The use of heavy metal concentrations and dendrochronology in the reconstruction of sediment accumulation, Mała Panew River Valley, southern Poland

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Abstract

Heavy metal concentrations were investigated in overbank sediments of the Malá Panew River, southern Poland. Samples were collected from seven vertical profiles located within channel infills of a 20th century floodplain at three sites, each up to 50 m wide. In each profile, 15–24 samples were collected and analysed for Ba, Cd, Cu, Pb, and Zn. Sequential extraction of these elements was carried out in the 0.063-mm fraction of selected samples. Additionally, the age of the oldest trees growing close to the profiles has been used to estimate the initiation of sediment accumulation there. Ba, Cu, and Pb, which occur mostly in less mobile, moderately reducible, and residual fractions, were used for sediment dating. Zn and Cd, which in 50–75% occur in the mobile exchangeable fraction, were not suitable for dating. Correlation of Ba, Cu, and Pb concentrations in vertical profiles with changes in the load of effluents discharged to the river showed abrupt changes in the thickness of the strongly polluted sediments across the floodplains. A comparison of the relative changes between heavy metal peaks in sediments of similar age in the different profiles suggests a variable rate of downward metal migration. In general, none of the heavy metals investigated seems to have been mobilised within the stratigraphic layers above the water table. In layers located at stratigraphically lower levels, the Zn and Cd peaks seem to migrate several centimetres to several decimetres down in the profile. In profiles inundated for several weeks every year, Zn and Cd, as well as the relatively less mobile Ba, Cu, and Pb, have migrated downward by several decimetres. The investigation shows that frequent fluctuations of the water table have blurred the original depositional metal patterns of metal concentrations within a period of less than 40 years.

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1. Introduction

The pollution of overbank sediments with heavy metals reflects past and present industrial activity. The highest metal concentrations usually occur in drainage basins affected by the excavation and processing of polymetallic ores (Macklin and Klimek, 1992; Swennen et al., 1994). Usually, peaks of Zn or Pb production, elucidated from the mining records, can be correlated with peaks in metal concentrations observed in vertical profiles from alluvial deposits. Additionally, the age of a stratigraphic horizon can

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be obtained if a sudden increase of production results in a parallel increase of metal concentrations in downstream sedimentary sequences (Macklin, 1985; Knox, 1987; Rowan et al., 1995).

The accuracy of such correlation relates strongly to river dynamics (Lewin and Macklin, 1987; Macklin, 1996). In valleys with braided rivers of high energy, which quickly rework alluvial sediments, it is often possible to distinguish only the pre-mining and post-mining era deposits (Miller et al., 1996). In incising river reaches with terraced valleys, sediment contamination is related not only to terrace age but also to terrace height and inundation frequency (Brewer and Taylor, 1997). Within meander bends of meandering rivers, metal concentrations vary considerably between lateral accretion deposits (Lewin and Macklin, 1987). The most polluted sediments accrete during the mining era (Wolfenden and Lewin, 1977). In laterally stable, regulated, and embanked river reaches, peaks of heavy metals can be correlated with periods of maximum pollution in the entire interembankment zone (Ciszewski, 2003). Moreover, in floodplain lakes, in which sediment accumulation has taken place for several decades, the metal record can be established using $^{137}$Cs and $^{210}$Pb (Middelkoop, 2000; Winter et al., 2001).

The use of metal concentrations as stratigraphic markers often provides satisfactory results. However, metal mobility affects the metal content in sedimentary layers. As a result of fluctuating water table elevation, acidification through pedogenesis, or atmospheric deposition, heavy metals are expected to migrate downward in vertical profiles (Salomons and Förstner, 1984; Hudson-Edwards et al., 1998; Van den Berg et al., 1998).

The aim of this study was to use spatial variations in heavy metal concentrations and dendrochronology to date overbank sediments in a laterally mobile river reach. Additional objectives were to identify the sediment layers that have pronounced metal migration, and to evaluate the influence of metal mobility on the accuracy of this dating technique.

### 2. Study area

The Mała Panew is a naturally meandering river, located in southern Poland. From its sources in the western part of the Silesia Upland to its confluence with the Odra River, its length is 132 km. The mean annual discharge in the middle reach, downstream the confluence with the Stola River, is ca. 10 m$^3$/s. The river channel is incised into semihomogenous fluvioglacial sands 2–12 m thick. Only along the middle reach does the river bed reach Lower Triassic shales. The river laterally migrates intensively, especially in the forested valley in the upper and middle reach. Between the map editions in 1912 and 1985, most of the river meanders migrated about 50 m downstream.

The largest sources of pollution are situated in the upper part of the drainage basin (Fig. 1). The town of Tarnowskie Góry was a lead and silver mining centre by the 16th century. About 20,000 small shafts were known to exist in the area (Drabina, 2000). After production collapsed in the 18th century, mining and smelting were revived in the 19th century. Industrial production was significantly expanded in the 20th century. In 1934, the chemical plants were established at Tarnowskie Góry and, after the World War II, the area became a primary producer of chemicals for dyeing and paints in Poland. Chemical production mostly included barium nitrates, sulphates, and carbonates. In 1959, the plants were expanded and started to produce 6000 tons of barium compounds as well as boric acid, borax, alum, copper, zinc, and natrium sulphates, as well as many others in lesser quantities. Since 1967, production has increased to 20,000–25,000 tons/year, and this continued until 1985, after which production decreased. In 1995, the plants were closed. Production of zinc sulphates reached 800 tons in 1960 and ceased in 1963. Production of copper sulphates generally followed changes in the production of barium compounds. The highest rates of production from 1970 to 1985 varied between 2000 and 3000 tons (Biernacki, 1983).

The zinc smelter plant in Miasteczko Śląskie, which began production at the end of 1968, was the second largest pollutant source in the Mała Panew drainage basin. During the first 6 years of activity, it discharged over 10$^8$ m$^3$ of effluents yearly to the Mała Panew River via the Stola tributary. The zinc load increased from 1968 to 1974 to as much as 80 tons/year. During the next 2 years (1975–76), zinc loads fell twice. In the same period, the cadmium and lead loads ranged between 3 and 6 tons/year. The amount of heavy metals in effluents increased once more in...
1980 as a result of smelter expansion. Significantly, the Pb releases increased to over 18 tons/year and decreased by over a factor of 4.5 during the next 2 years. Since 1989, the quantity of effluents released to the river has been on the order of several tens of thousands of cubic metres per year, and zinc, cadmium, and lead loads amount to several tens of kilograms per year (Zinc Smelter, unpublished data).

In addition to contaminant releases at Tarnowskie Góry and Miasteczko Śląskie, the cellulose plant in Kalety discharged huge amounts of effluents containing ligninosulphonates and cellulose fibres between 1960 and 1990. This plant, closed in 1992, as well as the town Tarnowskie Góry (60,000 inhabitants) were considered to be the main sources of organic matter transported to the Mała Panew River (Reczyńska-
In Tarnowskie Góry, several small electromechanical plants have been operating since the early 1970s. The paper mill in Boruszowice may also have been a source of river contamination. This extensive industrial activity caused the pollution of the river sediments by heavy metals. Investigations carried out in the early 1970s showed that the concentrations of Ba, Cd, Cu, Pb, and Zn were elevated above background values and (in bulk samples) reached 2500, 116, 200, 490, and 5000 ppm, respectively (Pasternak, 1974). Monitoring of river sediments in the lower Mała Panew river course also confirmed high metal contamination, especially by Cd (Bojakowska and Sokolowska, 1994, 1996; Bojakowska et al., 1998). Extensive pollution of both sediments and soils in the upper part of the drainage basin by cadmium, zinc, and lead was also reported in the Geochemical Atlas of Upper Silesia 1:200,000 (Lis and Pasieczna, 1995).

3. Materials and methods

A comparison of channel positions on the maps of 1912 (1:25,000, Meßtischblatt 3202, Königl Press) and 1985 (1:25,000, no. 521.22, PPWK) showed several regular meander bends, which shifted significantly during this period. These 20th century floodplains were selected for investigation and, in the field, three sites were sampled. Samples were collected from seven vertical profiles situated within overbank sediments of the middle reach of the Mała Panew River (Fig. 1). Profiles BI and BII were located at site B (5 km downstream from the junction with the Stola) 1.5 and 30 m from the channel, respectively. Profiles CI, CII, and CIII were situated in the floodplain of site C, 10, 30, and 45 m from the channel, respectively. Profile CIV outcrops in the opposite river bank. Profile DI was situated in the floodplain of site D. It is a bank section located 200 m downstream of site C.

The outer edge of the channel, from the beginning of this century, is well marked in the floodplain topography at sites B, C, and D. Floodplain height at investigated sites reaches about 2 m. At sites B and C, two paleochannels, partially filled with sediments, are present. A narrow 1.5-m-wide shelf forming one level in topography occurs only at site D.

The floodplains investigated have sparsely been colonised by trees. The age of the trees was used to partition their surfaces into age zones. The trunks of the oldest trees were sampled using a Pressler’s corer and the number of rings within the cores was counted. The age of the oldest tree growing on the geomorphic surface approximates the time when the deposits were stabilized. The deposits are always older than the oldest trees (Sigafoss, 1964; Hupp, 1987). The oldest trees and their ages are shown in Fig. 2.

At the sampling locations, pits were dug with spade to the ground water level. Also two outcrops were sampled to the water level in the river. During sampling, a mean high discharge of river waters was recorded at the gauging station in Krupski Młyn. The depth of the profiles varies between 1 and 2.2 m. Samples were taken at 2–30-cm intervals at every profile. The top sections were sampled more densely, at several centimetres in intervals. In sections where distinct layers occurred, the sampling density depended on their thickness. Throughout profiles BI, CI, and DI, interbeds of black, organic, and bright sandy layers were collected. Samples were placed into polyethylene bags and then dried at 105 °C and homogenised. The fraction smaller than 0.063 mm was obtained using a polyethylene sieve. About 0.5-g samples of this fraction were digested in Teflon bombs using a microwave technique (100% power; pressure 70 psig; time 20 min), with 10 ml of concentrated HNO₃ and 2 ml of H₂O₂. The extracts were then filtered and placed in 50-ml volumetric flasks. The concentrations of Ba, Cd, Cu, Pb, and Zn were subsequently determined using inductively coupled plasma mass spectrometry (ICP-MS). Analytical precision and accuracy were determined by inserting a blind duplicate and Canadian-Certified Reference Sample LSKD-4. The organic matter content was estimated by loss on ignition at 450 °C for 5 h.

Analyses for Ba, Cd, Cu, Pb, and Zn on a phase-specific, operationally defined basis were carried out in 12 samples, which were selected from the upper, middle, and lower parts of the BI, CI, CIV, and DI profiles. The method of Kersten and Förstner (1986), as applied here, partitions metals into six fractions:

I. Exchangeable, 1 M NH₄OAc, solid:solution ratio of 1:20, shaken for 2 h;
II. Specifically adsorbed, 1 M NaOAc, solid:solution ratio of 1:20, shaken for 5 h;

III. Easily reducible, 0.1 M NH₂OH-HCl, solid:solution ratio of 1:100, shaken for 12 h;

IV. Moderately reducible, 0.2 M (NH₄)₂C₂O₄ with 0.2 M H₂C₂O₄, solid:solution ratio of 1:100, shaken for 24 h;

V. Oxidizable, 1 M NH₄OAc with 30% H₂O₂, solid:solution ratio of 1:100, shaken for 12 h;

VI. Residual, 65% HNO₃, heated for 2 h, solid:solution ratio of 1:100.

After each extraction step, samples were centrifuged at 3500 rpm for 10 min. The supernatant was decanted off, filtered, and made up to 50 ml with 0.02 HNO₃ and analysed by ICP-MS. Blind duplicate and reference samples were used to check precision. The total contents of all metal contents were generally within 10% of the metal contents determined by single-stage HNO₃.

4. Results and discussion

4.1. Sediment stratigraphy and pollution

Profiles BI, CI, CIV, and DI, situated close to the channel, comprise a series of relatively thick layers of bright sandy sediments intercalated with fine, sand silt layers rich in organic matter (Fig. 3). The distinct organic layers are common in sediments accumulated by rivers, which drain coal mining regions (Macklin and Klimek, 1992; Klimek, 1999) or highly industrialised areas (Swennen et al., 1994). In the Mała Panew River basin, they are undoubtedly connected with the huge organic load discharged in the second
half of the 20th century from cellulose plants in Kalety and also with effluents from Tarnowskie Góry. Usually the sands accumulate during floods, whereas the organic sediments accumulate when the flood waves have receded (Macklin and Klimek, 1992). Hence, the number of couplets of the sand and organic layers approximates to the number of floods, as represented in any particular profile. In BI, CI, and DI, it is about 20, and in CIV, it is probably higher. In profiles DI and CI, the thickness of sandy layers reaches about 20–30 cm at the bottom of the section, but only several centimetres at the top; the organic layers never exceed 1–2 cm. The thickness of sandy layers in BI varies between 10 and 15 cm. In CIV, layered sediments occur only in the top 70 cm. The laminae get thinner toward the surface and in no case does the couplet exceed several tens of millimetres. In the lowermost part of the profile, there are massive sands, probably of a former channel bar. The sediments in CI and DI are among the most polluted in Poland. Maximum concentrations of Cd exceed 1000 times the values in unpolluted Polish soils (Lis and Pasieczna, 1995). Similarly, Zn, Pb and Ba, and Cu exceed unpolluted soils by 200, 150, and 40 times, respectively. In profile CIV, pollution of the same magnitude appears at 70 cm, where distinct layering starts to occur. Both maximum and average concentrations of Zn, Cd, and Pb are much lower in BI.

In profiles BII and CII, fine, black layers are less visible. This could be due to organic matter degradation and translocation. The top 30 cm in BII and the upper 50 cm in CII are apparently rich in organic matter (up to 20% and 25%, respectively, in the 0.063-mm fraction). Lower sandy sediments are relatively bright with 7–10% organic matter. At a depth of about 100 cm, where the water table frequently fluctuates, brownish sands with characteristic Fe-oxide precipitations occur. Average concentrations of heavy metals are generally lower here than in profiles located closer to the river channel. However, the maximum concentrations of Ba and Cu in BII are even higher and reach 14,000 and 600 ppm, respectively.

Fig. 3. Sediment stratigraphy and losses on ignition of the investigated samples (<0.063 mm). Arrows indicate distances between profiles investigated, and between river bank and profile CI. (1) Sand; (2) silty sand; (3) organic layers.
In profile CIII, which is situated 45 cm from the present channel position, no sand-and-organic layer is present (Figs. 2 and 3). A surface dark layer 15 cm thick, with high organic matter content and reaching 25% in a 0.063-mm fraction, is easily distinguished from the more uniform, underlying brown sands. In the lower levels, the organic matter content does not exceed 10%. In the CIII profile, the maximum metal concentrations are more than two times lower than in the channel banks. Also, the thickness of the highly polluted layer is relatively small and does not exceed 20 cm.

4.2. Dating sediments with tree rings

The dendrochronologic dating of sediments provided the best time resolution at site C. Profile CIII is located in the infill of the river channel, which is shown on the 1912 map (Fig. 2). However, the 100-year-old oak (Quercus robur), which grows on its edge, suggests that sediments may have started to accumulate at the site before about 1901. This date agrees with channel position shown on an earlier version of the map, as surveyed in 1883. It is possible that the map of 1912 simply redrew the same channel position without recording this fact. The upper limit of the initial sediment deposition within this paleochannel is given by the 72-year-old oak (Q. robur), which is located about 10 m closer to the present river channel than the 100-year-old oak. Because the meander bend had been shifted downvalley southwestward, the channel was unlikely to be in the position shown on the 1912 maps (Fig. 2). Moreover, the 72-year-old oak suggests that the lateral accretion deposits must have been deposited since ca. 1929. Profile CII is located in a shallow channel infill. This infill, situated further westward, is undoubtedly younger than 1929 but older than the 43-year-old elm (Ulmus effusa), which grows on the fill. Hence, bottom sediments in CII must have started to accumulate before 1958. The deepest CI profile was dug in the levee of a chute, which is active only during a flood. Relatively rapid sediment accretion, as the relatively significant thickness of the sediment layers suggests, probably made tree growth close to the profile CI impossible. However, groups of tens or dozens of alders (Alnus glutinosa) grow in the lowest part of this surface in which sediment accretion rate could be slower (Fig. 2). The oldest is 35 years old, so this form is older than 1967. At the channel bank of profile CIV, sediments accumulated for about 70–80 years. The bottom sediments started to accumulate before 1932 as the age of the pine (Pinus silvestris) suggests, but after 1912.

At site B, the oldest trees, alder (A. glutinosa) growing at the profile BI and pine (P. silvestris) growing at profile BII, are 43 years old (Fig. 2). However, it is obvious that the age of both forms in which profiles are located differs significantly. Channel infill along the 19th/20th century floodplain edge must be older than the age of the pine suggests. In this case, a date is, in principle, unsuitable for partitioning of this floodplain into age zones. In contrast, alder is considered to be a pioneer tree on the river banks in southern Poland. This tree species, less sensitive to persistent high water table (but not to inundation), can start to colonise newly formed point bars much more quickly than pine or oak; however, in North America, poplar can be established even faster (Everitt, 1968; Nanson and Beach, 1977). Also, the age of the alder at profile BI could approximate better the time when the initial bar appeared. Moreover, the relatively thick sediments in profile DI, which are only weakly polluted by Ba and Cu, suggest that the 40-year-old pine started to grow much later than when initial layers accumulated and does not approximate this date well.

4.3. Sequential extraction

The partitioning of heavy metals is very similar in all samples taken from the highly polluted upper and middle parts of the profiles, but different from the lower, usually less polluted sediments (Fig. 4). However, significant differences occur in the metal speciation of analysed metals.

Only a small percentage of Ba (usually 3–6%) is present in exchangeable, specifically adsorbed, or easily adsorbed fractions of the strongly polluted sediment. In contrast, in the lower part of the CI, CIV, and DI profiles, as much as 60–70% of the Ba was associated with these three fractions. These data indicate that Ba, if present in sediments in high concentrations, is rather immobile and may be particularly valuable for dating.

The highest proportion of Cu (60–70%) appears in the moderately reducible phase regardless of whether the sediments are highly or slightly contaminated. In
Fig. 4. Sequential extraction data of Ba, Cu, Pb, Zn, and Cd in selected samples (in percent).
those samples with lower proportions of Cu in the moderately reducible phase, Cu also occurs in the more mobile fractions: 10–20% exchangeable and specifically adsorbed on average.

Lead also belongs to the generally less mobile elements in the Mała Panew sediments. Partitioning of this element strongly depends on its concentration—a trend common also for other metal-polluted sediments (Helios-Rybicka Strzebońska 1999). The higher the concentration (over 1000–2000 ppm), the higher is the proportion at which Pb is present in the mobile exchangeable fraction. In some samples, it reaches 45%. The very high Pb concentrations in the vertical profiles occur as sharp peaks. For dating purposes, it was assumed that, even if as much as 40% of Pb concentration migrated downward, the peaks would remain in their original positions.

Very high portions of Zn (30–60%) and Cd (60–78%) were found in the exchangeable fraction. This correlates well with very high concentrations of these metals in all but one investigated sample. Most concentrations of Zn vary between 3000 and 12,000 ppm, and those of Cd vary between 3 and 460 ppm. In the one, a relatively weakly polluted sample from the bottom of the CIV profile, the Zn concentration is 1368 ppm and Cd reaches 12.3 ppm. Thirty-seven percent of Zn was extracted in the organic/sulfidic fraction (step V) and 15% in residual fraction (step VI). Also, 73% of Cd occurs in the residual fraction and only 10% in the exchangeable fraction. Owing to the high mobility of Zn and Cd, neither of these elements was considered to be suitable for dating purposes.

4.4. Dating sediments with heavy metals

A marked upward increase of Ba concentrations occurs in all investigated profiles except BI (Figs. 5 and 6). This change is well correlated with the marked increase of Cu concentrations. It is more likely related to the expansion of the chemical plants in Tarnowskie Góry in 1959 and the production of chemical compounds containing these elements. Thus, the first occurrence of those elements in the profiles can be dated at 1960. Also, above this level (1960) in the CI, CIII, CIV, and BI profiles, a very high peak concentration of Zn is observed. In spite of 30–60% of this element occurring in easily soluble fractions, this peak correlates well with the maximum production of zinc sulphates in 1959–1962. However, the concentrations of Zn in much older sediments are on the order of several hundreds ppm in these profiles. Considering the fact that production of this compound must have been several times less before 1955, the portion of Zn found in the lower levels is probably related to elemental migration from the upper layers. Perhaps this portion prevails over Zn, which had originated from the previous industrial activities in Tarnowskie Góry.

The most pronounced and regular peaks in Ba concentrations occur in profiles BII, CI, DI, CII, and CIV, at depths 15, 60, 30, 15, and 25 cm, respectively. The maximum Ba concentrations within these profiles are related to the greatest pollution of the Mała Panew River in the 1970s. This resulted from both the highest production of Ba compounds during this period and the almost regular discharge of untreated effluents from sewage treatment plants within the chemical plants (S. Malik, personal communication).

In almost all profiles, except BI, within the layers most polluted with Ba, there is a significant increase in Pb concentrations. This increase, which is related to the start of the production at the zinc smelter plant in Miasteczko Śląskie at the end of 1960s, supports the proposed dating of these layers. Moreover, within these layers, very high Cd concentrations occur and, in profiles CI, DI, and CIV, its concentrations increase regularly upward. Cd concentrations are probably related to zinc smelter activity. The increase of Pb concentrations peaks sharply in all profiles, except BI, at values exceeding 2000 ppm. These peaks are perhaps the most reliable marker of the investigated sediments and are well correlated with the exceptionally high load of this element in the effluent discharged from the zinc smelter in the period 1979–1981. Peak Pb concentrations date these layers to 1980. The decrease of Pb concentrations in younger sediments followed the significant drop of Pb load discharged from zinc smelter. Moreover, Cu and Ba concentrations in those sediments accumulated after 1980 slowly decreased as a result of more efficient pollution controls and an improved operational efficiency of the sewage treatment in the chemical plants. The drop in Pb concentrations after 1990 occurs only in the surface layers accumulated in the CI and CIV profiles and
could be correlated with closure of the chemical plants at the beginning of the 1990s, following the severe decline in production.

The relative differences between positions of particular metal peaks in the profiles suggest that the accuracy of this dating generally falls within the range $\pm 5$ years. However, the accuracy depends both on sediment stratigraphy and sampling density. The real age of the sediment layer may be younger than estimated if its accumulation is delayed by the absence of flooding. If separate couplets of sand-and-organic layers were taken, as in profiles CI and DI, the dates suffer only from such a delay. But if several such couplets or massive sediments are collected, the dates cover longer accumulation periods and are, therefore, less accurate. The accretion of the investi-
Gated sediments became progressively slower with time and the layers became thinner toward the top of the floodplain. For this reason, dating accuracy could change within the same profile.

The tree-ring dating confirms, to some extent, the dates of the sediments determined by the heavy metals. In floodplain C, the thinnest sediment layer is polluted with Ba and Cu the earliest date of the initial deposition shows the oldest tree. In profile CI, the Ba/Cu increase suggests that the lowermost 60 cm accumulated before 1960, whereas the oldest tree started to grow 7 years after this date. A comparison of these two ages proves that vegetation on a newly formed bar could be established in as much as 10 years. This also gives the order of general error with tree-ring dating in CII and CIII profiles. Thereby, the sediments in CI could have begun to accumulate in the first half of the 1950s, whereas in CII, about 10 years earlier. The similar depth of the Ba/Cu increase in profiles BII and CIII shows that sediment sequence in BII started to accumulate much earlier than the tree age suggests, probably at the end of the first quarter of the 20th century.

4.5. Dating sediments and metal migration

Changes in the Cu, Ba, and Pb concentrations appear to be mainly of a depositional nature and enabled sediment dating. However, in some profiles, there is evidence of downward metal migration, which makes such dating difficult or even precludes such dating. The distribution of these metal concentrations within the BI profile differs markedly when compared with the CI and CII profiles (Figs. 5 and 6), which are
generally of similar age. Obviously atypical are very high Ba, Cu, and Pb concentrations, which correspond with a relatively high Cd, and a rather low Zn content. The tree age gives the important information that these sediments accumulated pre-1958. Hence, the occurrence of sharp Ba/Cu concentrations is to be expected in the profile presumably only at a depth of ~ 40 cm. Surprisingly, below this horizon, there is a very high Pb maximum, but not in the 1980 sediments as in the other profiles. This element, present in the lowermost 50 cm, could have been migrated from the upper levels and, with Ba and Cu, gives postdepositional peaks. The downward migration of Pb is consistent with a particularly high portion of this element (44–46%) in a mobile exchangeable form. A high portion of the exchangeable fraction in the lower levels of BI does not occur in cases of Ba and Cu. Also, Zn in the lowest layer occurs in smaller amounts in the exchangeable fraction than on top. It is perhaps significant that throughout profile BI, the Zn concentrations are much lower than in BII and other profiles. This suggests that Zn was washed out of the entire BI profile, whereas Ba, Cu, and Pb mostly migrate downward and are retained.

The frequency of the water table fluctuations may explain the postdepositional metal distribution in profile BI. This profile is situated in a strongly eroded bank outcrop between channel and chute (Figs. 2 and 3). It is inundated below the bankfull stage at least once a year. Also, the changes of water levels at the gauge station in Krupski Mlyn suggest that the lowermost 0.5 m are inundated for at least 15–20 days/year. This frequent inundation by quickly flowing flood waters apparently affects metal distribution much more than in profile BII situated at a similar height. The latter is affected mainly by groundwater fluctuations. It is possible that only a portion of the Ba within the most often inundated bottom 0.5-m layer migrates from the upper levels of the profile, while the other part comes from upstream and was introduced into the highly permeable, sandy sediment by flood water.

However, the BI profile is the best example of metal migration of all the profiles investigated, detailed analysis of the relative changes in metal concentrations within sediment sequences suggests more evidences of this process. At site C, the accumulation of high Cd concentrations in layers accumulated before 1970 does not agree with the beginning of zinc smelter activity post-1968. Certainly, the small electroplating plants and chemical plants that operated at that time have not reworked Cd compounds and could not have caused concentrations that may be as much as 50–200 ppm. These concentrations seem to be postdepositional. Moreover, the Cd peak in the CI and CIV profiles occurs in layers accumulated in 1980; in CII profiles, it occurs earlier, i.e., in the 1970s, and in CIII, it occurs much before 1970 (Figs. 5 and 6). Also the peak in Zn concentrations changes its position with similar regularity; in CI, it is post-1970; in CII, it is just before 1970; and in CIII, it shifts before 1960. These changes seem not to be depositional in origin but, rather, are related to groundwater fluctuations. The frequency of these fluctuations is the greatest in CIII, which is situated at the lowest location (Fig. 3). In the highly located CI profile, the water table changes within the sampled deposits are relatively rare and Zn and Cd peaks seem to be in their original positions. By contrast, in the CII profile, which is located at an intermediate height, moderate water level changes caused only a small downward migration of the Cd peak.

In general, heavy metals are stored in the Mal Pano Panew sediments for a rather short period of about 50 years and appear to be moderately affected by processes of downward migration to date. The investigated concentrations of Ba, Cu, and Pb seem to be not more than about 10%, and Zn and Cd of several tens of percent less than the original. In the sediments accumulated at the average level of water table, the quantity of heavy metals remobilised could have increased up to 100%. Frequent fluctuations of water table within these layers have blurred considerably the spatial patterns in the original heavy metal concentrations within the period of less than 40 years. Metal fractionation (Fig. 4) suggests that postdepositional mobilisation is more widespread than the changes in heavy metal distribution described above show. In particular, the occurrence of Ba, Cu, and Pb in all profiles in sediments of different ages, predominantly with amorphous Fe-oxyhydroxides, indicates that dissolution and reprecipitation of these metals have taken place. Similar metal partitioning was also observed in sediments accumulated in an incised river system, which was also affected by water table fluctuation. This was explained by a breakdown and subsequent precipitation of metal-bearing minerals (Hudson-
Edwards et al., 1998). Unfortunately, in the present studies, the original metal minerals are unknown. Moreover, organic matter degradation can explain the occurrence of Zn and Cd mainly in the exchangeable fraction (Hudson-Edwards et al., 1998). Also, in the investigations carried out here, a decrease of organic matter content with depth in all profiles as well as the disappearance of black organic layers support this explanation. Apparently, metals mobilised during each inundation migrate only very slowly and, perhaps, precipitate in these same layers. Probably, sediment stratigraphy controls this process much more than it is generally considered, and dense, fine, organic laminae are able to hamper metal migration quite efficiently.

5. Conclusions

The correlation of Ba, Cu, and Pb concentrations changes in vertical profiles with Cu and Ba compound production and with Pb load, discharged in effluents, enabled dating of the 20th century Mała Panew River sediments. The variable thickness of the polluted sediments within meander bends shows that, in order to eliminate spurious results in routine sediments dating with heavy metals, the examination of the metal concentrations in a series of several profiles in each floodplain is necessary. Sharp peaks of weakly mobile metals, especially of Pb and Ba, which exceed by at least two orders of magnitude the background values, are the most reliable markers. An incremental annual series of 1- to 2-cm-thick layers better reflects river pollution changes than those rarely accumulated layers, which are several decimetres thick. Sediments inundated once a year are the most suitable for dating with heavy metals.

The dating of these sediments revealed that the Mała Panew River pollution was generally the greatest in the 1970s. In the period 1960–1985, the river was probably one of the most polluted with heavy metals in Europe.

In some river valleys, the limited number of map editions precludes a dating of sediments cartographically. In such cases, tree-ring dating can give an alternative for dating the 20th century floodplains in which contemporary landforms are clearly distinguishable in the topography. In the investigations carried out, the dendrochronologic data provided a basis for the general age of the deposits and the geomorphic evolution of the tree sites, whereas the geochemical data provided insights into the age of the vertically accreted floodplain sediments.

A comparison of the relative changes between heavy metal peaks in sediments of similar age in different profiles suggests that the rate of downward metal migration is variable. Generally, in layers that occur high above the water table, none of the heavy metals investigated seems to have been mobilised. In the layers that accumulated at lower positions, the Zn and Cd peaks seem to have moved down several centimetres or several decimetres. In profiles inundated for at least 2–3 weeks every year, both Zn and Cd, as well as the relatively less mobile Ba, Cu, and Pb, are translocated down by several decimetres. Also, the very high contribution of Zn and Cd in the exchangeable fraction, 50–75% on average, testifies to the higher mobility of these elements within Mała Panew sediments. This is greater than in the cases of Ba, Cu, and Pb, which predominantly occur in moderately reducible phase. The investigation shows that frequent fluctuation of the water table is the principal factor in the blurring of the downward trend in the original heavy metal concentrations. These can be quite marked, even in periods of less than 40 years.

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