



Glacial morphogenesis of uplands of the Warta Glaciation in Poland as a control on heavy metal distribution in deposits

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The investigations were carried out to determine the relationship between Cr, Co, Cd, Cu, Zn and Pb content and glacial morphogenesis that implies the geomorphological position of outcrops of Quaternary deposits. The analysis deals with parts of two glacial uplands whose relief developed during deglaciation of the Warta ice sheet and which are characterized by similar relief and lithology of surface deposits. These are the Nidzica Upland near Grzebsk and the Bielsk Plain near Bielsk Podlaski. These areas show distinct regularity in pattern of geomorphological units, proving their areal deglaciation. Melt-out depressions, side valleys, ablation covers, kame terraces and kames as well as glaciofluvial plains are observed. The typical geomorphological element is isolated morainic hills (mesas). The investigations enabled determinations of regularity in the distribution of chemical elements in the soil environment of the geomorphological units. Among mineral sediments, clay interlayers observed within kame terrace and kame deposits were the most susceptible to concentrations of heavy metals, regardless of the region and the element to be determined. Lower Cd, Cu, Co, Pb, Zn and Cr contents were associated with morainic mesa and ablation cover deposits. The lowest contents of heavy minerals were measured in glaciofluvial plain, kame and kame terrace sands. Among landforms filled with organic deposits, the highest abilities to fix Cr, Co, Cu and Zn were shown by ice-dammed basins within upland deposits (Nidzica Upland) and side valley deposits (Bielsk Plain). Peats and muds of melt-out depressions were found to be most active in retaining Cd and Pb.

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INTRODUCTION

Contents of heavy metals in sediments depend on a number of both natural and human-induced processes. By affecting the mineral composition of rocks, lithogenetic processes define the range of their physico-chemical properties, which, in turn, determine the possible level of concentration of individual elements. Distribution of these elements in sediments is uneven and dependent upon many factors, including the content and mineral composition of clay minerals, as well as the contents of organic matter and iron oxides and hydroxides, *etc.* (Helios-Rybicka, 1986; Petterson *et al.*, 1993; Pittman and Lewan, 1994; Kyzioł, 1994; Velde, 1995).

The occurrence of individual types of Quaternary deposits, dominant in the European Lowlands, is associated with definite geomorphological units. By determining the relation of the origin and geomorphological position of outcrops of specified deposits to the concentration of heavy metals in these deposits,

we can improve the procedures of estimation of concentration of the elements in the geological space. We are also able to identify zones susceptible to retaining heavy minerals and to determine regularity in the occurrence of the zones.

The image of distribution of heavy metals in surface sediments of the Polish Lowlands, presented in the geochemical atlases of Poland (Lis *et al.*, 1997) published by the Geological Survey (Polish Geological Institute) is highly generalized. It does not include the origin and geomorphological position of the sediments, although these factors can affect the dynamics of changes in concentrations of the elements (often generated by human activity). However, the relationship between the morphogenesis of the area and the accumulation of heavy metals is often presented for areas of non-glacial provenance. An example of such analysis is the study of slope loess deposits in the Lublin Upland (E Poland) (Zgłobicki and Rodzik, 2007). Heavy metals concentrations (Cd, Cu, Pb and Zn) in the deposits are considered to be associated with the presence of both organic matter and clay minerals. However, the influence of the relief-dependent process of surface washing out on the distri-

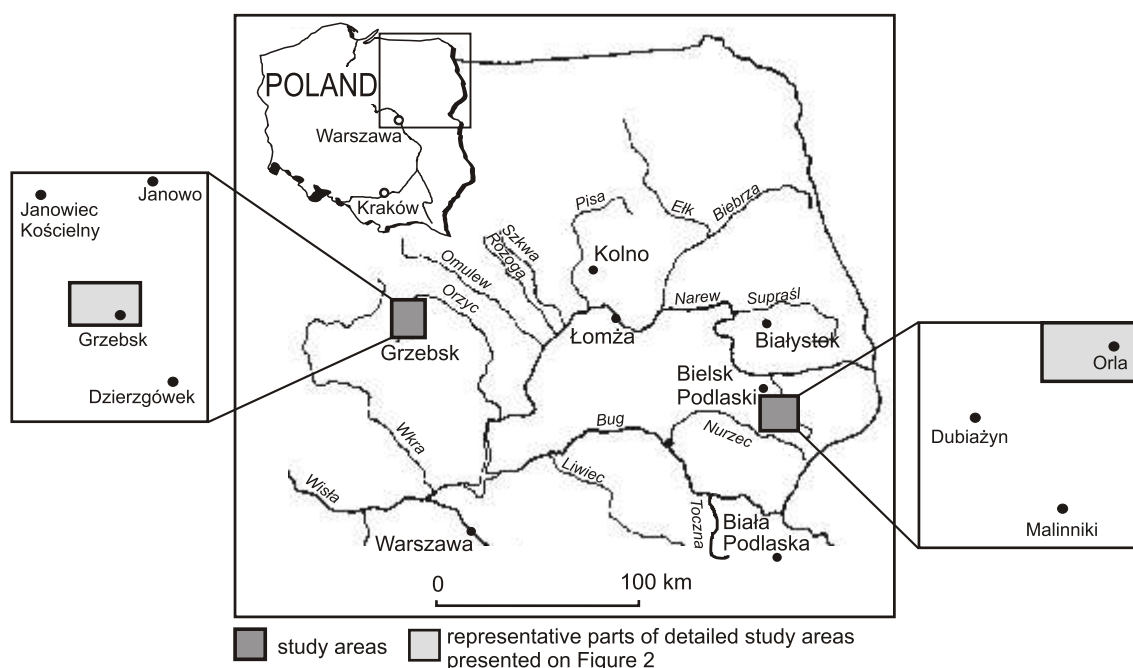


Fig. 1. Location of the study area

bution of heavy metals is also emphasised for that area (Zgłobicki and Rodzik, 2007).

The dependence of accumulation of heavy minerals in surface sediments on the pattern of geomorphological units is commonly exposed in geochemical analyses of river valley bottom deposits.

Distribution of contaminants in various landforms and types of river-channel and flood deposits as well as in longitudinal sections of urbanized river valleys was presented in Evans and Davies (1994), Rhoads and Cahill (1999), Ciszewski (2001, 2003), Sharma *et al.* (2003) and Akcay *et al.* (2003). Ciszewski and Malik (2004) claimed that heavy metals concentrations are due to some features of deposits composing terraces of the Mała Panew River. Ciszewski *et al.* (2004) suggested their association with whole geomorphological landforms of the river. Helios-Rybicka (1986) pointed out that there is a relation of heavy metals accumulation to the lithology of river channel deposits composing the Vistula River valley bottom. Concentrations of these elements in river valley sediments are considered to be also due to the fluvial transport mechanism (Helios-Rybicka, 1986; Galán *et al.*, 2008; Conde Bueno *et al.*, 2009). Moreover, regularities in concentrations of heavy metals, which result from both the character of sedimentary processes and mineral composition, have been proved in a lacustrine environment (Bojakowska and Sokołowska, 1997; Sobczyk and Siepak, 2001, Bilali *et al.*, 2002). There are few papers concerning the relationship between concentrations of heavy metals in glacial deposits and morphogenesis of outcrop zones, because such deposits often make up structurally very complex geomorphological units.

Variability in concentrations of heavy metals in genetically different sediments of Finland, including glacial deposits, was discussed by Salonen and Korkka-Niemi (2007). Analysing glacial till, glaciofluvial or littoral sand, clay, peat and marine

mud from the area near Turku, they proved variability in concentrations of the elements and found out that parent material determines the chemical composition of sediments in uncontaminated areas. The type of parent material has a crucial effect on the amount of accumulation of toxic components. Those authors claimed that the dominant role in the distribution of heavy metals should be attributed to the mineral composition of individual genetic types of the deposits.

The goal of the investigations presented in this study was to determine the significance of glacial morphogenesis in the development of susceptibility of surface sediments to concentration of selected heavy metals, which are used in anthropogenic pressure gradation. The investigations focused on parts of two glacial uplands whose relief developed during deglaciation of the Warta ice sheet. These are part of the Nidzica Upland near Grzebsk and part of the Bielsk Plain near Bielsk Podlaski (Fig. 1). The areas represent the same type of geological structure of the near-surface zone. Because of similarity in relief and lithologies composing individual geomorphological units between these areas, they can be considered typical of the regions where ice-sheet retreat was of areal type. Both the areas are agricultural regions with similar levels of agrotechnical measures.

The present investigations included geomorphological analysis of some areas. Concentrations of chromium, cobalt, cadmium, copper, lead and zinc were determined in sediments composing the identified geomorphological units. Regularities in the distribution of these elements in the soil environment were also analysed.

MORPHOGENESIS OF THE STUDY AREA

The analysis was performed in two areas of the Polish Lowlands, whose topography was shaped during deglaciation of the

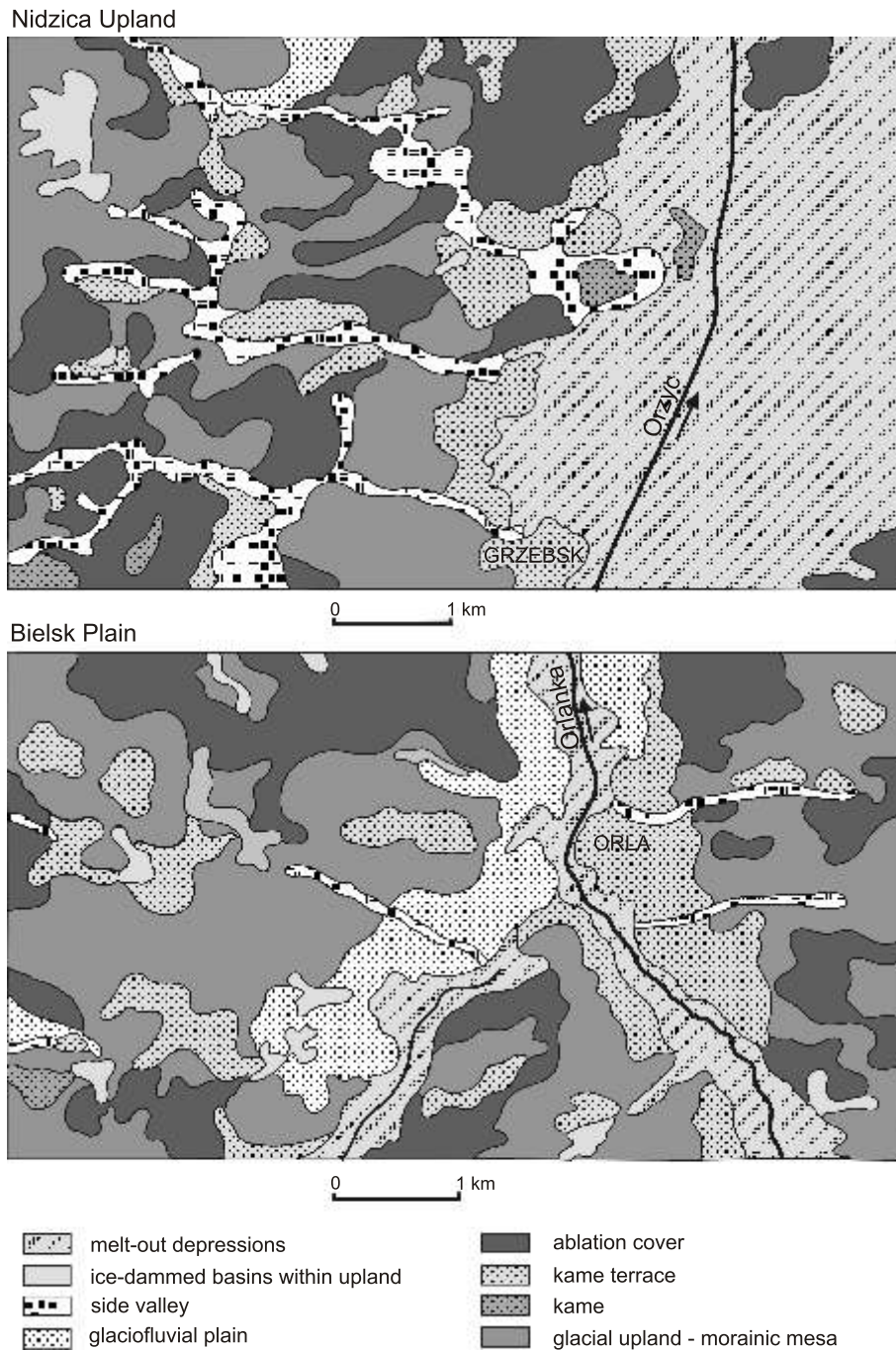


Fig. 2. Geomorphological sketches of the representative parts of the investigated areas (based on Falkowska, 2009)

Warta ice sheet. The main relief features of the area situated south of Bielsk Podlaski within the Bielsk Plain (190 km²) developed as a result of deglaciation of the Wkra Stadial ice sheet (Mojski, 1972; Lindner and Marks, 1999; Brud and Kupryjanowicz, 2002). Glacial morphogenesis of the Nidzica Upland near Grzebsk (180 km²) is associated with the retreat of the Mława Stadial (Różycki, 1972; Michalska, 1967). Both the areas are characterized by a distinct regularity in the geological structure and pattern of geomorphological units, indicating areal deglaciation (Figs. 2 and 3). This type of deglaciation of the Nidzica Upland during the Warta Glaciation was already sug-

gested by Michalska (1967), Bałuk (1991) and Uniejewska (2001). The predominance of processes related to areal retreat of the ice sheet in the Bielsk Plain was underlined by Mojski (1972), Falkowski *et al.*, (1988), Musiał (1992), Brud (2000) and Brud and Kupryjanowicz (2002).

The feature of the near-surface geological structure in common to both the areas is the occurrence of melt-out depressions, kame terraces, kames and ablation covers. There are also distinct morphological levels observed in the slopes of the glacial till upland (Fig. 2) represented by a succession of levels, coming down stepwise towards melt-out depressions (Fig. 3). They

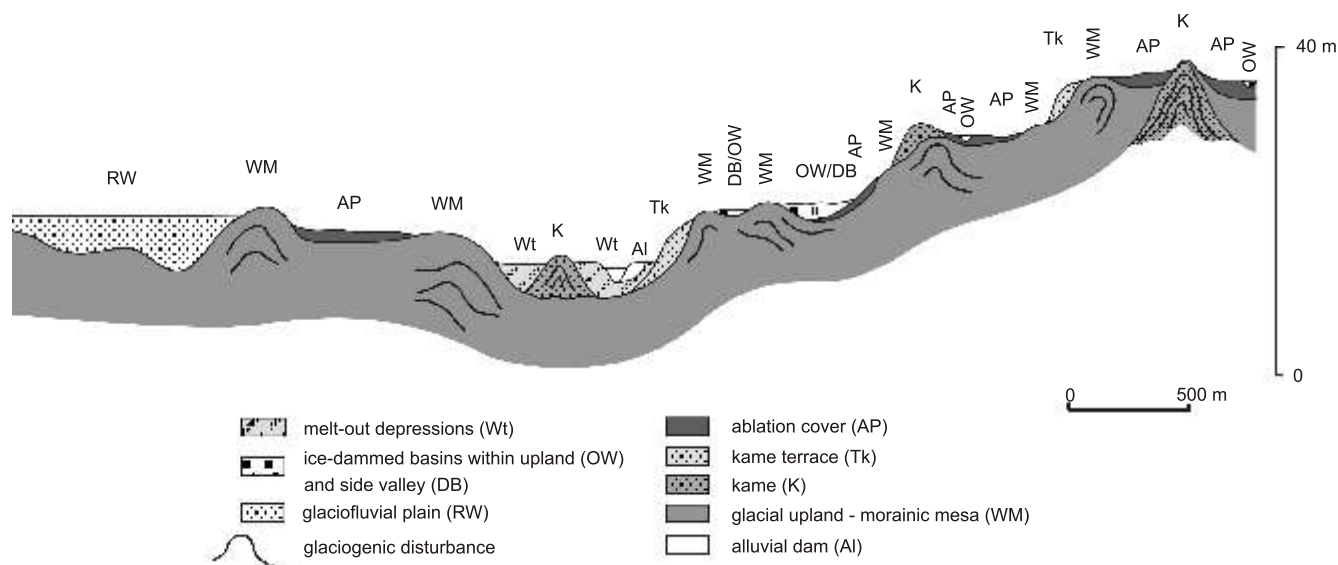


Fig. 3. Model of the geological structure of the surface zone of the investigated regions (scales approximate; after Falkowska, 2009)

are a record of successive phases of dead-ice melting. In many places at the edges of the levels, there are small elongated hills composed of morainic material glaciostatically thrust near dead-ice blocks. Commonly, these are also sites of small sand hills or narrow terraces, well-marked in the topography. They can be considered as small kames and kame terraces marking the pathway of meltwater flows in ice crevasses (Falkowski *et al.*, 1988). Landforms of similar origin and structure have been found within the uppermost parts of moraine hills. They form small hummocks composed of sands and gravels with intercalations of muds and tills, described by Bałuk (1979).

The glacial upland near Grzebsk and Bielsk Podlaski consists of vast hills composed of 5–20 m thick glacial tills (Uniejewska, 2001; Brud and Kmieciak, 2006). These cohesive deposits form “glacial icelands” — morainic mesas (similar forms to kame mesa), because in many areas they are overlain by a silt-sand layer. They form extensive covers that developed probably as a result of very slow meltwater flow in already widened ice crevasses in which kames were previously deposited. Silt sediments of the covers may have been deposited also in ablation puddle zones upon the ice surface. Variability of flow dynamics in such zones affected the selection of deposited material. Similar plains were described by Rdzany (1997) from the NE Łódź Upland between the upper Rawka and Pilica rivers, and defined as ablation covers. Sedimentary structures observed in exposures within these landforms indicate that they are similar in lithology to top layers of flow-tills deposited under conditions of water saturation of morainic material (Boulton, 1972; Marks, 1992). Structural and textural features (e.g., granulation and bedding) of the deposits around the slopes of island tills in the glacial upland (morainic mesa and kames) suggest that ablation material was deposited either in ablation puddle zones that developed in widened ice crevasses or on the surface of melting ice. Thus, they can be considered, like the landforms from the Łódź Upland, to represent ablation covers (Falkowska, 2007).

In the glacial upland area, there are also depressions after small dead ice blocks — ice-dammed basins (Figs. 2 and 3). Currently, most of the depressions are filled with organic deposits. Many of them have been included in the drainage system of the upland through permanent or intermittent streams. Some of side valleys are narrow erosional landforms, incised into the basement. Their bottoms are composed of mineral sediments.

The lowermost areas in the topography are extensive melt-out depressions filled with lacustrine and boggy deposits: peats and peaty muds. After the ice had melted, they were incorporated into the system of surface drainage and adapted as flow pathways for the largest streams of Orłanka and Białka (Bielsk Plain) and Orzyc (Nidzica Upland).

The flow of water causes permanent transformation of organic deposits in the depressions' bottoms, which relies mainly either on the enrichment of redeposited peats and peaty muds in sand material, as observed near Grzebsk (Falkowska, 2008), or on the formation of a distinct alluvial zone in an incision within the organic deposits, as reported from Białka near Orła (south of Bielsk Podlaski; Falkowska, 2009).

Small hills composed of bedded fine- and medium-grained sands occur within melt-out depressions filled with organic deposits (Fig. 2). These are valley kames observed in the bottoms of polygenic sectors of river valleys, characteristic of the eastern Polish Lowlands (Falkowska, 2001). They developed probably as a result of meltwater flow from the last, lowermost-situated dead-ice blocks.

Marginal zones of the depressions are also areas of numerous kame terraces (Figs. 2 and 3). They form elongated kame terraces composed of sand and gravel, variable in grain size. In topographic lows, there are also flat glaciofluvial sand plains that developed when melting ice water flowed between dead ice blocks during the successive deglaciation phases (Brud and Boratyn, 2006).

SAMPLING AND ANALYTICAL METHODS

Table 1

Mineral composition of the particle <0.002 mm (clay fraction) of sediments of the investigated regions (after Falkowska, 2009)

Regions of investigation	Bielsk Plain	Nidzica Upland
Mineral composition of the particle <0.002 mm	S>Kt = I (WM, AP) S>Kt>I ~ Cl (Tk, K, Wt, OW)	S>Kt>I

S — smectite, Kt — kaolinite, I — illite, Cl — chlorite, WM — glacial upland (morainic mesa), AP — ablation cover, Tk — kame terrace, K — kame, Wt — melt-out depression, OW — ice-dammed basin within upland

Lithologic investigations included granulometric (areometric and grain-size sieve) analysis, determination of CaCO₃ content using the Scheibler method, organic matter content using the loss-on-ignition (LOI) method (heating at temperature of 550°C) and pH (in H₂O) of soil using the potentiometric method (Mylińska, 2001). Mineral composition of the clay fraction was determined by the X-ray diffraction method (Table 1). The analysis was carried out only on oriented samples. There were three groups of these: sedimented, after glycol treatment and heated.

Measurements of content of selected elements, including heavy metals, were made on 145 sediment samples representative of each lithological type of deposit making up the geomorphological units identified (Table 2). Samples were collected after detailed analyses of the geological structures of the investigated regions according to ISO 10381-2:2002 (Soil quality — sampling, part 2: Guidance on sampling techniques), and Stuczyński *et al.* (2004) from a depth of 50 cm. They were taken directly from the walls of outcrops or by means of a core of 10 cm in diameter taken by a sampler. Next the samples were dried at a temperature of 105°C, sieved through a 1.0 sieve and then ground in ball mills. They were subsequently subjected to wet decomposition in a closed system, and finally microwave heated (*Paar Physica MULIWAVE* mineralizer). While decomposing the sediments, the following agents were used: HCl — diluted 6/100, HNO₃ — 2/100 and H₂O₂ — 1/100. Contents of the main and trace elements were measured in the obtained solutions using Inductively Coupled Plasma-Atomic Emission Spectrometry (*ICP-AES, Perkin Elmer Optima 5300 DV* spectrometer).

RESEARCH RESULTS

LITHOLOGICAL CHARACTERISTICS OF THE INDIVIDUAL GEOMORPHOLOGICAL UNITS

The present investigations prove a lithological similarity between the deposits of individual geomorphological units in both the regions under study. Small differences result from both slightly different ranges of contents of individual constituents and variability in the mineral composition of the clay fraction.

Deposits from all the geomorphological units of the Nidzica Upland have a similar mineral composition of the clay fraction. Smectites are the most common, prevailing over kaolinite. Illites are the rarest minerals in these deposits (Table 1).

The clay fractions of clay intercalations in kame and kame terrace sands, as well as of the sediments underlying peats and peaty muds of melt out depressions, are also similar in composition. Within the morainic mesa areas of the Bielsk Plain, there is an admixture of chlorite in cohesive deposits.

Different contents of individual clay minerals are observed in island tills of glacial uplands and ablation covers. Smectites are definitely dominant in these deposits, whereas kaolinite and illite occur in smaller but comparable amounts.

THE BIELSK PLAIN

In the Bielsk Plain near Bielsk Podlaski, morainic mesas are composed of cohesive deposits of variable clay fraction contents ranging from 4 to 65% (Table 2). However, the most common are deposits containing >25% of the clay fraction, as indicated by the values of both the mean and the median (Table 2). These are tills, sandy tills, clayey tills and clays. Organic matter contents vary between 1.1 and 7.1%. The values of the mean (6.3%) and the median (3.8%) suggest, however, that the tills are composed mainly of material enriched in organic matter.

Most of the tills and clays of morainic mesas contain calcium carbonate. The CaCO₃ content in these deposits reaches 28.8%, with mean of 7.5% and median of 3.7%. The pH of the deposits composing these geomorphological units varies from slightly acid to basic (5.85–8.52).

Ablation covers consist of sands to silty tills, variable in grain size. The clay fraction content ranges from 0 to 25% (Table 2), with both mean and median of 9%. The organic matter content exceeds 2% only in some places, normally being below 1%. Ablation cover deposits are locally enriched in calcium carbonate. The pH values vary within a wide range of between 4.99 and 8.83.

Kame, kame terrace and glaciofluvial plain deposits are represented mainly by fine- to coarse-grained sands and sandy gravels containing small amount of organic matter (average 0.6%). Calcium carbonate admixture was observed only sporadically. These sediments show slightly acidic to basic pH (Table 2).

Non-cohesive kame deposits are interbedded with tills and clays containing 9 to 45% of the clay fraction (mean 26%, median 31%). The interbeds are characterised by high cohesiveness and increased organic matter contents reaching 9.2%, with mean of 4.0% and median of 3.6%. Kame terrace, kame and glaciofluvial plain deposits show acidic to basic pH (4.84–8.57).

The largest melt-out depressions are filled with a wide range of organic deposits including peat, peaty mud and humic sand, containing variable amounts of organic matter (4.2–83.8%). Clay fraction admixture (<7%) is observed only in peaty muds and humic sands commonly composing the basal part of the deposits. These deposits contain less than 0.1% of calcium carbonate.

Table 2

Characteristic of the investigated sediments

Geomorphological unit number of samples Bielsk Plain/ Nidzica Upland		Content of particle <0.002 mm [%] min-max average median		Loss-on-ignition [%] min-max average median		Content of CaCO ₃ [%] min-max average median		pH	
		Bielsk Plain	Nidzica Upland	Bielsk Plain	Nidzica Upland	Bielsk Plain	Nidzica Upland	Bielsk Plain	Nidzica Upland
Glacial upland (morainic mesa) 15/14		4–65 27 26	12–34 23 24	1.1 6.3 3.8	0.4–3.2 1.7 1.7	0–28.8 7.5 3.7	<0.1	5.85–8.52	6.25–7.48
Ablation cover 12/13		0–25 9 9	0–27 8 6	0.8–4.3 1.4 0.9	0.5–4.1 1.0 0.7	0–24.2 2.2 0	<0.1	4.99–8.83	5.28–7.81
Kame, kame terrace, glaciofluvial plain	sand 9/8	0–2	0–2	0.3–1.0 0.6 0.6	0.1–2.3 0.8 0.6	0–10.0 0.7 0	<0.1	6.16–8.41	5.92–8.54
	clay inter- calation 9/7	9–45 26 31	14–20 16 15	0.6–9.2 4.0 3.6	1.0–2.5 1.6 1.6	0–32.2 6.7 0	<0.1	4.84–8.57	6.05–8.00
Ice-dammed basin within upland 9/10		7–14 11 12	5–68 25 13	3.7–62.2 16.0 4.7	4.6–62.3 2.1 8.0	<0.1	<0.1	6.24–7.08	5.18–8.06
Side valley 11/11		1–37 16 14	0–58 16 4	0.7–6.5 4.0 5.0	3.9–61.8 17.3 8.1	<0.1	<0.1	5.76–8.30	4.73–7.99

Similar deposits fill small ice-dammed basins within the glacial upland. However, they contain less organic matter. Its mean content is 16.0% (ranging from 3.7% to 62.2%) and the median is around 5%. The basal peaty muds and humic tills are characterised additionally by the presence of a clay fraction of 7–14%.

Organic deposits also occur in side valleys. They are represented mainly by sandy muds, argillaceous humic sands, tills and humic clays containing 0.7–6.5% of organic matter. The clay fraction content varies from 1 to 37%. The deposits of vast melt-out depressions, side valleys, and ice-dammed basins within glacial upland contain less than 0.1% calcium carbonate. Organic deposits of these geomorphological units are characterized by acidic to neutral pH (4.90–8.30).

THE NIDZICA UPLAND

The glacial upland (morainic mesas) of the Grzebsk region (Nidzica Upland) is composed of cohesive deposits: tills, sandy tills, clayey tills and clays. These deposits have a clay fraction of 12–34%, with mean of 23% and median of 24%. The organic matter content is small in these deposits, ranging between 0.4 and 3.2%, with both mean and median of 1.7%. Surface deposits of the morainic mesas typically show low pH variability within the range of 6.25–7.48.

The surface zone of ablation covers is composed of deposits containing smaller amounts of both the clay fraction and organic matter as compared with sediments of morainic mesas. These are silty and fine-grained sands as well as tills, sandy tills

and clayey tills with mean clay fraction content of 8% and median of 6%. The average content of organic matter is about 1.0% (the median is 0.7%). The pH values of the deposits vary between 5.28 and 7.81.

Kame hills, kame terraces and glaciofluvial plains of the Nidzica Upland are at the surface composed of fine- to coarse-grained sands and silty sands. They are only slightly enriched in organic matter accounting for up to 2.3% (the mean is 0.8%, the median is 0.6%). CaCO₃ is observed sporadically and its content is below 0.6%. Till interbeds within the deposits constituting the near-surface zone of the kames, kame terraces and glaciofluvial plains contain 14–20% of the clay fraction and 1.6% of organic matter on average. The pH values of the deposits range from 5.92 to 8.54, indicating slightly acidic, neutral or basic conditions.

Vast melt-out depressions are filled with various types of organic deposits containing 7.6–76.1% organic matter, with a mean value of about 43.7%. Peaty muds and humic tills forming the lower parts of these landforms are composed of 7–29% of the clay fraction (with mean of about 13% and median of 9%).

Ice-dammed basins within the upland are filled with deposits in which the organic matter content falls within a similar range of 4.6–62.3% (Table 2). The clay fraction content in these deposits ranges within an interval of 5–68% (averages 25%).

The bottoms of side valleys are lined with peats, peaty muds and organic tills. The measured values of organic matter content vary within the range of approximately 3.9% to almost 61.8%, with a median of 8.1%. The clay fraction content falls within the

interval of 0–58%. The median is 4%, indicating sediments with a smaller clay fraction content. The pH values of organic deposits from the Grzebsk region vary between 4.43 and 8.06.

Calcium carbonate is sporadically observed in the deposits of the geomorphological units in the Nidzica Upland.

CONTENTS OF SELECTED HEAVY METALS

The study areas are agricultural regions. The contents of heavy metals determined by the analyses do not exceed the region's average values presented in the geochemical maps of Poland. The lead content is 18–25 ppm, whereas the chromium contents are below 10 ppm (Lis *et al.*, 1997). The values also fall within the ranges of average concentrations for various arable soils of Poland (Dobrzański *et al.*, 1973; Dudka, 1992). Moreover, they are lower than allowable concentrations recommended by the Regulation of the Ministry of the Environment on the standards of soil and ground quality (Regulation of 9 September 2002, point 1359). The contents of elements measured in soils also fall within the ranges of the so-called standard Dutch List optimum values. There are only two samples showing increased contents of heavy metals. However, they were collected in the immediate vicinity of a high-traffic road.

Distribution of the elements is very uneven in these postglacial areas. Variability in the contents of heavy metals within the individual geomorphological units is high. In these units very significant regularity of distribution of investigated elements is observed (Fig. 4): there are convergence of distribution of means and medians of content of each heavy metal in the individual landforms. The lowest concentrations of heavy metals were recorded in sandy deposits building glaciofluvial plain, kame sands and kame terrace. The highest concentrations occur in clay interlayers of kames, kame terraces and glaciofluvial plains (Cr, Co, Cu, Zn) and in sediments filling the largest melt-out depressions (Pb, Cd).

THE BIELSK PLAIN

Determinations of contents of heavy metals carried out in the Bielsk Plain deposits indicate a recurrent distribution in the individual geomorphological units (Fig. 4A). In surface deposits of the area, the highest Cr, Zn, Co, Cd, Pb and Cu contents were recorded in clay interlayers of kames, kame terraces and glaciofluvial plains (Fig. 4A).

Among the landforms filled with organic deposits, relatively high Cr, Co, Cu and Zn contents were measured in side valley deposits in comparison with other landforms. A different phenomenon was observed in regards to Cd and Pb contents. The greatest amounts of these metals are fixed by peats and peaty muds of melt-out depressions (Fig. 4A).

Slightly lower Cr, Co, Cu and Zn contents were measured in soils of melt-out depressions, as compared with deposits of ice-dammed basin within glacial upland, with zinc showing the widest range of content values (12–43 ppm). Similar contents of heavy metals were observed in mineral sediments composing the morainic mesa surfaces.

Smaller amounts of Cr, Zn, Co, Cd, Pb and Cu occur in ablation cover deposits that, however, locally show increased

concentrations. They are characterized by a wide range of content values of these elements, accompanied by low values of both the mean and the median. The lowest concentrations of heavy metals were recorded in sands of glaciofluvial plain, kame and kame terrace (Fig. 4A).

THE NIDZICA UPLAND

The distribution of contents of heavy metals in the geomorphological units of the Nidzica Upland near Grzebsk is conspicuous by its distinct regularity.

Within the landforms composed of mineral sediments the most active in attracting these elements are till and clay interlayers within kame, kame terrace and glaciofluvial plain sands (Fig. 4B). Cohesive deposits of morainic mesas are also characterized by high activity. Low Cr, Co, Cd, Cu, Pb and Zn concentrations are observed in silty and argillaceous deposits of ablation covers. The smallest concentrations of heavy metals were measured in kame, kame terrace and glaciofluvial plain sands (Fig. 4B).

In the case of landforms built up of organic deposits the greatest amounts of Cd and Pb occur in sediments filling the largest melt-out depressions. The other elements are most easily fixed by the ice-dammed basin within upland deposits of upland areas. Among organic deposits, peats and peaty muds of melt-out depressions exhibit the lowest content of these elements, with values close to those typical of mineral sediments. Cr, Co, Cd, Cu, Pb and Zn contents determined in side valley deposits are lower than those measured in ice-dammed basin deposits of upland areas (Fig. 4B).

The results of investigations prove that there are differences in the regularities observed in each of the regions. Contents of heavy metals determined in sediments of this region are higher (excluding Zn) than those measured in the Bielsk Plain, although the sediments contain lower amounts of the clay fraction, calcium carbonate and organic matter. This is manifested by higher values of both the mean and the median calculated for these elements. Moreover, the Nidzica Upland differs from the Bielsk Podlaski region in having a wider range of Cr, Co, Cd, Cu and Pb contents in organic deposits filling melt-out depressions, ice-dammed basin within upland and side valleys (Fig. 4).

DISCUSSIONS

The present investigations prove that the distribution pattern of concentrations of heavy metals in the glacial geomorphological units depends on the type of element. The distribution pattern of Cr, Zn, Co and Cu differs from that of Cd and Pb. Results of the geochemical measurements were examined with a distribution test, which showed that the investigated heavy metals follow a normal distribution. This is a general trend of geochemical data (Krumbein, 1937). It was found that in both of investigated areas the contents of Cr, Zn, Co and Cu were very strongly correlated with each other (correlation coefficient $r > 0.7$, probability p -value < 0.05) and weakly or not at all correlated with the contents of Cd and Pb. The value of correlation coefficient r for content of these two

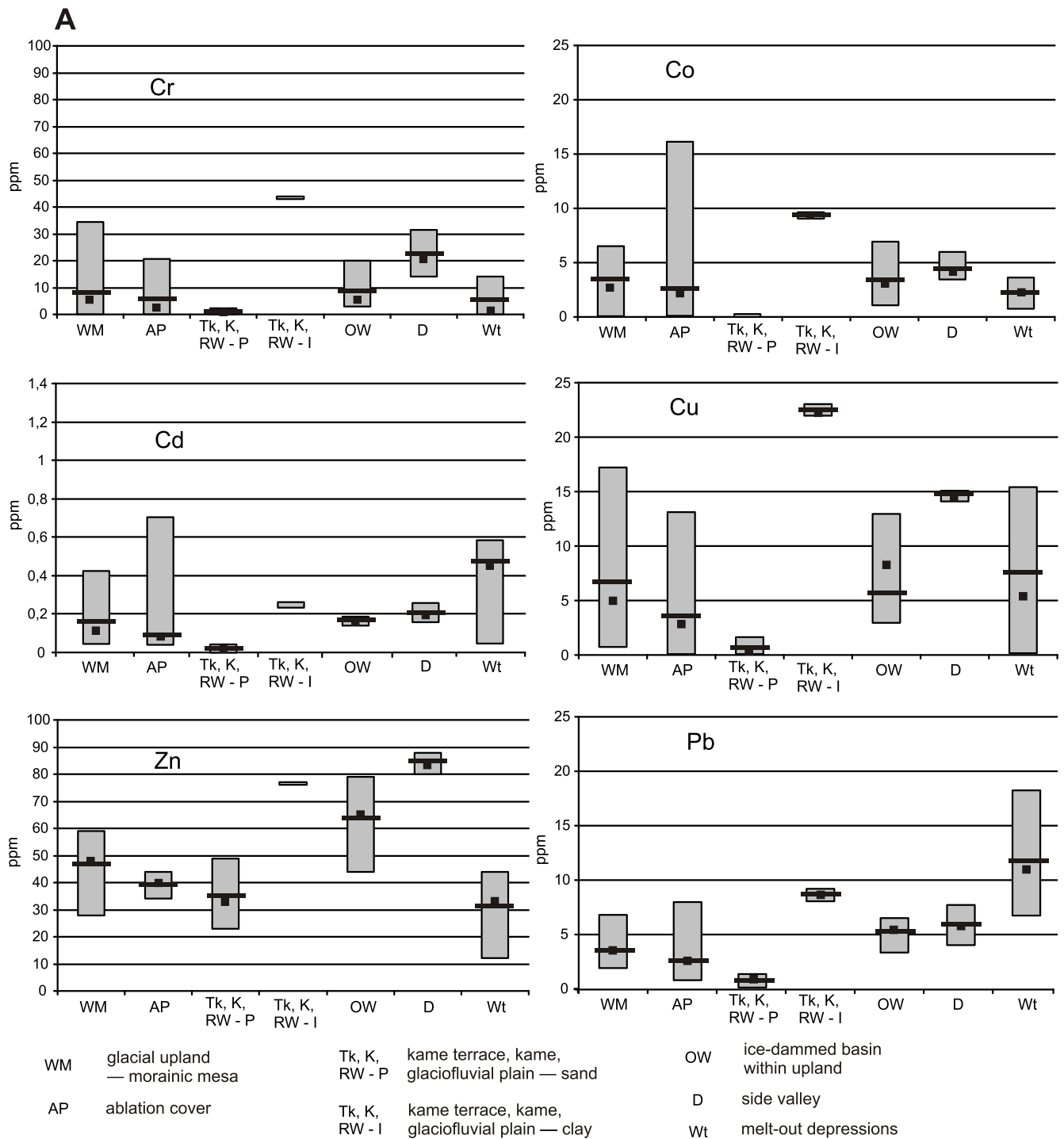
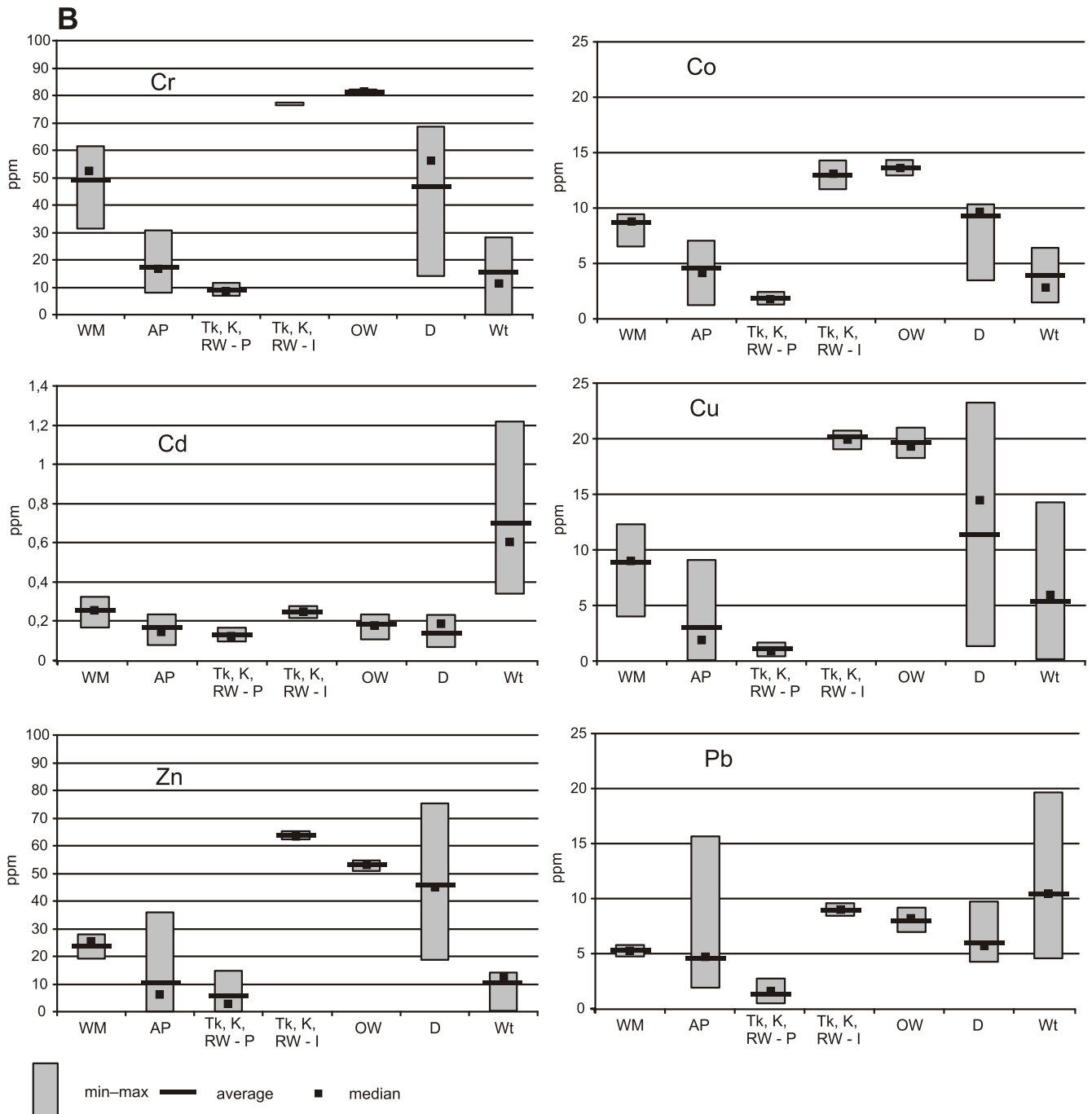


Fig. 4. Content of heavy metals

A — geomorphological units of the Bielsk Plain in the Bielsk Podlaski area;

elements and Cr, Zn, Co and Cu is less than 0.51 (p -value <0.05 ; Table 3). But there is also a strong correlation of the concentration of Cd with the concentration of Pb ($r = 0.97$ for Bielsk Plain and $r = 0.77$ for Nidzica Upland with p -value <0.05). It was observed that this regularity was caused by the factors which dominate process of sorption of heavy metals by deposits. The concentrations of Cr, Cd, Zn and Cu strongly depends on the content of the clay fraction ($r >0.7$, p -value

<0.05). On the other hand, the organic matter content has a crucial influence on content of Cd and Pb in all investigated deposits (Table 4). But in deposits in which LOI $>10\%$ organic matter has an influence on sorption of all investigated heavy metals because a strong correlation was observed between content of Cr, Zn, Co, Cu, Pb, Cd and content of organic matter ($r >0.7$, p -value <0.05 ; Table 4).



in the sediments

B — geomorphological units of the Nidzica Upland in the Grzebsk area

So, contents of heavy metals in geomorphological units filled with peats depend on the organic matter content as well as on the degree of decay and special composition of the peats (Sapek, 1980; Twardowska *et al.*, 1999). In mineral and organic-mineral sediments (LOI <10%) of the postglacial areas, the granulometric composition (content of the clay fraction) affects more strongly the concentrations of heavy metals than the organic matter content.

In postglacial areas of equal anthropogenic pressure, the basement lithology (parent material) is the crucial factor influencing the concentrations of heavy metals, as evidenced by research carried out by Salonen and Korkka-Niemi (2007) in the Turku region of Finland and by Palumbo *et al.* (2000). The parent material composition of individual landforms depends on their origin. Hence, also the susceptibility to accumulate heavy metals is dependent on the origin. The presented investigations

Table 3

**Correlation matrix of heavy metal content for sediments
(number of samples = 145, *p*-value — probability)**

Bielsk Plain						
	Cr	Cd	Zn	Co	Cu	Pb
Cr	1.00					
Cd	0.17	1.00				
Zn	0.80	0.16	1.00			
Co	0.96	0.19	0.71	1.00		
Cu	0.98	0.34	0.79	0.94	1.00	
Pb	0.36	0.97	0.14	0.35	0.51	1.00
Nidzica Upland						
	Cr	Cd	Zn	Co	Cu	Pb
Cr	1.00					
Cd	0.31	1.00				
Zn	0.95	0.28	1.00			
Co	0.99	0.29	0.93	1.00		
Cu	0.96	0.18	0.97	0.97	1.00	
Pb	0.31	0.77	0.36	0.33	0.46	1.00

Correlation coefficients are statistically significant (*p*-value <0.05)

Table 4

Correlations of the contents of heavy metals with content of clay fraction and organic matter in the sediments (*p*-value — probability)

	Content of particle <0.002 mm (clay fraction)	Loss-on-ignition of deposits	Loss-on-ignition of organic deposits (>2%)	Loss-on-ignition of organic deposits (>10%)
Cr	0.94	0.37	0.37	0.75
Cd	0.37	0.84	0.79	0.70
Zn	0.79	0.12	0.38	0.81
Co	0.90	0.41	0.63	0.85
Cu	0.73	0.16	0.24	0.84
Pb	0.12	0.85	0.80	0.70

Correlation coefficients are statistically significant (*p*-value <0.05)

show that the distribution trend of individual metals in each area is constant. The research results suggest regularity in the distribution of heavy metals within the deposits of topographic landforms typical of glacial areas. Areal deglaciation of the Warta ice sheet resulted in the formation of geomorphological landforms consisting of sediments showing specific physico-chemical features i.e. specified susceptibility to Cr, Co, Cd, Cu, Zn and Pb concentrations.

It was observed that both regions show similarity in the distribution of contents of heavy metals in the geomorphological units. However, the ranges of content values are slightly differ-

ent. Despite a certain difference in the anthropogenic pressure level, the distribution trend of these elements is constant. Regional variations are observed mainly in the landforms composed of organic and mineral-organic deposits of melt-out depressions, side valleys and ice-dammed basins within upland areas (Fig. 4).

The highest contents of heavy metals were observed in clay interlayers of kame and kame terrace sands. However, the range of content values is small due to low lithologic variability (Fig. 4). The high concentrations observed in these deposits result also from the fact that they play a role of a filter preventing chemical compounds from downward migration. They are the active horizon within low-activity deposits, able to fix heavy metals.

Among the landforms composed of mineral sediments, morainic mesas (till outcrops) also show high Cd, Cu, Co, Pb, Zn and Cr contents, however the values are lower than those measured in tills and clays occurring within kames and kame terraces (Fig. 4). This phenomenon takes place although deposits building morainic mesas were characterized by higher contents of clay fraction and organic matter (Table 2). Sediments of morainic mesa reveal also higher concentrations of heavy metals than those measured in ablation cover

This is caused by smaller amounts of elements which have a crucial influence on content of heavy metals (clay fraction, organic matter and calcium carbonate) in deposits of ablation covers as compared with the deposits of island tills of glacial uplands. The lowest values are observed in sandy deposits of kames, kame terraces and glaciofluvial plains. The range of contents of heavy metals in these geomorphological units (built up of mineral deposits) depends on both the variability in the clay fraction content (Table 4) and its mineral composition (Pittman and Lewan, 1994; Kyzioł, 1994; Velde, 1995).

The units filling with organic deposits (melt-out depressions, side valleys, ice-dammed basins within upland) show variability in the regularity of heavy metals distribution, depending on the type of element. Among these landforms deposits of ice-dammed basins within uplands of the Nidzica Upland and side valley sediments of the Bielsk Plain show the highest ability to attract Cr, Co, Cu and Zn. The greatest amounts of Cd and Pb were accumulated in peats and peaty muds of melt-out depressions (LOI >10%). High concentrations of heavy metals in organic deposits of side valleys and ice-dammed basins of glacial upland are due to the joint presence of the two components showing high sorption properties: clay fraction and organic matter. These two components are the key factors in attracting heavy metals in this type of sediments. In addition, these are zones of concentrated runoff from the glacial uplands, vulnerable to the supply of a greater load of the elements measured.

Surface deposits of the glacial areas reveal regional variability in contents of heavy metals. Higher Cd, Cu, Co, Pb and Cr concentrations are observed in the Nidzica Upland near Grzebsk than in the Bielsk Plain (Fig. 4), although the geomorphological units of the Nidzica Upland are composed of sediments containing smaller amounts of clay minerals and organic matter than those from the Bielsk Plain. Smectites, attracting sorption of heavy metals, are definitely dominant in the clay fraction of deposits from Bielsk Plain and this element also occurs in the clay

fraction of deposits from Nidzica Upland, although in lesser quantities. Moreover, deposits in Nidzica Upland contain no CaCO₃ whereas sediments building geomorphological units in Bielsk Plain (Table 2), whereby their ability to attract heavy metals is increased. It is very significant that deposits of all geomorphological units in both investigated regions are characterized by similar pH. So, the variability in contents of heavy metals in both investigated areas can be explained by differences in the levels of agricultural management, and thus by differences in the effects of anthropogenic factors. But in both regions the anthropogenic pressure is rather low. On the other hand this variability in contents of investigated heavy metals in Nidzica Upland and Bielsk Plain can be also caused by chemical composition of the parent material, because this material strongly influences soil chemical properties (Palumbo *et al.*, 2000; Salminen and Gregorauskiene, 2000).

The research results suggest that the use of a regular sampling network (Lis *et al.*, 1999) in constructing geochemical maps can deliver only a fortuitous image, especially in areas of complex geological structure, such as lowland areas of postglacial relief. It seems justified to postulate the use of a geomorphological key in preparing regional geochemical reports. This key allows to optimization of sample collection and obtains reliable evaluation of contents of chemical elements.

CONCLUSIONS

In areas of areal deglaciation, there is a relationship between concentrations of Cd, Cu, Co, Pb, Zn, Cr in surface deposits and the origin of individual geomorphological units.

Among mineral sediments, the highest susceptibility to accumulate heavy metals is manifested by clay interlayers observed within sands of kame terraces and kames, regardless of both the region and the type of element. Lower amounts of Cd, Cu, Co, Pb, Zn and Cr were attracted by till deposits composing the morainic mesa surface, however, they show higher concentrations than those measured in ablation cover deposits. The lowest concentrations of heavy metals were recorded in sands of glaciofluvial plain, kame terrace and kame.

As concerning the landforms filled with organic deposits, there is variability in the regularity of heavy metals distribution depending on both the type of element and the region. Deposits of ice-dammed basins within upland (Nidzica Upland) and side valley sediments (Bielsk Plain) show the highest ability to attract Cr, Co, Cu and Zn. The greatest amounts of Cd and Pb were accumulated in peats and peaty muds of melt-out depressions.

In mineral and mineral-organic deposits (LOI < 10%) the concentrations of Cr, Cd, Zn and Cu strongly depend on the content of the clay fraction. The organic matter has a crucial influence on the content of Cr, Cd, Zn Cu in deposits in which LOI > 10% and on content of Cd and Pb in all types of investigated deposits.

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