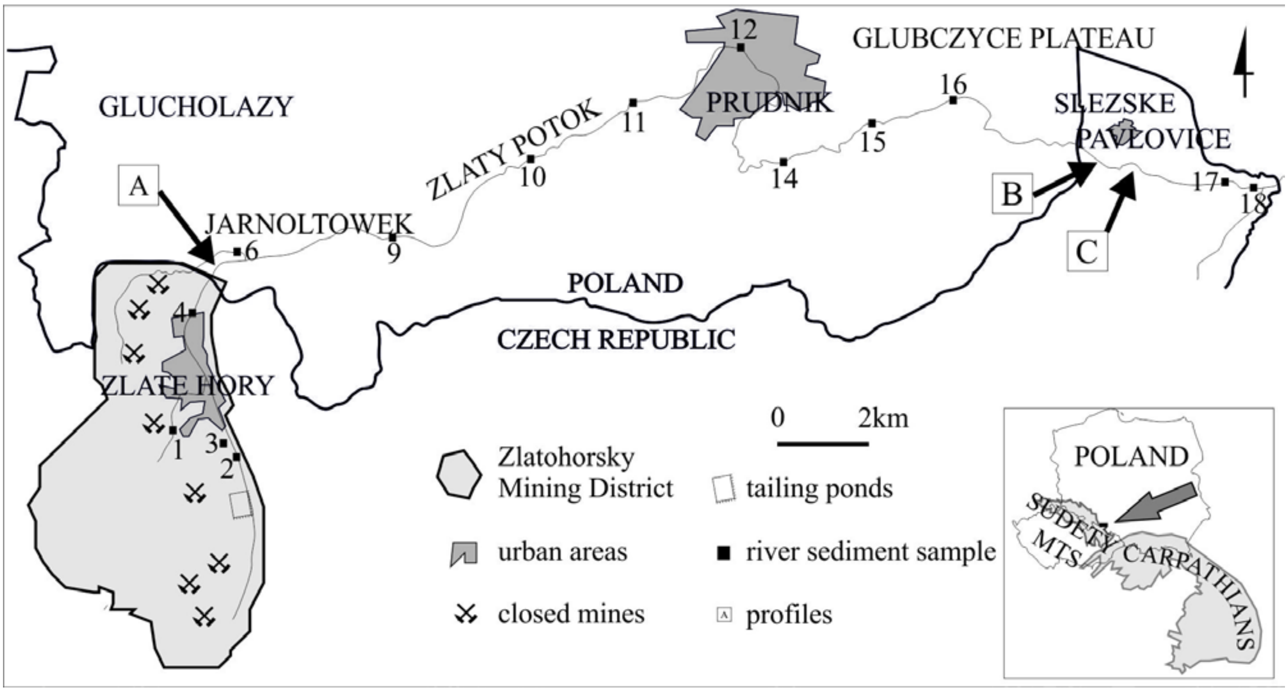

Figure 1. The study area with location of sediment samples

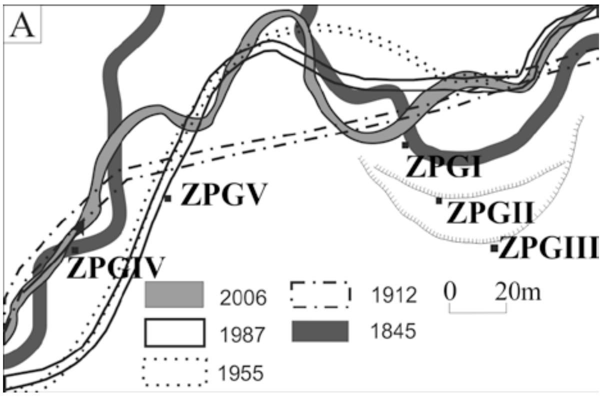

Figure 2. Location of overbank profiles in upper reach of the Zlatý Potok.

The ZPI profile was dug on the lowest level of the meander to the depth of 70 cm. Each of the consecutive profiles was dug in higher floodplain levels up to the depth of 3 m. Also on the highest, 3 m level, an additional ZPVII profile was outcropped on the opposite river bank about 200 m downstream.

Moreover, along the entire course of the Zlatý Potok and its tributaries draining the mining district, fine grained bottom sediments were sampled at the banks of the channel (Fig. 1). For this sampling quiet embayments and slack water deposits were selected.

2.3. Sediment analyzes

Sampling of river bed sediments was focused on estimation of the contemporary metal content and by comparison with metal content in sediments of the mining era in vertical profiles the rate of post-mining changes in sediment pollution was evaluated. Sediment profiles were outcropped with a spade or were drilled with a hand auger. The profiles were sampled at 2–10 cm intervals, in particular in their upper sections. In those profiles where distinct layers occurred, sampling density was related to the differences in sediment stratigraphy. Sediments without distinct stratification were sampled at 10–20 cm intervals. The samples were divided and one portion of each sample was wet sieved through 0.063 mm sieve and the content of fine fraction was determined.

In the other part of a sample that passed through 1mm sieve the losses on ignition at 550ºC were determined. Metals were brought into solution in Teflon bombs using a microwave digestion technique (10 cm^3 of 65% HNO_3 and 2 cm^3 of 30% H_2O_2). Concentrations of metals: Zn, Cd, Cu and Pb were measured with an atomic absorption spectrometer (ICE 3500 Thermo Scientific). Changes of the channel position and the maximum age of deposits were determined by comparison of the present channel position on ortophotomaps of 2009 with that of 1955 and on topographic maps: two from 1936 and 1880 (1:25 000) and a map from 1845 (1:28 800).

3. RESULTS

Pollution of the Zlatý Potok channel bed sediments decreased markedly from the upper reach downstream (Table 1). There were very high concentrations of Cu, Zn and Cd in the Zlatý Potok and its tributaries on the area of the ore district (marked in grey in the Table 1).

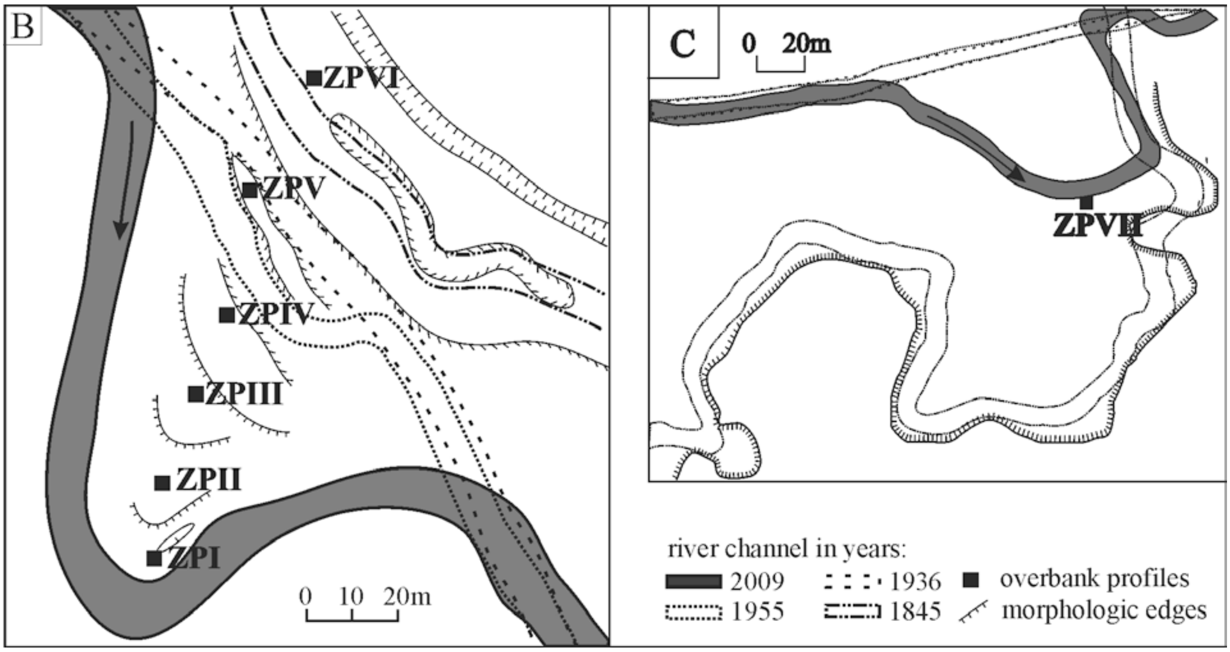

Figure 3. Location of overbank profiles in lower reach of the Zlatý Potok.

Table 1. Content of heavy metals in the sediments of Zlatý Potok.

Sample	Metal concentrations [mg·kg^{-1}]			
	Cu	Zn	Pb	Cd
1	1111.7	5948.0	55.7	22.18
2	3534.2	8764.0	72.9	47.44
3	755.2	1807.1	97.0	6.34
4	158.6	1163.3	66.1	6.38
6	224.1	977.0	133.4	4.68
9	162.4	914.0	79.3	1.49
10	186.5	1016.5	69.2	3.15
11	199.9	1018.8	74.9	5.02
12	67.4	50.5	10.1	0.28
14	112.8	727.2	64.3	1.87
15	150.0	716.8	62.27	2.31
16	110.0	534.9	64.28	1.71
17	79.8	465.0	64.50	3.48
18	79.5	474.3	65.02	3.39

In the Zlatý Potok downstream the former flotation pond and in the Zámecký Potok (Zamecky brook) which formerly received mine waters, concentrations of Cu, Zn and Cd exceeded about 100 times the values usually considered as a natural background (Lis & Pasieczna, 1995). Concentrations dropped several times below Zlaté Hory village and decreased slowly to the Prudnik city.

There, concentrations decreased over a short reach downstream the mouth of the relatively clean tributary (Prudnik river). Downstream the city of Prudnik, in the lower course of the river, sediments were moderately polluted with metals, with Cu, Zn and Cd content exceeding several times the geochemical background. Over the entire river reach, Pb concentrations remained at the same low level. This indicates that the mining activity was not an important Pb pollution source. However, comparison of this metal content to its average values in alluvial deposits of Poland (Lis & Pasieczna, 1995) suggests, that the background values of this catchment were naturally elevated because of drainage of a metamorphic bedrock.

Sediment profiles in the upper reach were located in the area of the dry water reservoir established in 1903. In this reach the Zlatý Potok flows across a bottom of the about 1 km wide, flat surface of an alluvial cone inclined eastward, which is dammed by up to 10 m high dike. The wide surface favored changes of the river channel position and accumulation of fine silty-sands which cover fine and medium gravels with a layer of up to about 2 m in thickness. The depth of these gravels is related to the position of the channel bed which was revealed in particular sampled sediment profiles. The ZPGI profile consisted of fine grained deposits with content of silt exceeding about 50% (Fig. 4). The deposits rested on gravelly pavement of the former bed. Apart from uniform grain size, the content of organic matter (expressed as LOI) varied only a little throughout the profile, between 5 and 7%, which resulted in lack of distinct stratification. Contrary to sediment stratigraphy, metal concentrations varied markedly in the profile (Fig. 4). There were marked peaks of Cu at the depth of 60 cm, which equals to 760 mg·kg^{-1} as well as those of Zn, which rose to about 1400 mg·kg^{-1} at the surface. Cadmium, with a peak of about 6.0mg·kg^{-1} at the surface, also followed the same pattern of changes as Zn. In contrast, Pb concentrations decreased about 2 times, from the bottom toward the surface.

Profile ZPGII was situated at the edge of the former channel, about 1.2 m high, and consisted of more differentiated deposits. Evidently, the topmost layer was almost exclusively composed of silt fraction containing over 7 % of organic matter. The stratum lying 0.5 m lower was more sandy and contained about 75% of silt fraction and about 5% of organic matter. Lower horizons were light brown and contained 2-5% of LOI with greater amount of sandy grains and the presence of fine gravels was recorded. Here, no particular peak of Cu was observed similarly to the previous profile. Instead, progressive, albeit small, decline of this metal concentration toward the surface was observed. In the profile almost the same distribution pattern of Zn and Cd occurred with raised metal content at the surface and its peak in the top 10 cm layer. Lead variability resembled that in ZPGI profile because, they changed from the highest values at the bottom to the lowest values on the top. However, the values were moderate to small and varied from about 300mg·kg^{-1} to about 80 mg·kg^{-1}.

Profile ZPGIII was situated about 25 meters from the previous profile and was composed of uniform, cohesive silts which covered gravels at the depth of about 90 cm. The LOI content equaled to 8% and was the highest in the topmost layer. It decreased gradually down the profile reaching 2.4% in the bottom 20 cm strata. The distribution pattern of all investigated metals was very similar (Fig. 4). Generally, Cu, Zn and Cd concentrations rose from the lowest values at the bottom to the highest at the top and peaks of Zn and Cd in the few-centimeter-thick layer were significantly higher than in lower lying deposits. As in all profiles investigated in the upper reach, Pb distribution pattern did not resemble that of the other metals. Lead content rose markedly at larger depth and at the surface there was a lack of peak, but small decrease of the metal content was observed.

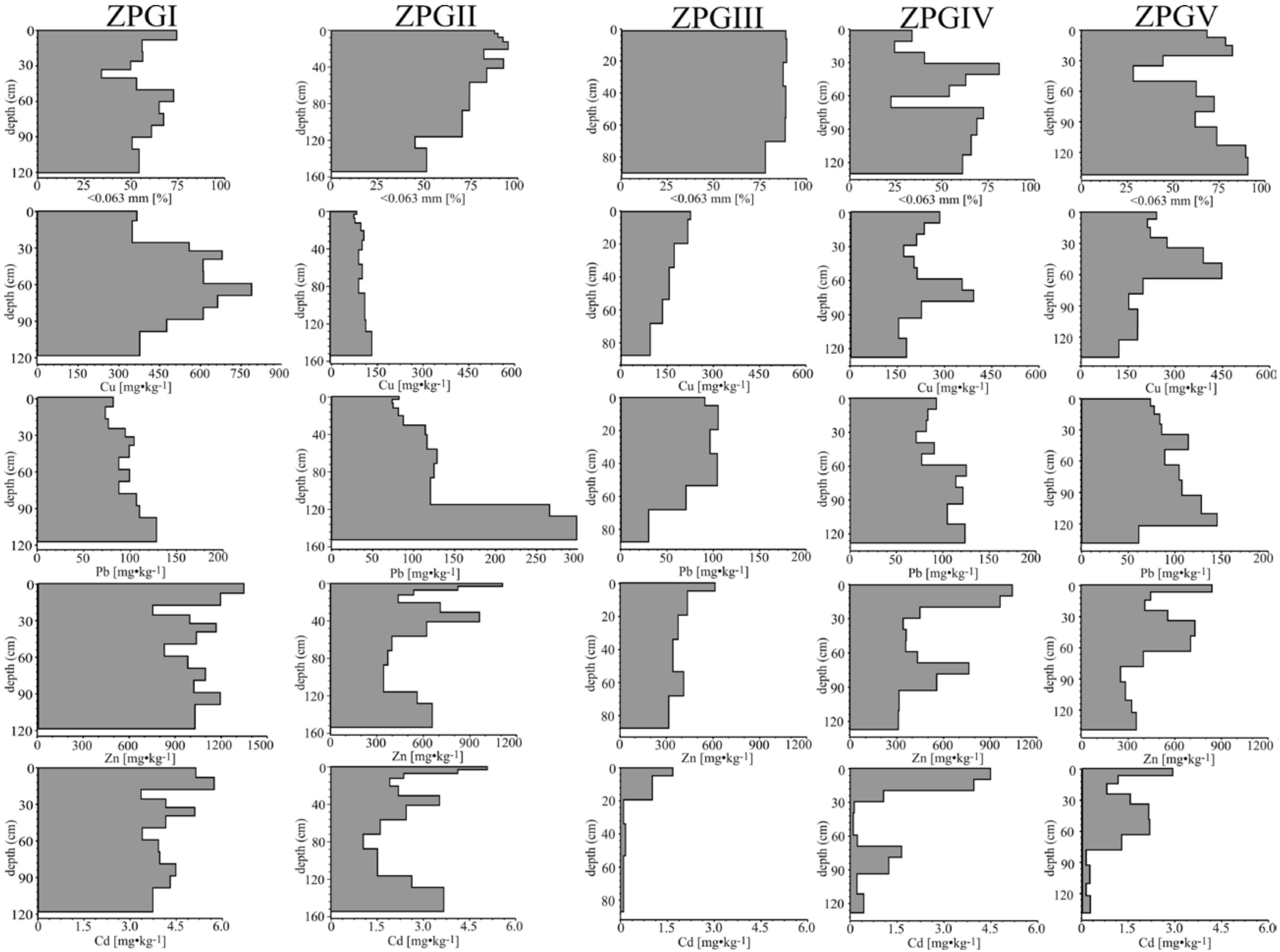

Figure 4. Content of heavy metals in <0.063 mm fraction in profiles from the upper reach of the Zlatý Potok.

The next two profiles were located about 100 meters upstream. The ZPGIV profile representing contemporary overbank deposits was situated in analogous position to that of the ZPGI profile. The floodplain sampled was of similar height, about 1.3 m, but it was lower by about 0.2-0.4 m from the floodplain level, which was sampled about 30 m further from the bank in the ZPGV profile. The deposits outcropped at the bank were similar also in respect of their stratigraphy. However, some changes in stratification were observed in the profile. The topmost deposits were composed of medium and coarse grained sands with silts. They covered muds with insets of very fine gravels and sands. Moreover, in the profile, except for the lowermost strata, organic matter content varied in range 6.6-7.6% and caused the dark color of these deposits. Distribution of metal concentrations repeated the pattern observed in the ZPGI profile. Peaks of Cu were observed at the depth of about 70 cm whereas, peaks of Zn and Cd occurred at the surface. Moreover, there were lower but marked peaks of all metals at the depth of about 70 cm and slightly raised content of Cu and Pb in the top 30 cm.

Profile ZPGV was outcropped in the bank of the channel, active in 1950s, which is now partially filled with sediments. The deposits of the profile were generally silty at the bottom and became more coarse-grained toward the profile top. The topmost deposits were composed of muds with organic matter content of about 6%, which decreased below 3% at the depth of 0.8 m. Characteristic features of the metals distribution were: the marked peak of Cu at the depth of about 60 cm, concurrence of peaks of Zn and Cd in the several-centimeter-thick surface sediment sample and smaller peaks of these metals at the depth similar to that of the Cu maximum. Lead distribution resembled that of the ZPGI profile, where its concentration decreased gradually toward the top.

Sediments in seven profiles in the lower course of the Zlatý Potok were much more differentiated in respect of their stratigraphy and content of heavy metals. ZPI profile was situated in the lowest near-bank part of the meander bend (Fig. 5). It represented the youngest deposits because of progressive meander migration and erosion of the opposite river bank. The entire profile was composed of coarse grained sands with fine gravels dispersed more densely at bottom levels. The depth of the profile to the water level was only 70 cm. Coarse grained deposits with LOI values of about 4% were covered with 10 cm silty-sand layer with organic matter content of up to 7%. Metal concentrations in this profile generally followed the same pattern with more or less proportional decrease of the content from the bottom toward the surface. In the ZPII profile the surface layer of mud, overgrown with grass, was about 25 cm thick. Content of organic matter in this layer was similar to that of the previous profile and dropped below the depth of 30 cm to about 1-3%. Lower horizons were composed of fine gravels in a matrix of coarse and medium grained sands. Content of silts was less than 10% throughout the coarse grained sediments, nevertheless, thick sediment stratification was well visible. Peaks of Cu, Pb and Zn were not distinct but occurred at the same depth of about 40 cm, whereas the maximum of Cd was observed lower, at the depth of about 60 cm.

The ZPIII profile was located about 20 m from the previous one, but on the floodplain level about 0.5 m higher. The older age of these deposits is confirmed by willows of Salix sp, 20 years of age, estimated based on their diameter. Deposits outcropped in a shallow pit were similar to the youngest ones. They were composed of about 0.5 m-thick dark muds on the top of the profile with organic content of about 4-6%; gravels with sandy matrix reached the water level at the depth of 1.2 m. The depth of peaks of all metals was the same and equaled about 0.7 m. However, Pb and Cd concentrations changed less regularly showing smaller peaks on the surface or subsurface horizons.

The deposits in ZPIV profile differed markedly with respect to their stratigraphy. The height of the floodplain level was higher by about 30 centimeters than that represented by ZPIII profile. The height of the edge, which split the two floodplain levels increased down the meander to over 0.5 m (Fig. 5).

The surface of the sampled level declined toward an up to one-meter deep chute in the inner part of the meander. Sediments consisted mainly of silty sands intercalated with some medium grained and bright sandy layers. In these layers organic content was about 2-4% and raised to 5-6% at the surface. Metal distribution in the ZPIV profile differed from the lower profiles in this meander. Peaks of Cu, Zn and Cd occurred at the depth of about 30 cm and then decreased up to the surface. The maximum of Pb was found at larger depth of about 75 cm but the content of this element and the other ones was not more than 2-3 times higher than the average values in sandy alluvia of Poland (Lis & Pasieczna, 1995).

The floodplain surface, where the ZPV profile was located, was confined by the 1-m-high edge of a chute, which separated it from the rest of the meander and from the other side by the elongated depression.

Behind this depression, floodplain raised by 1.5 m to the height of 3 m over the average water table. The age of willows on this surface could be estimated at 30-40 years.

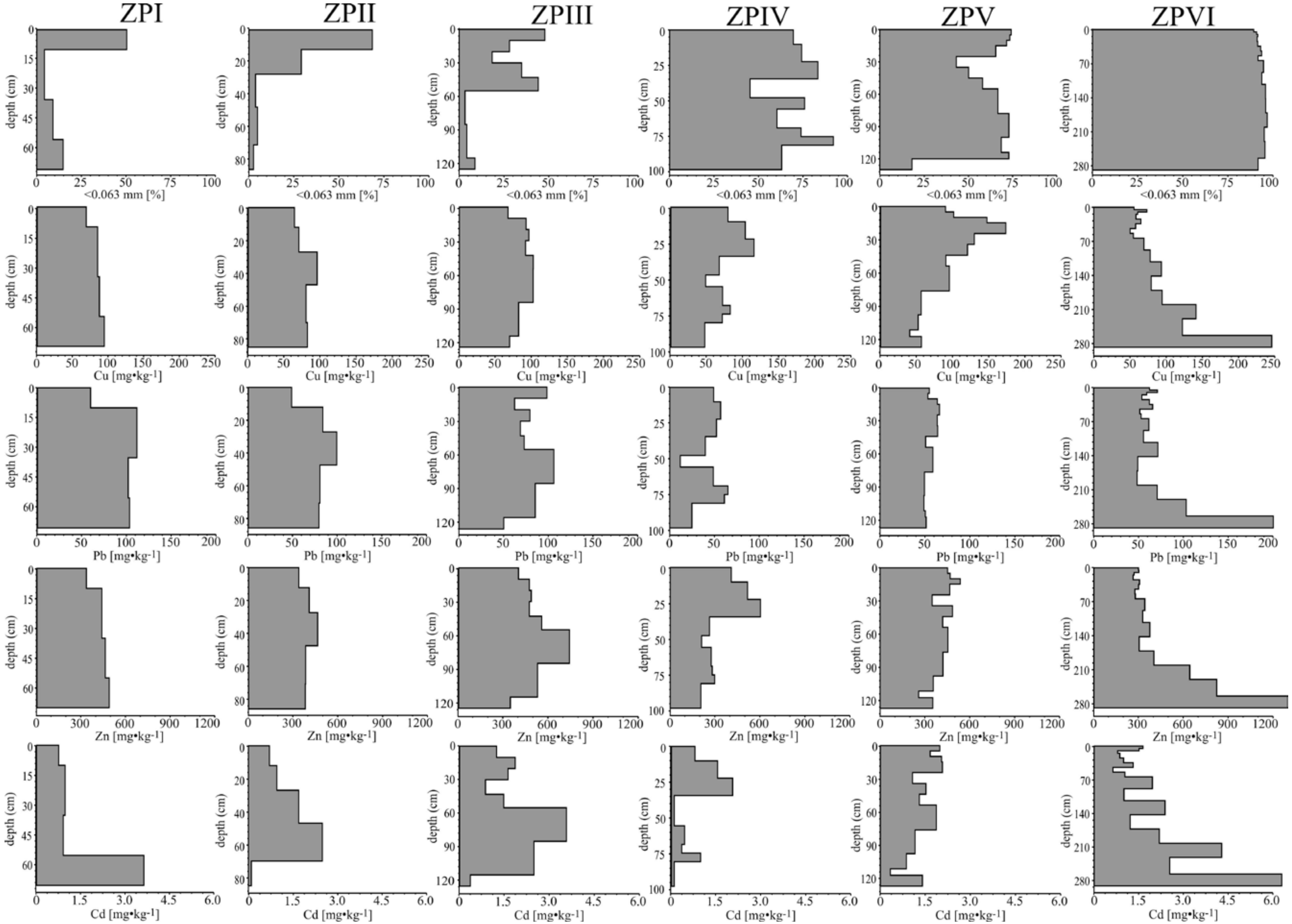

Figure 5. Content of heavy metals and <0.063 fraction in the lower reach of the Zlatý Potok.

The deposits which occurred in this profile with the predominance of brown silts were very similar to those observed in the previous profile. Also, ZPV profile had the same concentration of organic matter in respective depth horizons. Maximum Cu concentration was determined at the shallowest depth of about 15 centimeters of the investigated profiles in the meander. The maximum concentrations of the other elements were found also at the same depth but their content rose slowly from the bottom of the ZPV and did not exceed 3-4 times the geochemical background.

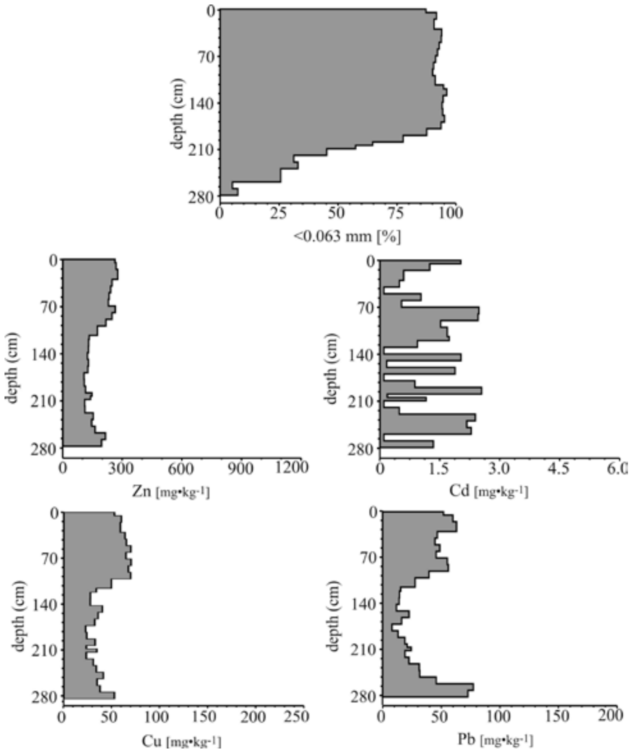

Figure 6. Content of heavy metals in <0.063 fraction in the profile ZPVII.

The ZPVI profile was located on the Holocene floodplain, several meters from the artificial channel which supplied a nearby mill with water until 1950s. The profile consisted of uniform loess-like deposits which are common in the lowest part of the drainage basin. They were fluvially reworked and accumulated on coarse gravels found at the depth of 3 m at the profile bottom. LOI values in this profile decreased progressively from about 7% at the surface to about 3-5% throughout the rest of the profile. All heavy metals investigated represented the same distribution pattern. The tendency of metal concentration changes were reversed if compared to the other profiles. Their values peaked at the very bottom and were comparable to the maximum concentrations observed in the profiles in the upper river reach, whereas surface sediments were characterized by concentrations close to minimal. Additionally, one more sediment ZPVII profile was outcropped on the about 3-meters-high floodplain, but on the opposite bank, about 200 m downstream (Fig. 5). The profile comprised medium grained sands progressively fining upward, underlying uniform loams 1.8 m thick (Fig. 6).

Changes in organic matter follow the changes observed in the ZPVI loess profile with the maximum at the surface of about 6.7%, slow decrease to about 3% over 90 cm and low variability at about 2-3% over the next 2 m of the profile. Distribution of Cu, Pb and Zn was very similar in the profile because maximum metal concentrations occurred in the upper 1 m and also the rise of metal content was observed at the bottom where base gravels were found. Cadmium content was low and varied between consecutive layers. The stem of woody debris found at the bottom of the profile was dated with ^{14}C method on 1740±70 BP (Klimek, 2010).

4. DISCUSSIONS

Distribution of the analyzed heavy metals in the investigated profiles exhibit differences which may be correlated with changes in metal production in the Zlaté Hory ore district. The highest peaks of Cu occur in profiles from the upper reach outcropped in the present river banks. Also, there is the distinct peak of Cu in the profile, which was located at the bank of the river channel documented on the map from the middle of 20th century. The proximity of the river channel favored deposition of fine particles polluted with Cu at the time of Cu production in years 1965-1990. However, the production peaked in 1980, therefore we cannot correlate it directly with the maximum in these profiles because of application of some measures reducing metal content in mine effluents. Probably the emission of this metal to surface waters was higher during the first 10 years of mine operation when no such measures were undertaken. Obtained dates indicate rapid accumulation of sediment in the near bank zone, the same in both profiles (ZPGI and ZPGIV). About 70 cm thickness of the sediment, which accumulated over 40 years, indicates quite high average deposition rate of about 1.5 cm/year. This may be confirmed by the lack of sediment compaction, which is not observed also in the other profiles in the upper reach and suggests sediment accumulation when rapidly flowing water slows down. The highest deposition took place during flash floods when normally dry reservoir at least partially fills with water. The most significant changes, including channel avulsion, could occur here approximately every ten years when rainfall intensity exceeds 100 mm within about 3 hours (Polach & Gaba, 1998). However, sediment deposition outside the near-bank zone is much slower because peak of Cu in the ZPGIII profile occurs in the surface sediment stratum.

Sediments with peaks of Cu in all but one (ZPGII) profile of the upper reach are overlaid by several to dozen centimeters thick stratum with maximum values of Zn and Cd. Increase of these metals contents in topmost sediment samples indicates recent increase of the Zlatý Potok pollution but their sources are less clear. It seems that this change is not directly related to the increase in Zn production which already ended 20 years before. Since there is no other pollution sources with these elements in the upper drainage basin the former mine must be responsible for this pollution. Cessation of the mining about 20 years ago resulted in periodical increase of heavy metals content in waters draining former adit Mir used as drainage of the mine. The highest Zn, Cd and Cu content was observed in years 1994-1996 as a result of raising of the water table and dissolution of the ore compounds in central part of the mine. Amount of waters 10-15 l/s discharged to the Zámecký Potok was in the following years reduced due to drilling and direction of highly mineralized waters to lower levels of the mine. The water was diluted with cleaner waters and with time its quality was markedly improved. From 1995 to 2000 the content of Cd decreased from 0.11 to 0.005 $mg{\cdot}L^{-1}$ and of Zn from 28 $mg{\cdot}L^{-1}$ to 1.77 $mg{\cdot}L^{-1}$ (Tisnovska, 2004). These activities were accompanied by liming of the spoil heaps and capping with loams, which eliminated erosion and leaching on the early stage of works. The discharge of highly polluted waters with cadmium and Zn is responsible for high content of these metals in the fine grained sediments presently observed in the Zlatý Potok and its tributaries in the Zlaté Hory mine district. For this reason for the last 15 years or so after marked reduction of metals content in waters, channel sediments are the main source of pollution which may be responsible for growth of metal content observed in the overbank sediments in the upper reach of the Zlatý Potok.

The respective growth of cadmium and Zn content over peaks of Cu is not observed in vertical profiles from the lower course of the river. Moreover, peaks of these metals are lower than in the upper reach, what could be related to the larger distance from the pollution source. This regularity is typically observed in most of streams as a result of losses of river sediment during transport and mixing of the carried sediment with the unpolluted one, eroded from river banks and the channel bed or dissolution due to oxidation of the sediment-associated heavy metals (Bird et al., 2008). It is known that valley geomorphology play an important role in winnowing of heavy metal pollutants from the catchment (Majerova et al., 2013). Fluvial processes are particularly efficient in catchments with high flood frequency leading to rapid removal of deposits in the post-mining period (Black et al., 2004). These processes are much less effective in channels of low capacity and small gradient where downstream attenuation is controlled mainly by slow sediment leaching (Ciszewski et al., 2012). Channelization of the prevailing course of the Zlatý Potok and mountain hydrological regime with rapid summer rainfalls favour the transfer of sediment down the channel.

Aforementioned up to 500 meters high northern slope of Zlatohorská Highland causes the snow cover duration. In the piedmont loess plateau, completely deforested, the snow cover duration is 20-40 days shorter than in the forested north facing mountain slopes. The snow melting events are more frequent here during mid-winter snow thawing events. The cultivated large fields, without permanent vegetation are exposed to water erosion during snow-melting periods. The cool waters deliver a lot of fine soil particles to the local periodical streams which supply the main channel of the Zlatý Potok.

This is the reason for the rapid drop of metals content down the Zlaté Hory ore district. The lack of enrichment of top sediment strata with Zn and Cd in profiles from the lower river course is also related to a small capacity of the most polluted tributaries of the Zlatý Potok. Hence, there is the relatively small volume of fine, strongly polluted sediments in these channels dominated by coarse gravels. This volume is markedly diluted by sediments probably mostly eroded from the channel banks and not from the catchment surface because most of the upper catchment is overgrown with forest. These sediments are effectively trapped in dry reservoir with significantly lower channel gradient.

The dating of the sediments with Cu peaks, although not accurate, confirm the rough age estimates based on channel changes on maps and ortophotomaps as well as with tree age, which changes from the youngest at ZPIII (about 20 years) to the very old (probably a 100 years old oak) at ZPVI profile. This dating is to some extent confirmed by the decrease of the depth of peaks in consecutive profiles from the youngest (ZPI) to the oldest (ZPV). The only exception from this rule is the specific peak of all metals at the very bottom of ZPVI profile and ZPVII. The radiocarbon date, 1750 years BP, obtained for the bottom of the profile PPM (Klimek, 2010) proves that it is the secondary metal peak preceding the mining in this region. This has to be related to secondary enrichment of the bottom sandy deposits close to the average water table. This effect is particularly known in case of Pb, which is an element of low solubility and may infiltrate from the channel or migrate downward within the profile associated with particles of the micrometer dimensions (Hurkamp et al., 2009). This phenomenon is better seen at the bottom of the ZPVI profile in the strata overlying coarse gravel and is associated with penetration of polluted waters in gravels and sorption/precipitation or entrapment of the very fine sediment particles (Ciszewski &Turner, 2009).

Ore mining and processing is the main source of heavy metals in the environment. Metals which escape from production processes may accumulate in river systems over a long period of time and pollute thick floodplain sediment sequences for a long time after mining cessation. The sediment pollution may be stable for many years to come and beat efforts in remedial activities at mine sites. In some cases it is estimated that natural decay of metals within a river channel may last several hundred years. Works aiming at reducing this time are usually expensive and may increase response time to success by only a little (Moore & Langner, 2012). Fluvial sediments may be an important secondary source of pollution. It was several times evidenced that content of some easily soluble elements increase downstream the polluted catchments both during average water stages (Ciszewski et al., 2012) as well as during floods (Žak et al., 2009). In the Zlatý Potok there are no observations of downstream metal content in river water. But considering channelization and lateral channel stabilization since the beginning of 20th century the storage of sediment-associated heavy metals was limited to short river reaches, which were sampled in the current investigations. Limited volume of sediments stored there appears not to be a significant source of river pollution. Instead, sediment-associated heavy metals which accumulate on the floodplain of the upper reach originate from small tributaries affected by mine water discharge at the end of mining activity.

5. CONCLUSIONS

The profiles from the upper reach situated about 7 km downstream the former mine revealed distinct peaks of Cu, which could be correlated with the ore mining period. Peaks occur at larger depth of dozen centimeters in bank outcrops and at the ground surface at locations more distant from the present channel. Moreover, distinct peaks of Zn and Cd were found in the top strata of all profiles. This indicates recent increase in pollution of the river channel which took place after mining cessation. The highest Zn and Cd content in mine waters discharged from the old adit to the Zlatý Potok was observed in 1995. Content of these metals dropped to low values before the year 2000 but resulted in the high and persistent pollution of stream bed sediments in the area of the Zlaté Hory ore district. Erosion of fine polluted channel sediments appear to be the main source of heavy metals, which have accumulated recently in the upper reach of the Zlatý Potok.

In the lower reach of the Zlatý Potok the concentrations of heavy metals are generally lower. Peaks of Cu are distinct only on the top of the older floodplain deposits which started to accumulate in the first half of 20th century. Progressive decrease of concentrations of all metals is observed in profiles representing the youngest deposits and there is a lack of Zn and Cd enrichment on the top of these profiles. This indicates lack of influence of the post-mining pollution on metal content in this reach because only small volume of heavy metal-associated sediments is stored in channels of the Zlaté Hory ore district, which were identified as the main pollution source. This confirms the observations of the Zlatý Potok bed which is dominated by gravels with only small amount of the fine fraction.

Restoration of spoil heaps and former settling pond mitigated post-mining pollution only partially by eliminating erosion of the mine site. The effects of these works were constrained by uncontrolled outflow of polluted mine waters and channel sediment pollution, which is expensive and difficult to eliminate. It affects only a short river reach and will decrease in the following years.

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