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GEOCHEMICAL CHARACTERISTICS OF LATE GLACIAL AND HOLOCENE BIOGENIC SEDIMENTS IN CENTRAL POLAND AND IMPLICATIONS FOR RECONSTRUCTING THE PALAEOENVIRONMENT

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Abstract. The chemical composition of lake and mire sediments can be used as proxies of past changes in different accumulation environments. Here, I present these proxies that can be used to reconstruct the palaeoenvironment of the past 16,000 years for many mineral-biogenic series from central Poland and establish regional similarities and differences. Past geochemical studies of biogenic sediments from this region were usually carried out in the context of the genesis of: individual accumulation reservoirs, the development of the relief of river valleys and watersheds; they were also used in combination with other methods of palaeoecological research also reconstruct climatic changes in individual phases of the Late Glacial and Holocene. However, due to the complexity of matter circulation in the lithological and hypsometrical diverse transitional zone between the belts of the Polish Uplands and the Polish Lowlands, an analysis was made to determine the relationship between the conditions of biogenic sedimentation at individual sites using selected statistical analyses. In addition to its description of the geochemical variability of biogenic sediments, this analysis was supplemented by its reference to the spatial differentiation in the relationships between geochemical landscapes and the landforms of various orders. In turn, the method of lithogeochemical facies used for several profiles along the transect from the west to the east of the region made it possible to determine: the origin of water supplying the studied biogenic accumulation reservoirs, the range of individual zones of their supply and the conditions of inflow of allochthonous mineral matter.

Key words: geochemistry, mires, palaeolakes, palaeogeography, the postglacial period, statistical analysis, Polish Lowlands

Introduction

There is a rich papers on the reconstruction of palaeoenvironmental changes based on the chemical composition of sediments deposited in the lake or mire environment of central Poland is extensive (e.g., Goździk, Konecka-Betley 1992; Ziułkiewicz *et al.* 2012; Borówka *et al.* 2014a,b, 2015a,b; Gałka *et al.* 2020; Petera-Zganiacz *et al.* 2022). Nevertheless, the results in this field have not been systematised in terms of the spatial variability of depositional processes, which are conditioned by the functioning and nature of elementary connections between geochemical landscapes. The differences in the sedimentological and geochemical records of the Late Glacial and Holocene events among sites result largely from the location of a given biogenic accumulation reservoir relative to neighbouring landscape units of an autonomous, transit or subordinate character; it is this character that, along with the geological structure and lithology of the catchment area, determines the kind and dynamics of the circulation of water and matter in the environment (Oświt *et al.* 1980; Żurek 1990; Borówka 1992; Wicik 1992a; Bezkowska 1997; Falkowska 2009; Hirsch *et al.* 2015; Okupny, Pawłowski 2021).

The results of spatial analyses of the chemical composition of biogenic sediments for various

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research sites to date have included cartographic studies at various scales and numerical values presented as histograms or centrographic measures. In the first case, however, these are usually single ecosystems, in which the geochemical topics discussed refer chronostratigraphic differences or differences between individual accumulation zones (Wojciechowski 1990; Bojakowska, Sokołowska 1997; Aleksander-Kwaterczak, Kostka 2011; Pawłowski *et al.* 2014; Adumitroaei *et al.* 2018; Adamek *et al.* 2021; Juśkiewicz, Gierszewski 2022); the sediments of several biogenic accumulation reservoirs within one morphogenetic or landscape zone have been compared less often (e.g., Wicik 1984; Borówka 1992; Owsianny *et al.* 2011; Kłapyta *et al.* 2016). In cases of statistical description, the most commonly used measures are averages, dispersion and asymmetry (Bojakowska, Lech 2008; Borówka *et al.* 2022). On the other hand, statistical inferencing to detect interdependencies between individual elements of the chemical composition of sediments and environmental factors is most effective for stations with long measurement series (e.g., Boryczka, Wicik 1983; Walanus 2000; Okupny *et al.* 2021; Zander *et al.* 2021; Płóciennik *et al.* 2022), or for larger areas covered by detailed monitoring (Marszelewski 2005; Sojka *et al.* 2022).

In the light of the literature, the variation in concentrations of geochemical components in biogenic sediments is mainly explained by: increased supply of allochthonous mineral matter to reservoirs (Borówka 1992; Enters *et al.* 2010; Mendyk *et al.* 2016; Lenz *et al.* 2021; Petera-Zganiacz *et al.* 2022); changes in habitat trophy (Woszczyk 2011; Zawiska *et al.* 2019; Mirosław-Grabowska *et al.* 2020); and the specifics of hydrogeological conditions and flow directions of water migration streams in landscape and geochemical systems often identified with the catchment (Kruk 1987; Wicik 1992b; Rycharski, Piórkowski 2001; Okupny, Pawłowski 2021). Specific arrangements of these conditions can also be used as the basis for distinguishing specific types of hydrogenic sediment-forming habitats (Okruszko 1983; Davis, Anderson 1991), which may nonetheless be subject to changes due to various human activities (Cieśla, Stupnicka 1980; Oonk *et al.* 2009; Zgłobicki *et al.* 2011; Płaza *et al.* 2013/2015; Szwarczewski, Smolska, 2013; Dörfler *et al.* 2020; Sobkowiak-Tabaka *et al.* 2022).

In turn, the nature and intensity of individual depositional processes are responsible for many elements within reservoirs precipitating as poorly soluble compounds (Kwiatkowski 1971; Grobelny, Mikulski 1981; Hildebrandt-Radke *et al.* 2011; Rydelek 2013). It should be emphasised that, when interpreting past environmental changes based on the concentration or mutual relationship of individual lithogeochemical components, it is necessary to take into account the geochemical background. The possibility of precisely determining natural concentrations of elements as reference values obviously depends on the geological structure and lithology of the catchment area, which therefore very often vary even locally (Gałuszka 2007; Zgłobicki 2010). For this reason, geochemical data can be considered in terms of positive or negative anomalies, which in areas of polygenic relief better inform us about excesses or deficiencies in individual elements (Lis, Pasieczna 2001).

In central Poland, which is transitional between highlands and the Polish Lowlands (Turkowska 2006), peatland coverage ranges between 0.6 and 2.9% and is almost twice as low as the national average (Żurek 1987; Okupny *et al.* 2014b). In addition, the contemporary mires of central Poland are located in depressions that differ greatly in origin and geological structure (Forysiak 2012), while the structure of biogenic sediments is dominated by fen peat deposits, mainly of reed and sedge beds (Żurek, Okupny 2015). The ratio of area of gyttja deposits to area of peatlands is quite high (from 4% in the Pilica River catchment to as much as 15.3% in the Ner River catchment). According to Forysiak (2013) and Żurek and Okupny (2015), this can be interpreted as an indicator of the past lake coefficient in this part of lowland Poland. The location of the area on the border of two morphological zones was also reflected in the multimodal distributions of the chemical composition of other surface environments (Czarnowska 1996; Pasieczna 2012).

However, the article was inspired by Geomorphological Map of the Łódź region by Turkowska (2006) and the commonly distinguished elementary geochemical landscapes, which, in Perelman's (1971) concept, correspond to the following areas: autonomous, transit and subordinate. The morphogenetic diversity of the wider Łódź area presented in the cited cartographic study is also reflected in existing physical geography regionalisations (Dylik 1948; Gilewska 1986; Kondracki 1991) and should, according to the author, be one of the key criteria for distinguishing geochemical landscapes. The relationships between the geomorphological features and the specificity of individual hydrogenic habitats are needed in order more fully to understand the processes by which matter is supplied to accumulation basins and their effect on chemical composition of biogenic sediments at the regional scale. However, this issue has not yet been discussed for this area, despite several attempts to determine the structure and nature of geochemical landscape relations for other parts of the Polish Lowlands (Sołowiej 1976; Sołowiej, Stryjakiewicz 1987; Kruk 1991; Wicik 1997; Rycharski, Piórkowski 2001).

Moreover, the studies to date have not allowed it to be identified to what extent geochemical landscapes identified with a landform or part thereof (i.e., characterised by lithological homogeneity and type of water circulation) should be treated as dynamic structures subject to continuous environmental changes of a global or regional nature. The importance of postglacial climate change is of particular importance here. On the one hand, it allows, for example, lakes and mires to function in a given place. On the other hand, it is responsible for changes in the vegetation cover and modifies the properties of the substrate, which in turn is reflected in the nature and volume of delivery of various dissolved and suspended substances to biogenic accumulation reservoirs (Apolinarska *et al.* 2012; Dietze *et al.* 2016; Pleskot *et al.* 2018; Ramisch *et al.* 2018; Müller *et al.* 2021; Petera-Zganiacz *et al.* 2022; Płóciennik *et al.* 2022), as well as changes in the rate of sediment accumulation (Żurek 1986; Hinderer 2001; Brisset *et al.* 2015; Żurek, Okupny 2015).

In the light of these remarks, the main aim of the article is to characterise the conditions of biogenic accumulation in the context of factors responsible for the circulation of matter in individual catchments rivers of central Poland, based on a statistical analysis of the geochemical composition of biogenic sediments for selected mires. The achievement of this goal required the use of a number of statistical methods whose results are presented in relation to lithology sediments and in relation to general trends in relief development expressed by the nature and dynamics of denudation processes in the postglacial period. The postglacial period for central Poland was delimited after Dzieduszyńska and Forysiak (2013). An attempt was also made to assess this type of analyses to distinguish lithogeochemical facies along an east–west transect of the research area, taking into account the reaction of the river valley network to environmental changes in the last several thousand years and the role of the geochemical background in interpreting the dynamics of these changes. The basic criterion for selecting nineteen peatlands for specialist palaeogeographical analyses was that their biogenic fills be thicker than the regional average, as this allowed the longest possible time range of postglacial environmental changes to be obtained. Another two research sites are endorheic biogenic accumulation reservoirs whose reactions to even relatively slight changes in the natural environment might be relatively quick changes in water level and water chemistry, trophism or rate of sediment accumulation. In terms of the classification of peaty concave forms developed by Żurek (1999), the studied geosystems represent all five types of mires with fluviogenic, fluviogenic-soligenic, soligenic-topogenic, topogenic and ombrogenic types of recharge.

Regional settings

The study area is approximately delimited by the geographical coordinates 51°00' and 52°20' north latitude and 18°30' and 20°30' east longitude. Thus, it covers a section of the Warta morphogenetic zone defined by Turkowska (2006) as the Łódź region (Fig. 1A). The names of morphological units and mesoregions of the analysed area include several terms referring to large landforms (Fig. 1B), among which valleys (e.g., Sieradz Valley) and basins (e.g., Koło Basin, Szczerców Basin) are most often mentioned. Data collected by Dylik (1948) already show that these forms, together with proglacial valleys, depressions and hollows, constitute 50% of the study area, while upland forms are dominated by low hills (22.6% of the area) and plains (21.3% of the area). Despite differences of opinion over the morphogenesis of individual parts of the study area (cf. Turkowska 2006), it is the diversity of geological and morphological features that is the most important criterion for the multi-stage development of mires (Żurek 1990; Forysiak 2012; Żurek, Okupny 2015).

Due to the relatively high density of the river network in the study area (Rdzany *et al.* 2021), as in the rest of the old-glacial (Saalian Glacial) zone, wetlands are the dominant type of hydrogenic habitat (Dembek *et al.* 2000). The map of the wetland index in Poland by Pietrucień (1991) shows that the study area has a meridional arrangement of zones (Fig. 2), which is comple-

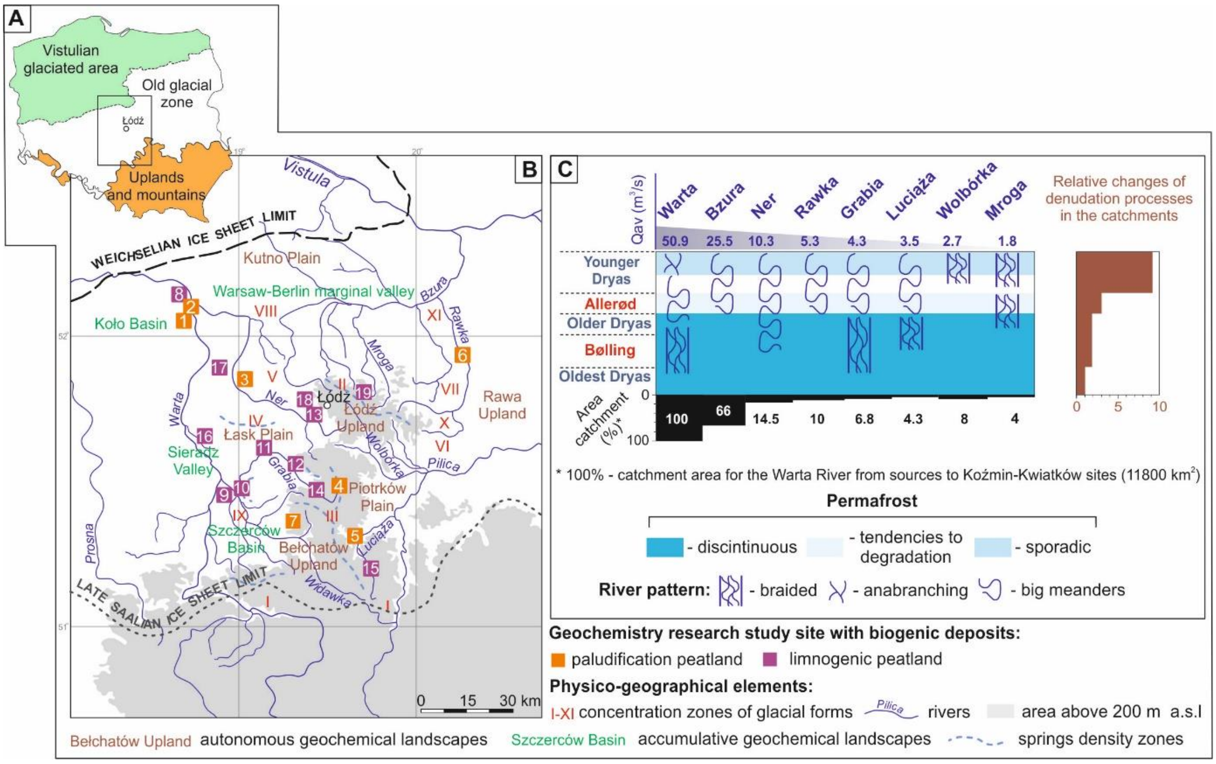

Fig. 1. A – Location of study region against the morphological zones Poland
B – Location study peatland against the selected physicogeographical features central Poland after Moniewski (2004) and Turkowska (2006) research
C – Stratigraphical changes of selected elements the fluvial environemnt in the Late Glacial period agains the contemporary hydrogeomorphological parameters if the main rivers central Poland after Turkowska (1988, 1997, 2006) and Okupny, Pawłowski (2021)
Numbers of research sites is accordance with Table 1

tely different than in the rest of the Polish Lowlands. Of the 1,210 peatlands included in the study by Żurek and Okupny (2015), the majority (95%) are eutrophic mires. On the other hand, there are only 34 mesotrophic and oligotrophic peatlands in the entire region that total less than 630 ha. Of the mires exceeding 10 ha, valley deposits dominate (Forysiak 2012; Żurek, Okupny 2015). The shape of the Lorenz curve, made by Okupny *et al.* (2014b), shows a high concentration of mires within the study area, and most are spread across the entire Szczerców Basin, the Bełdówka River catchment and the Warta River valley from the mouth of the Widawka River to the Jeziorsko reservoir.

The largest of all the examined valley peat-forming wetlands are the deposits in Wilczków (300 ha) and Będczkowice (202 ha), while the smalllest are at Ldzań (4.4 ha) and Okup (7.2 ha). The first two mires mentioned above cover almost the entire width of valley bottoms (Balin-Chropy and Luciąża, respectively), and the remaining ten peat deposits (in order along the west–east transect: Korzeń, Świerczyna, Mianów, Okup, Ldzań, Kolonia-Bechcice, Pawłowa, Grabica, Rozprza, Kopanicha) are located at the edges of floodplain terraces in valleys of rivers that, in the region, are smaller but strongly differentiated in terms of runoff conditions (Jokiel, Stanisławczyk 2012; Jokiel 2016) (Fig. 1C). In the middle section of the Rawka River valley, the Kopanicha mire is the object furthest from a contemporary riverbed (over 800 metres). In other river valleys, these distances range around 500 m, and, in gorge sections of the middle or lower Grabia River, they do not even exceed 200 m. The following fens have a completely different character: Ługi, located within a fluvial form excluded from fluvial activity (Forysiak *et al.* 2023) and Podwódka, which fills an extensive basin depression with the greatest outflow of waters of the HCO_3-SO_4-Ca type in the entire region (Burchard, Maksymiuk 1997). Due to the unique nature of its Late Glacial organic series in the middle Warta River valley near Koźmin (Petera-Zganiacz, Dzieduszyńska 2007), research on the ele-

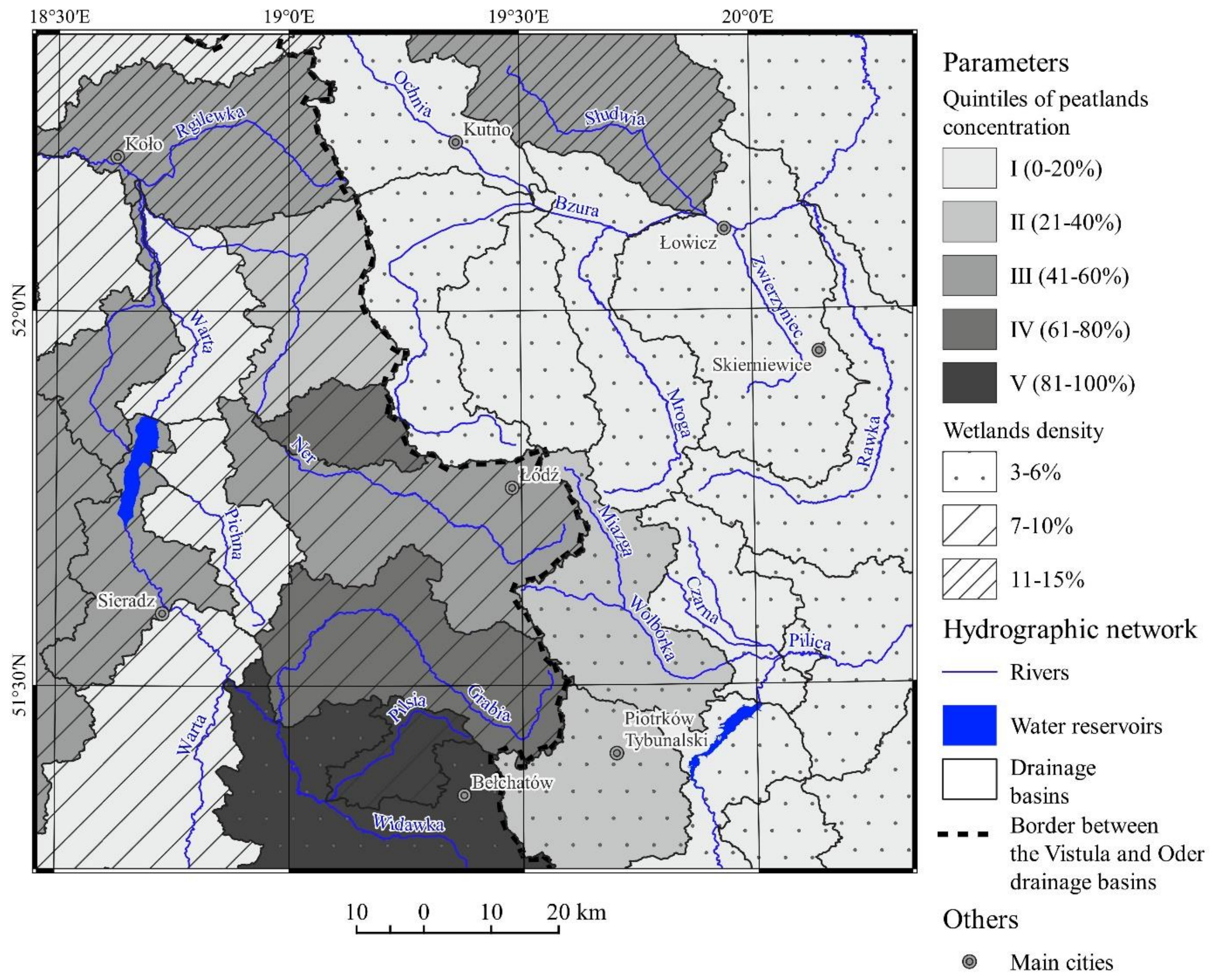

Fig. 2. Map of the share wetlands after Pietrucień (1991) against the quuntiles of peatlands concentrations in the catchment areas of main rivers of central Poland after Okupny *et al.* (2014)

ments cycle was carried out on as many as four profiles here, of which only one has been published by Okupny *et al.* (2014a) while another three are under development (Majecka et al. 2014; Krąpiec *et al.* 2020a).

Among the upland mires, detailed geochemical studies have been carried out for only two sites to date (i.e., Rąbień and Żabieniec). The first is located in an oval closed depression of glacial origin in the watershed zone of the Vistula and Oder River catchments (Forysiak *et al.* 2012a), further surrounded on three sides by dunes intensively inhabited by hunter-gatherers in the Mesolithic (Płaza *et al.* 2013/2015). On the other hand, the small Żabieniec mire (2.4 ha) on the watershed between the Mroga and the Mrożyca River catchments has repeatedly been studied to reconstruct biotic and abiotic changes (Lamentowicz *et al.* 2009; Forysiak 2012; Okupny *et al.* 2021; Petera-Zganiacz *et al.* 2022; Rudna *et al.* 2023). This is because it has the thickest biogenic sediments in the entire region (slightly over 16 m), which accumulation mostly in favourable water conditions and periodically intensive supply of mineral matter to a steep-walled bowl typical of kettle-holes (Forysiak, Twardy 2010).

As a result, the above-described geological and geomorphological conditions of the catchment area of individual peatlands in conjunction with selected climatic parameters (Tomczyk, Bednorz 2022) are responsible for the spatial differentiation of river runoff seasonality (Jokiel, Tomalski 2015) and are confirmed by the research of Andrzejewski *et al.* (2018) on the role of inland runoff and surface runoff in the circulation of matter. Geomorphological research to date suggests that the postglacial circulation of matter in the study area was strongly differentiated, as it concerned subenvironments of not only fluvial (Starkel 1997; Turkowska 1997), slope (Dzieduszyńska *et al.* 2020) and aeolian character (Goździk 1991; Manikowska 1995) but also watershed zones with locally varied post-Saalian relief (Majecka *et al.* 2018). According to Turkowska (2006), the greatest transformations of the relief in this period concerned the morainic plateaux and uplands and higher valley levels, where, alongside mechanical and chemical denudation processes, aeolian sand covers accumulated and dunes formed.

The above-mentioned examples of changes that occurred in the relief of the transitional zone between the belt of the Polish Highlands and the Polish Lowlands in the Late Glacial and Holocene have repeatedly been interpreted based on the geochemical and sedimentological parameters of sediments filling biogenic accumulation depressions (Goździk, Konecka-Betley 1992; Forysiak, Twardy 2012; 2021; Pawłowski *et al.* 2015b; Petera-Zganiacz *et al.* 2022). This is because depressions of this type, acting as depositional receivers, are of particular importance in landscape and geochemical systems and in denudation balance, regardless of the morphogenetic zone in which they are located (Drwal 1975; Borówka 1992; Wicik 1992a; Kłapyta *et al.* 2016; Karasiewicz 2019).

Research methods and materials

Fieldworks and sampling strategy

Profiles for detailed palaeogeographic studies, including geochemical analysis, were collected from where biogenic sediments were thickest for each site using: Instorf sampler (sites in alphabetical order: Bęczkowice, Grabica, Kopanicha, Korzeń, Ldzań, Ługi, Mianów, Okup, Pawłowa, Podwódka, Świerczyna, Wilczków), Więckowski probe (Rąbień and Żabieniec) and directly from the excavation walls (Kolonia Bechcice, Koźmin Głowy, Koźmin Las, Kwiatków KWI and Rozprza). The location of the profiles was preceded by detailed documentation of sediment thicknesses by manual and mechanical drillings, the results of which have been presented as sketches and geological cross-sections by Forysiak (2012), Pawłowski *et al.* (2014; 2015a; 2016b), Petera-Zganiacz and Andrzejak (2014), Okupny and Pawłowski (2021) and Antczak-Orlewska *et al.* (2023).

The chronology of the biogenic sediments was established on the basis of a series of published results of radiocarbon dates and age-depth models documenting, among others, the filling rate of accumulation reservoirs and a number of geodynamic processes within their catchment areas, which occurred in conditions of regional hydroclimatic changes in the last 16,000 years. The past work by Forysiak (2012), Dzieduszyńska (2017, 2019), Pawłowski (2017), Krąpiec *et al.* (2020a,b), Okupny and Pawłowski (2021) and Antczak-Orlewska *et al.* (2023) shows that the radiocarbon age was most often determined from bulk samples for organic silts, peats with varying degrees of decomposition, fine-detritus and clay-detritus gyttjas, and wood fragments. However, these databases were collected for the Late Glacial and early Holocene stages of the development of lake reservoirs and peatlands are restricted to 18,000–9,150 cal BP. In the case of Holocene sediments, charcoal, humic substance from fossil soil horizons and peats were most often dated. In addition, from those compiled by Forysiak (2012), Forysiak and Twardy (2012), Twardy (2013/2015) and Twardy *et al.* (2014) data show that Holocene organic sediments mostly underlay series of sediments of terrigenous origin, which is evidence of breaks in the sedimentation of autochthonous organic matter caused by hydrological changes and growing human impact. In the set of 153 radiocarbon dates used for the purposes of this article, ^{14}C analyses performed by scintillation prevail (53%), while the remaining 72 samples were tested by AMS technique.

The chemical composition findings for biogenic sediments discussed here have already been published by interdisciplinary research teams (Borówka *et al.* 2014a,b; 2015a,b; Okupny *et al.* 2014a, 2021; Pawłowski *et al.* 2015a, 2016a; Antczak-Orlewska *et al.* 2023) for most sites, but without a synthesis aimed at palaeoenvironmental interpretations of the spatial and temporal circulation of metals. Geochemical tests on 1537 samples from 19 profiles totalling nearly 67 metres thick involved determining percentage of organic matter by loss on ignition, calcium carbonate by volumetric method using the Scheibler apparatus and the content of biogenic and terrigenous silica by dissolving ash in alkaline compounds. For this purpose, fresh sediment samples were lyophilised in a Chrust Alpha 1-1 LD plus device and dried at 105°C before being dry mineralised to a constant weight by roasting at 550°C in a Gallenkamp muffle furnace. The ash obtained after roasting, identified as primary and secondary mineral matter after Kwiatkowski (1971), was wet mineralised by dissolving in a mixture of: 8 ml concentrated nitric acid (HNO_3), 2 ml 10% hydrochloric acid (HCl) with the addition of 2 ml of perhydrol (H_2O_2). This mineralisation was performed in Teflon bombs using a Berghoff twelve-column ultrasonic mineraliser. The concentration of selected elements (Na, K, Mg, Ca, Fe, Mn, Cu, Zn and Pb) in the obtained solutions was determined by atomic absorption spectrometry (AAS) on a Solaar 969 Unicam company. To avoid interactions between the individual elements, a lanthanum solution was used in the concentrations specified by Pinta (1977). The concentrations of most metals were expressed in mg/g d.m. except for Cu, Zn and Pb, which were converted to μg/g d.m. In addition, in order to determine the share of total carbon (C), total nitrogen (N) and total sulphur (S) for 180 samples, the VarioMax CNS apparatus by Elementar was used, and the results (expressed in %) were determined on the basis of high-temperature combustion of fresh organic samples placed in ceramic crucibles. Moreover, the grain-size composition of the mineral matter admixture from 319 research samples was determined using the laser particle size analyser Mastersizer 3000 with a Hydro MU dispersion unit (Malvern).

It is worth noting that, when determining the share of organic matter in sediments, different ranges of roasting temperature are often given, which results from the decomposition of some minerals and water loss by clay minerals (Wicik, Więckowski 1991; Myślińska 1999). On the other hand, the universality of the loss-of-ignition method results from its utility for sediments of either low or high content of organic matter, which is crucial in research aimed at comparing physical, chemical and biotic conditions in various sedimentary environments (Wójcicki 2010; Kordowski *et al.* 2014; Kittel *et al.* 2020).

There are also methodological differences in the second stage of geochemical research, i.e. the dissolving of samples. In this case, it is possible to obtain solutions for determining the concentration of elements using: hydrofluoric acid (HF) or tetrafluoroboric acid (HBF4), aqua regia, i.e. a mixture of concentrated H_2SO_4 or HNO_3 acids with HCl in a volume ratio of 3:1, or HCl alone with different concentrations (Cook *et al.* 1997; Woszczyk *et al.* 2009; Bojakowska, Tołkanowicz 2015; Parker *et al.* 2022). It should be emphasised that the first two of these methods is not often used in research in the field of dynamic geomorphology and Quaternary geology due to its complete dissolution of silicates and resultant overestimation in reconstructed intensity of denudation processes. The ongoing discussion on the geochemical methods used relates to, among other things, research objectives, the nature of examined sediment, and technological progress in research equipment (Borówka 2007; Zgłobicki 2010; Woszczyk, Spychalski 2013); nevertheless, this paper presents the results of analyses of the chemical composition of sediments that were performed with the highest accuracy and, in order to obtain comparability of results, that employed uniform and consistent laboratory procedures described detailed by Borówka (1990, 1992) and Okupny *et al.* (2020). The outcome was a database of results of various geochemical parameters for nineteen sites within a relatively small area, which makes the study area unique among geochemically developed parts of the Polish Lowland.

GIS and statistical analysis

The degree of peat cover within the study area was characterised based on data from preliminary documentation on sediments and the analysis of several tens of sheets of the 1:50,000 scale Detailed Geological Map of Poland compiled by Okupny *et al.* (2014b) and Żurek and Okupny (2015). These results were supplemented with an analysis of digital data, taking into account regional and local conditions of the water and matter cycle. For this reason, the morphometric parameters were obtained in the GIS environment using Quantum GIS and GRASS GIS software and spatial materials – maps and elevation models.

The diversity of relief in the distinguished catchments of the Łódź region was analysed based on a study of distributions of three topographic indicators derived from the digital elevation model as digital terrain models: slopes, Topographic Wetness Index (TWI) model and its modification, i.e. SAGA Wetness Index (abbreviated as SAGA WI). These indicators were generated based on the Airbone Laser Scanner data from Polish ISOK program (Geoportal 2023). Then, the spatial distribution of these indicators was examined in the catchment areas in the studied region using raster zonal statistics tools. A detailed description of the assumptions and the possibility of using the calculated indices can be found in the works of Migoń and Kasprzak (2014) and Okupny and Jucha (2020).

Table 1

Sites locations and basic information about genesis and relief features, thickness of sediments and the number of samples with geochemical research

No.	Genesis of the peatland	Site name	Latitude	Longitude	Altitude [m a.s.l.]	Location	Length of core [cm]/ ca. length of Late Glacial period [cm]	Number of samples	Source
1	Paludification	Koźmin Las	52°04’51” N	18°40’30” E	97	river valley	50/30	13	i
2		Kwiatków (KWI)	52°05’59” N	18°40’52” E	95.6	river valley	100/65	75	p
3		Mianów	51°49’00” N	18°40’52” E	128.8	river valley	190/35	40	g
4		Grabica	51°29’11” N	19°32’12” E	215	river valley	200/80	96	n, r
5		Rozprza	51°18’07” N	19°40’04” E	182.5	river valley	214/41	109	u
6		Kopanicha	52°01’01” N	20°11’20” E	101	river valley	306/0	59	k
7		Podwódka	51°21’19” N	19°14’49” E	183	inactive river valley	480/240	48	d
8	Limnogenic	Koźmin Głowy	52°04’51” N	18°40’30” E	96	river valley	200/200	99	h
9		Korzeń	51°28’44” N	18°53’25” E	139	river valley	200/90	42	b
10		Świerczyna	51°28’02” N	18°59’89” E	146	river valley	336/176	106	ł, n, r
11		Okup	51°58’50” N	19°06’96” E	164	river valley	400/200	100	r
12		Ldzań	51°35’31” N	19°13’58” E	173	river valley	100/44	41	n, r
13		Kolonia Bechcice	51°45’12” N	19°14’26” E	154	river valley	139/30	32	o
14		Pawłowa	51°30’19” N	19°19’59” E	184	river valley	450/160	114	m, r
15		Bęczkowice	51°11’05” N	19°42’45” E	209	river valley	300/160	60	j, t
16		Ługi	51°43’52” N	18°42’46” E	123	inactive river valley	300/150	76	d, w
17		Wilczków	51°56’40” N	18°53’20” E	115	inactive river valley	494/40	97	f, l
18		Rąbień	51°48’20” N	19°18’05” E	189	upland hills	620/65	127	c, e
19		Żabieniec	51°51’01” N	19°46’38” E	180	upland hills	1600/320	219	a, s

Based on: a – Borówka, Tomkowiak (2010); b – Borówka i in. (2011); c – Forysiak *et al.* (2012b); d – Okupny *et al.* (2013); e – Płaza *et al.* (2013/2015); f – Borówka *et al.* (2014a); g – Borówka *et al.* (2014b); h – Majecka *et al.* (2014); i – Okupny *et al.* (2014); j – Borówka *et al.* (2015a); k – Borówka *et al.* (2015b); l – Płóciennik *et al.* (2015); ł – Pawłowski *et al.* (2015a); m – Pawłowski *et al.* (2016a); n – Pawłowski *et al.* (2016b); o – Płóciennik *et al.* (2016); p – Krąpiec *et al.* (2020); r – Okupny, Pawłowski (2021); s – Okupny *et al.* (2021); t – Płóciennik *et al.* (2021); u – Antczak-Orlewska *et al.* (2023); w – Forysiak *et al.* (2023)

The geochemical landscapes were distinguished into autonomous, transit and accumulation landscapes on a regional scale using the procedure proposed by Sołowiej (1987) and Rycharski and Piórkowski (2001). Slopes were reclassified into the ranges: 0–2°, 2–5°, 5–8°, 8–15° and >15° for the relief types of the Łódź region distinguished by Turkowska (2006), thus illustrating the different intensity of land surface erosion. Moreover, according to the proposal of Sołowiej (1986), the coefficient of landscape stability was calculated for the catchment area of the examined mires. This parameter is the relation of the area of autonomous landscapes to the area of subordinate landscapes.

In accordance with the classification procedure described in detail by Okupny and Pawłowski (2021), a set of 1537 samples of sediments representing limnic, telmatic and fluvial environments was divided by hierarchical grouping method into 11 lithogeochemical facies forming three basic groups of sediments: organic, mineral and mixed. Twelve lithogeochemical components were assumed as grouping variables: these were nine elements and the share of organic matter, terrigenous silica and calcium carbonate, which reflect, *inter alia*, the type and dynamics of denudation processes and the method of supply. To assess the prevailing trends in the dynamics of the Late Glacial environment, selected geochemical indices (i.e.: share of organic matter, calcium carbonate, sandy fraction in the mineral admixture; results of TOC/N, Na+K+Mg/Ca relations; and extreme values of the sum of metal concentrations: ΣK) and sedimentological indices (results of grain-size indicators such as: GSI1, GSI2 and SPAN indices) are compared against the lithology of sediments for the chronostratigraphically best-recognised profiles. The characteristics of other geochemical indices, often including biotic indices that record changes in the environment, have been presented in earlier works listed in Table 1.

Results and interpretations

Macro- and mesoscale relationships between relief and the functioning of mires

With reference to the assumptions of the geomorphological map of the region in the research of Turkowska (2006), the distinguished elements of the pre-Pleistocene, glacial, periglacial and Holocene reliefs were assigned to three basic types of geochemical landscapes, i.e. autonomous, transit and subordinate. Although the cartographic material cited above is typical for large-scale maps, the sheer number and spatial relationship of landforms she distinguishes allow us to treat the analysis of the structure of the distinguished geochemical landscapes as a kind of physical and geographical characterisation of the research area. This was also confirmed by the results of the spatial distribution of two parameters origin from the digital elevation model, i.e. terrain slope (Fig. 3) and Topographic Wetness Index (TWI) (Fig. 4). The extent of wetlands, however, is most faithfully reproduced by the SAGA WI parameter, which takes into account not only the surface slope, but also supply higher-lying areas (Fig. 4). Comparing this picture against the range of geologically documented mires (cf. Forysiak 2012; Okupny *et al.* 2014b; Żurek, Okupny 2015) allowed for the first regional-level determination of the nature of the processes responsible for supplying allochthonous mineral material to the studied biogenic accumulation reservoirs that occurred in periglacial and temperate climate conditions.

The group of autonomous geochemical landscapes that cover the highest-lying areas of the region (usually above 180 m a.s.l. and with an inclination of less than 2°), comprises zones of supply of weathering and soil material for lower-altitude locations (usually below 120 m a.s.l.). According to Wicik (1992a), mineral components are not accumulated in landscapes of this type because weathering processes occurring in different climatic conditions favour their mobilisation and leaching. Thus, autonomous landscapes include upland areas. Turkowska (2006), however, draws attention to the large lithological diversity and varying degree of preservation of these landscape units in the vicinity of Łódź, which translated into the possibility of selected substances migrating in dissolved form (e.g., calcium carbonate, silica, iron and manganese ions) and was reflected in the grain-size distributions of the terrigenous admixtures of bottom sediments. This is confirmed by the latest results of geochemical and sedimentological studies for mires in Rąbień (Forysiak *et al.* 2012a; Płaza *et al.* 2013/2015), in Żabieniec (Okupny *et al.* 2021; Petera-Zganiacz *et al.* 2022) and Wolskie Bagno (Petera-Zganiacz *et al.* 2023). Also, the very low values of landscape sta-

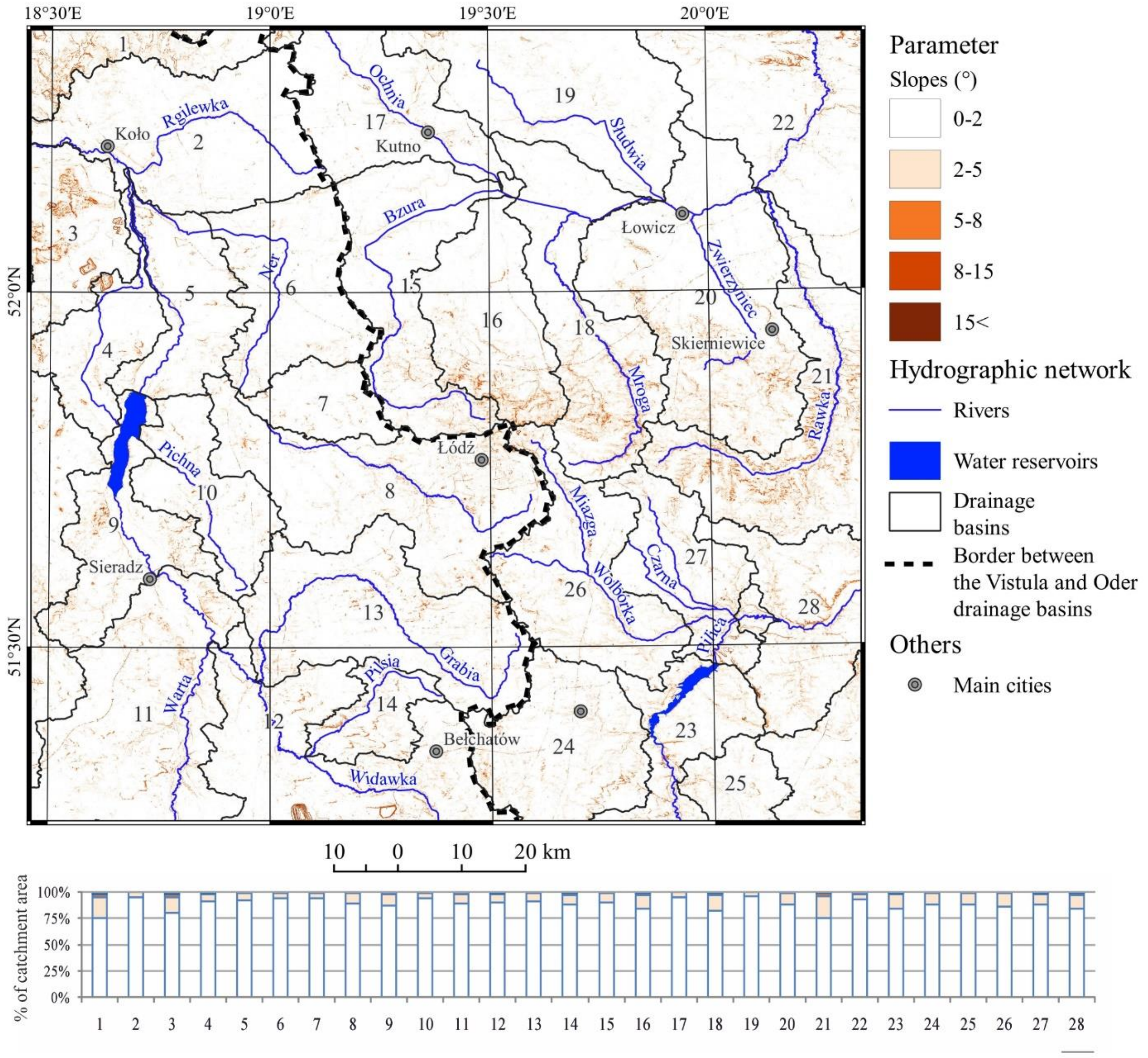

Fig. 3. Map of the slope gradients in the catchments of main rivers of central Poland

bility coefficients in both cases (Fig. 5) confirm the possibility of intensive environmental changes with the dominant role of substance transit within the catchment area. As a result, many endorheic thaw depressions were filled with sediments of various ages and are therefore poorly preserved in today's watershed landscape (Klatkowa 1997; Roman 2016; Forysiak *et al.* 2017). The situation described above constitutes evidence that the autonomous landscapes were internally morphologically differentiated and that the specific hydrogeological system and continuous denudation processes in the biogenic accumulation reservoirs are thus dominated today by the accumulation of acidic sediments. Data collected by Żurek (1990) for the eastern part of the Polish Lowlands show that the decrease in sediment pH is from 7.5 to even 2.8; a similar order of change for the research area is described by Forysiak (2012).

In the case of valley forms and clearly inclining slopes (Fig. 3), the transit nature of the link between geochemical landscapes is manifested by the leaching and horizontal conduction of mineral and organic substances. Research by Wicik (1992a) shows that the high lithological and morphological homogeneity of geochemical transit landscapes does not necessarily limit the dynamic transport of matter. A good example here is the valley forms studied in detail in central Poland that often cut through alternating extensive flats and much narrower fronts of steps (Turkowska 2006). This feature is visible in, among other things, the longitudinal profiles of the rivers of the study area, which are typical of the transi-

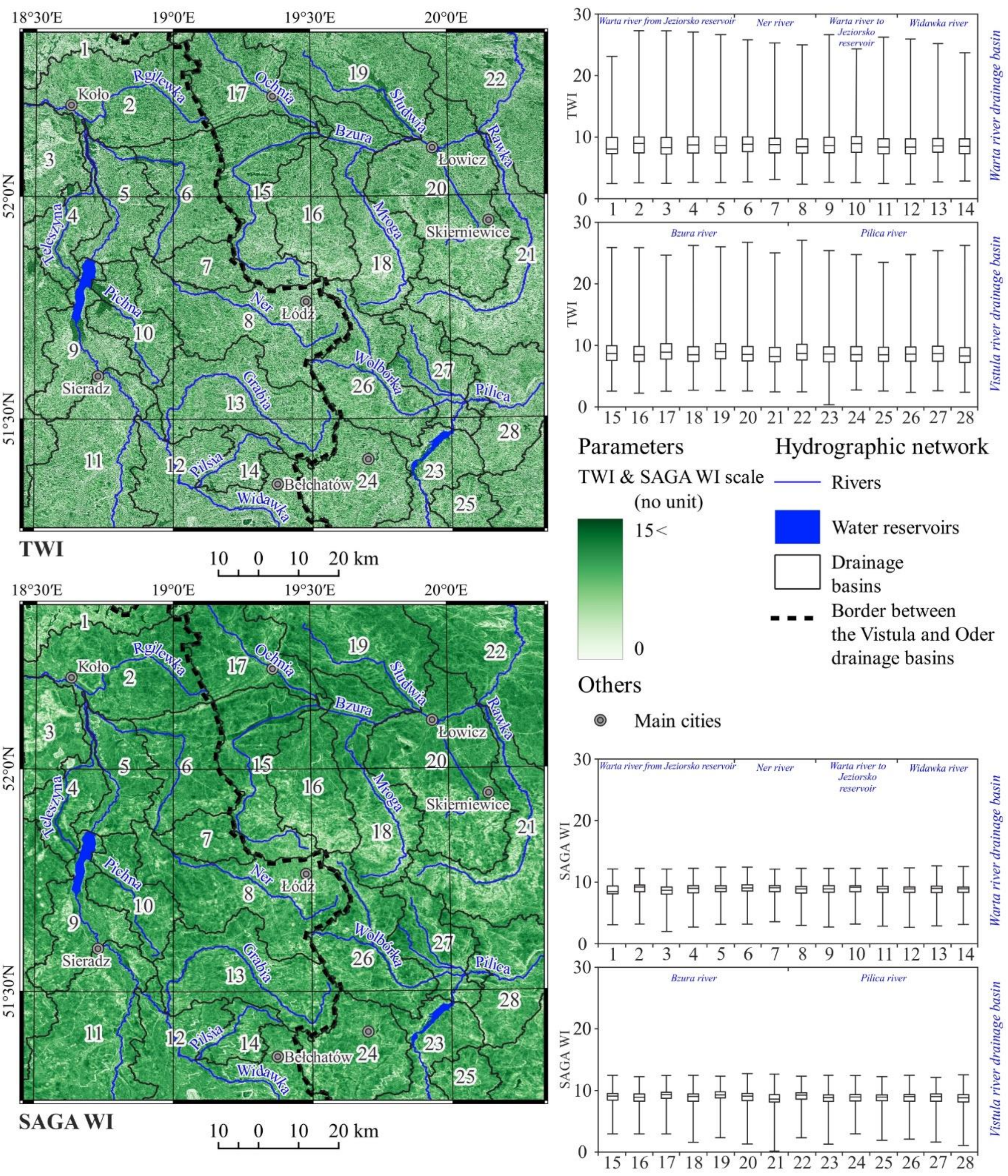

Fig. 4. Spatial distribution of Topographic Wetness Index and SAGA Wetness Index in the catchment areas of main rivers of central Poland. Numbers of catchments as in Figure 3

tion zone from the Polish Highlands to the Polish Lowland (Maksymiuk 1980; Moszczyńska 1986; Wachecka-Kotkowska 2004). Key in this case are the quite large drops in the channel and a poorly leveled profile with clear bend not only in the upper sections but also the lower sections of the river valleys. This arrangement exhibits the features of a cascade structure, and, at the scale of the entire river basin, it has been most fully discussed based on the chemical composition of the sediments forming the deposits of five mires located in different sections of the Grabia River valley

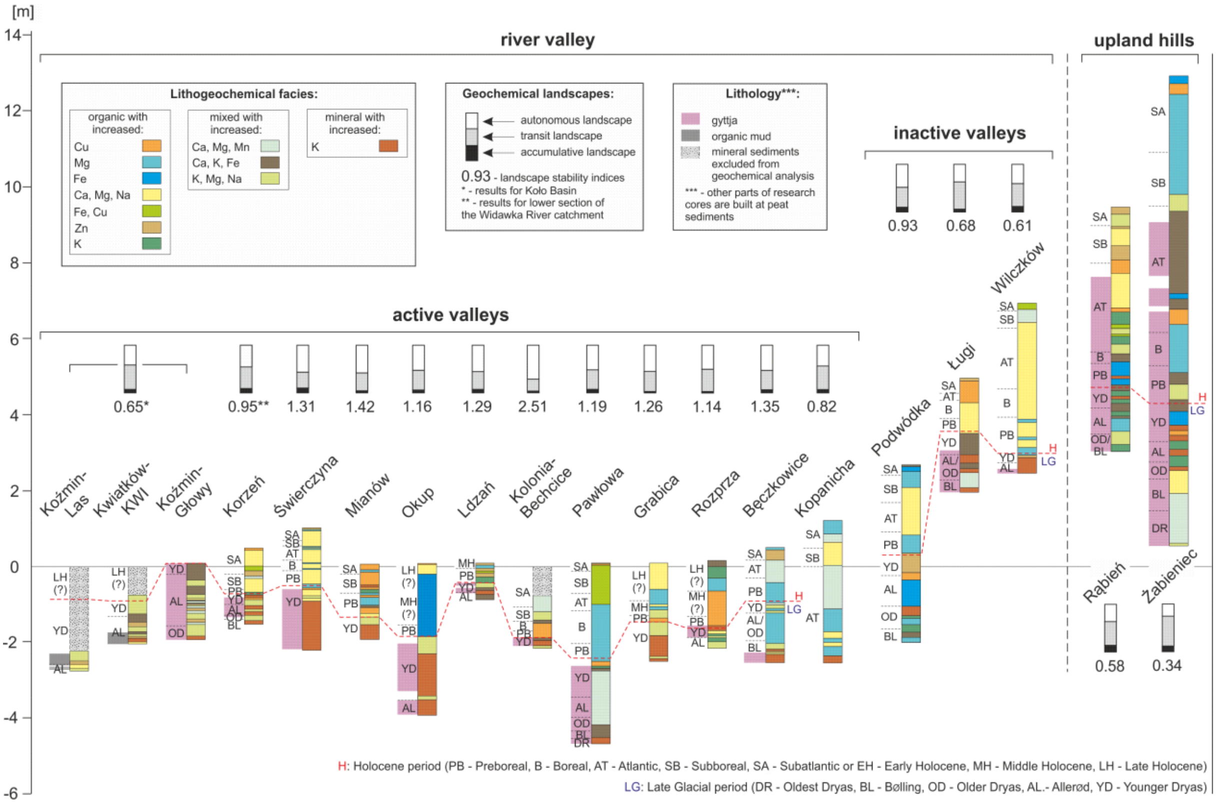

Fig. 5. Spatial pattern of lithogeochemical facies separated with the Okupny and Pawłowski (2021) description against the geomorphological features, lithology sediments and results of the landscape stability index as defined by Sołowiej (1986)

Vertical axis – relative height [m] in relation to mean water level in a stream draining the peatland area – Forysiak (2012)

(Okupny, Pawłowski 2021). In the Luciąża River valley, the system of functioning of transit geochemical landscapes differs according to three major hypsometric and geological units (Radomsko Hills, Dobryszyce Hills and Piotrków Upland), from which the allochthonous mineral component delivered to the mires in Bęczkowice (Borówka *et al.* 2015; Płóciennik *et al.* 2021) and Rozprza (Antczak-Orlewska *et al.* 2023) show even greater differences. Similar conditions of geochemical circulation apply to the Warsaw–Berlin marginal valley, where the meridional transport of matter determines a drop of 60 metres over a distance of a few kilometres (Krajewski 1977).

With reference to the geomorphological division of Gilewska (1986), it is worth emphasising that the surface share of landscape-geochemical units of transit nature decreases most quickly towards the northern and western peripheries of the study area. This patterns applies mainly to areas drained by the Bzura, Ner and Widawka Rivers systems. This is also confirmed by the high values of the relative peatlands occurrence in vast depressions and plains of various origins (Żurek, Okupny 2015) and the spatial differentiation of the terrain slope on either side of the watershed zone of the Vistula and Oder River catchments (Fig. 3). For example, within the study area, the indices of relative wetlands and peatlands occurrence in the Pilica River catchment are as much as three times lower than in the other catchments (Fig. 2), while it also has a predominance of undulating and inclined landscape (>2°) over flat areas with slopes of <2° (Fig. 3).

The last group of geochemical landscapes is that of depressions with limited outflow, in which matter of terrestrial or aquatic origin is accumulated. Sediments deposited at the bottom of reservoirs may be terrigenous, biogenic or chemogenic (Borówka 2007). The possibility of a particular sediment type accumulating – and its distribution – depend on factors both regional (Żurek 1981, 1990, 2001; Borówka 1992; Marszelewski 2005) and local (Okupny *et al.* 2020; Adamek *et al.* 2021). In both cases, however, fluctuations in the quality and levels of ground and surface water, changes in water quality, and the conditions of water flow through a lake or mire are key factors, as reflected in the stratigraphic differentiation of deposits of many mire profiles (Oświt *et al.* 1980; Żurek 1993; Forysiak 2012).

Within the study area, the functioning of subordinate geochemical landscapes should be associated with extensive glacial depressions, which Turkowska (2006) includes dead ice moraines, terminal basins, glacitectonic depressions and depressions related to the uneven accumulative activity of the ice sheet. Due to their age (the Warta stadial of the Saalian Glaciation) and size (up to several tens of kilometres across), they played a significant role in the postglacial development of the relief. As local denudation bases, some of them were filled with sand and silt material in periglacial climate conditions, and therefore the subordinate nature of the landscapes transformed towards geochemical accumulation-transit landscapes. Despite this, the right-bank side of the middle Warta River catchment, including such macroforms as the Szczerców Basin, Sieradz Valley and Koło Basin, are among the areas of the greatest peat coverage in the region (Lipka *et al.* 2008; Forysiak 2012; Okupny *et al.* 2014b). It is dominated by flat surfaces cut by valleys that are wide but usually hypsometrically poorly defined. In the north-south-oriented valleys, peatlands rarely exceed 5 ha, while east-west-oriented valleys (now often inactive functioning) peat deposits reach maxima of as much as 300 ha (Forysiak *et al*. 2012b).

The development of the peatlands was also majorly affected by the geological structure of the aforementioned basins. This is confirmed by the fact that the eastern part of the Warsaw–Berlin marginal valley, which has the most monotonous surface of anywhere in the study region has a very low share of peatlands, slightly exceeding 1% according to Żurek and Okupny (2015). So too, Rycharski and Piórkowski (2001) emphasised the transit nature of this part of central Poland, thereby explaining it have the lowest share of peatlands (in total area of hydrogenic habitats) of any mesoregion of the old-glacial zone. Within the entire research area, Okupny *et al.* (2014b) found fewer than 20% of the region's individual peatlands were spread over more than ten third-order river catchments (incl. the Bzura, Mroga, Mrożyca and Rawka) (Fig. 2). Summarising the basic physical geographical features of the mires in the study area, those of 5–20 ha predominate numerically; moreover, all of those of 20–50 ha are located at less than 180 m a.s.l. Of the peat deposits of less than 5 ha (which account for as much as 31% of the total number of the region's mires, but only 2.19% by total area), most are located within the boundaries of periglacial denudation plains at 180–200 m a.s.l.

With reference to the research assumptions presented in the introduction herein, it should be emphasised that the character of individual geochemical landscapes changed over time in the Late Glacial and Holocene. The most important factor modifying the matter cycle both in valleys and on moraine plateaus was aeolian processes. They led to the formation of aeolian covers, dunes and deflation depressions. This allowed dunes to mask the relief, divide valleys and inhibit the free flow of surface water, as well as to create new autonomous landscapes at the microscale (e.g., along the watershed on the crests of dunes), transit landscapes divided into windward and leeward slopes, and subordinate landscapes (e.g., small-area closed depressions and their catchments). Changes of this type mainly relate to the Warsaw–Berlin marginal valley (Krajewski 1977; Okupny 2009) and the Szczerców Basin (Gawlik 1969; Stępień, Forysiak 2017).

So too, Wicik (1992b, 1997) emphasises that Late Glacial and Holocene dune development should be seen as a major determinant of changes in the environmental metal cycle. On the one hand, the overlaying of a thick series of sands onto the bedrock and soils preserved their chemical composition, but on the other, it significantly increased groundwater retention. As a result, the conditions determining the leaching of metals, environmental pH, the intensity of weathering processes and the potential for iron compounds to migrate and precipitate in the hypergenic zone also changed, which is very well recorded by the results of geochemical studies on fossil soils within the research area (Manikowska 1999) and on biogenic sediments from the mire in Rąbień (Forysiak *et al.* 2012a; Płaza *et al.* 2013/2015).

The influence of regional vs local environmental drivers on the geochemically-based reconstructions

Data presented by Żurek and Okupny (2015) show that most geochemically processed peatland deposits in central Poland (27, which is almost half of all peatlands examined in the region) have a relatively high ash content of 25–50%. Next are 16

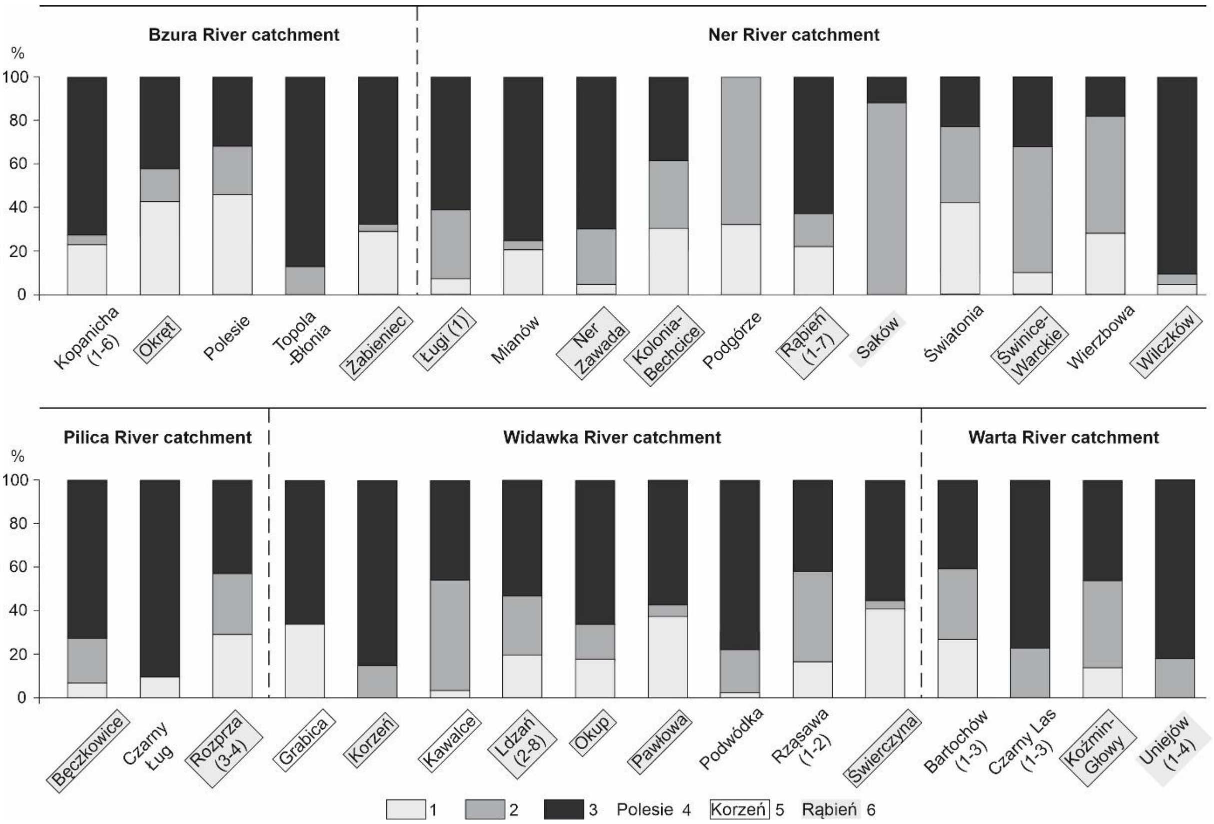

Fig. 6. The degree of silting Late Glacial and Holocene deposits for selected study sites from central Poland (based on results of loss on ignition procedure and following by Okruszko (1977)

1 – deposits strongly silting (organic matter between 25–50%), 2 – deposits medium silting (organic matter between 50–75%), 3 – deposits non silting (organic matter above 75%), 4 – study sites with only Holocene sediments after, 5 – study sites with Late Glacial and Holocene sediments, 6 – limnogenic peatlands

Based on the references cited in the Tab. 1 and Okruszko, Duch (1957); Okupny (2009); Domińczak, Okupny (2010); Forysiak *et al.* (2011); Białczak, Forysiak (2012); Forysiak (2012); Pawłowski *et al.* (2014); Stępień, Forysiak (2017); Kittel *et al.* (2018)

deposits with a moderate ash content (10–25%), and in last place are 6 deposits with an average admixture of mineral matter of less than 10%. These results are also spatially varied (Fig. 6). There are more profiles with a low degree of sediment silting in the river catchments to the east of the first-order watershed than to the west. On the other hand, in the catchments of the Ner and Widawka Rivers, conditions were more favourable to the siltation of hydrogenic habitats, with samples with a high degree of silting being documented in all profiles from this part of the region. Also, the number of samples with a moderate degree of silting is two to three times higher than at the sites in the Bzura or Pilica Rivers catchments (Fig. 6). In addition, compared to other regions of Poland (cf. Żurek 1981, 1987, 1999; Borowiec 1990), the degree sediment silting is several percent higher and results mainly from a greater degree of organic matter decomposition and increased supply of mineral particles due to various morphogenetic processes. These processes were characteristic of the first evolutionary stage of the studied reservoirs, and their intensity was higher in the Widawka and Ner Rivers catchments than in the east of the study area due to differences in the impact of climatic and non-climatic geographical environmental factors.

The climate factors includes local differences in annual precipitation (of up to 150 mm), which are due the rain shadow in the axial part cast by upland areas lying between 200 and 250 m a.s.l. (Podstawczyńska 2010). The non-climatic factors, meanwhile, are more numerous and complex, as they include the size and shape, geological structure, substrate permeability and topography of the catchment area. The right-bank tributaries of the Warta River more frequently exhibit watersheds breaking almost at right angles to one another and greater diversity of selected morphometric parameters between upper and lower parts of the catchment (Turkowska

1988; Okupny, Pawłowski 2021), which determine the conditions of the water and matter cycles in these areas. Even greater variation in morphometric characteristics is found in subcatchments of the Ner, Grabia, Widawka and Wolbórka Rivers (Maksymiuk 1980; Moszczyńska 1986; Krzemiński 1989; Jokiel, Bartnik 2020). This, in conjunction with the geological structure, significantly changes and differentiates the formation conditions and rate of groundwater drainage in valleys even in close proximity to one another.

In the light of data collected to date for the Polish Lowlands (Okruszko 1969; Oświt *et al.* 1980; Kalisz, Łachacz 2008), it should be stated that the division presented above may have some drawbacks. First of all, the term "degree of silting" used in the literature is interpreted differently by different disciplines of natural sciences (cf. Okruszko 1977; Tobolski 2004). As a result, a number of types of hydrogenic sediments are distinguished that suggest that most of the silt fraction was supplied mainly due to annual water level fluctuations but that exclude the possibility of the abundant development of diatoms during periods of more intense denudation processes. Also, the grain-size indices of the of terrigenous admixture and SiO_{2biog} content in the sediments from central Poland studied to date do not attest to their high homogeneity (Pawłowski *et al.* 2015a; Petera-Zganiacz *et al.* 2022; Antczak-Orlewska *et al.* 2023). Therefore, an approach based on determining the origin of minerals supplied to biogenic accumulation reservoirs, e.g., using SEM/EDS methods, seems to be correct. Only then will it be possible to identify ingredients of allochthonous origin, autogenic ingredients and minerals of biogenic origin (Ewing, Nater 2003; Rydelek 2013; Kalińska-Nartiša, Gałka 2018). As a result, the multitude of distinguished components translates into a high diversity of types of biogenic sediments in the temperate climate zone (Borówka 2007; Kanbar *et al.* 2021), and as many researchers correctly claim (Sobczyński, Siepak 1998; Woszczyk, Spychalski 2013) is a reason to distinguish and quantify the forms in which metals occur in reservoir sediments.

The research results shown in Figure 5 prove to some extent the synchronicity of sedimentation of biogenic sediments of a specific chemical composition in the profiles of mires in central Poland. The similarity in thickness, time of occurrence and order of occurrence of the distinguished lithogeochemical facies can be treated as an effect of regional changes. This is most clearly recorded in the bottom sections of valley mire profiles, regardless of any local modifications in the course of a given type of biogenic sedimentation as a result of, for example: differences in the genesis of the basin (paludification of the mineral substrate or limnic phase); location in a given section of the river valley (upper/middle/lower); or the variable relationship between autonomous, transit and accumulation landscapes (the landscape stability coefficient ranges from 0.61 to 2.51). It should be emphasized that the Late Glacial biogenic sediment series contain as many as ten of the eleven total lithogeochemical facies distinguished (Fig. 5). The appearance of more organic lithogeochemical facies at the turn of the Late Glacial and Holocene attests to the lake reservoirs progressively filling with sediments, which in turn led to their complete disappearance and a change in deposition processes from biogenic sedimentation to sedentation of autochthonic organic matter.

However, there are major discrepancies in the presented list that relate to two issues of the metal cycle. The first is the increase in frequency of lithogeochemical facies, such as organic facies with increased of Mg concentration and mixed facies with increased of Ca, Mg and Mn at the sites in the highest parts of the Łódź Upland and the eastern part of the first-order division (such sites as: Pawłowa, Grabica , Rozprza, Bęczkowice, Kopanicha, Podwódka and Żabieniec). The second issue concerns the sediment profiles from inactive valleys (the Podwódka, Ługi and Wilczków sites), which record a lower frequency of changes in the course of specific lithogeochemical facies, despite complex environmental changes in the postglacial period.

The regional differences in chemical composition presented above can probably be explained by the temporally and spatially changeable relationship between surface runoff and underground runoff in supplying particular sections of river valleys or endorheic depressions. Research by Borówka (1992) shows that key in this case is the occurrence of favourable infiltration conditions in the catchment area (as reflected in the concentrations of metals that migrate more easily in aqueous solutions) alongside the weakened role of mechanical denudation associated with e.g., surface runoff and passive atmospheric supply of terrigenous material. So too, Kruk (1991) and Wicik (1992a) have emphasised the need to treat hydrogenic habitats as geochemical barrier zones. The functioning of such ecosystems is particularly important in the transition zone between transit and accumulation landscapes, which, together with a significant decrease in the waterborne migration of matter and a dense network of river valleys, favours intensive leaching of the weathering-soil cover and long-distance migration of Mg and Ca (Wicik 1972). The role of local hydrogeological determinants of Ca, Na or Mg environmental circulation has to date been emphasised only in studies of locally functioning cupola spring mires (Ziułkiewicz *et al.* 2012; Dobrowolski *et al.* 2017).

Palaeogeographical interpretations of the groundwater circulation system and the occurrence of soligenous reservoirs of biogenic accumulation, should also consider the meso- or macroform scale. After all, peatlands of this type can be supplied with free or pressurised groundwater from dissected aquifers in clusters of convex glacial and fluvioglacial forms (usually identified with autonomous geochemical landscapes) or polygenetic concave forms (occupying an intermediate place between uplands and valleys). Turkowska (2006) distinguishes eleven such clusters in central Poland (Fig. 1B), which are differentiated in terms of location on uplands or in valley depressions, total area and origin of individual landforms. In addition, analysis of the digital terrain model (Fig. 3) shows that the rate of groundwater drainage and feeding of biogenic accumulation reservoirs was very spatially variable. The average heights for the main concentrations of glacial and/or fluvioglacial accumulations distinguished by Turkowska (2006) range from 94 m a.s.l. (zone XI) up to 230 m a.s.l (zone I), and therefore differ by as much as 136 m. There are also differences in average surface slope in individual parts of the catchment, from below 1° in zones IX and XI, to more than 2°30' in the edge zone of the Łódź Upland (zone II) and watershed areas of smaller rivers (zones IV, VI and VII).

The soligenous supply of the fens in the study area is also confirmed by comparing the list of groundwater outflow locations (Fig. 1B) against the spatial differentiation of the TWI and SAGA WI parameters (Fig. 4). This is clearest in the 180–220 m a.s.l. range. The analysis of the geomorphological map of the Łódź region by Turkowska (2006) shows that this height range corresponds spatially to the edge zones of individual morphological units, valley slopes and numerous small erosional undercuttings. As a result, with significant slopes in the terrain (often exceeding 4°, Fig. 3), the incision of water tables not only favoured frequent flooding on floodplains in valley-like depressions, but also guaranteed high groundwater outflow and highly stable water outflow through rivers (Maksymiuk 1980; Krzemiński 1989). In addition, due to the presence of a fluvioglacial series of gravel and sand in the subsoil, often of more than 25 metres thick (Konecka-Betley, Czępińska-Kamińska 1979; Rdzany 2009; Wachecka-Kotkowska 2013), autonomous and transit geochemical landscapes in the above-mentioned height range have the highest water retention capacity of anywhere in the study area.

In turn, in the catchments of the upper and lower Grabia River, lower Widawka River and upper Luciąża River, the significant surface runoff caused by the terrain (Fig. 3) and the predominance of poorly permeable deposits (Maksymiuk 1970, 1980; Krzemiński 1989; Wachecka-Kotkowska 2004; Okupny, Pawłowski 2021) may have caused the more frequent changes in the lithogeochemical facies. In addition, the division of sites along the E–W transect presented in Fig. 5 shows that mineral facies with increased K concentration dominate in biogenic sediments in the west of the first-order watershed. This lithogeochemical facies was first distinguished by Okupny and Pawłowski (2021) in the Oldest Dryas at the Pawłowa site, though its range of thickness at individual sites before 11,500 cal BP is closely related to the occurrence of clayey gyttja or other types of biogenic sediments, but with admixture of sand (Tab. 2).

Compared to other morphogenetic zones of Poland, clay gyttja deposits in the vicinity of Łódź are relatively often distinguished, although the geochemical criteria for the division of biogenic deposits often disagree and may therefore give cause for doubt (cf. Markowski 1980; Rzepecki 1983; Maciak, Liwski 1996; Myślińska 2003). In the case of the study area, the interbedding of clay gyttja is treated as abiotic evidence of increased flood activity in the Late Glacial (Pawłowski *et al.* 2015a; Okupny, Pawłowski 2021). However, the sedimentological analyses carried out for this series indicate a significant share of sand fraction, with a very large range of GSI1, GSI2 and SPAN indices (Fig. 7). The results of the first two indices, which mainly result from changes in the share of coarse and fine silt fraction with a relatively constant clay fraction content, record a high variability of material delivery from short- and long-distance transport. The diversity of results for the second index,

Table 2

Lithogeochemical facies of the Late Glacial and Holocene deposits in the central Poland

Lithogeochemical facies		Lithology	Facies	Depositional environment	Total thickness for all sites in m (% of sum)
Organic	with Cu	peat	telmatic	mire, kettle-hole	4.32 (6.5)
	with Mg	peat, clay gyttja, clay-detritous gyttja, detritous gyttja	telmatic, limnic	mire, oxbow lake, kettle-hole	10.8 (16.2)
	with Fe	peat, clay-detritous gyttja, detritous-clay gyttja	telmatic, limnic	mire, oxbow lake, kettle-hole	3.58 (5.4)
	with Ca, Mg, Na	organic mud, peat, clay gyttja, detritous gyttja	telmatic, limnic	mire, oxbow lake, kettle-hole	12.05 (18)
	with Fe, Cu	peat, detritous gyttja	telmatic, limnic	mire, oxbow lake, kettle-hole	1.40 (2.1)
	with Zn	peat, clay-detritous gyttja	telmatic, limnic	mire, oxbow lake	2.25 (3.4)
	with K	peat, clay-detritous gyttja, detritous-clay gyttja, detritous gyttja	telmatic, limnic	mire, oxbow lake, kettle-hole	3.61 (5.4)
Mixed	with Ca, Mg, Mn	peat, calcareous gyttja, clay-calcareous gyttja, clay gyttja	telmatic, limnic, fluvial	mire, oxbow lake, kettle-hole	6.08 (9.1)
	with Ca, K, Fe	peat, clay gyttja, clay gyttja with sand, calcareous gyttja, detritous gyttja	telmatic, limnic, fluvial	mire, oxbow lake, kettle-hole	6.11 (9.1)
	with K, Mg, Na	peat, detritous gyttja, clay gyttja, clay gyttja with sand, peat with sand	telmatic, limnic, fluvial	mire, oxbow lake, kettle-hole	9.07 (13.6)
Mineral	with K	peat, peat with sand, clay gyttja, clay gyttja with sand, detritous gyttja, river sand	telmatic, limnic, fluvial	mire, oxbow lake, kettle-hole	7.52 (11.3)

in turn, attests to the varied dynamics and high variability of the force transporting mineral material, which, according to Kordowski *et al.* (2014) and Petera-Zganiacz *et al.* (2022) are typical of Late Glacial sedimentary environments.

In addition, in the presented correlation of chemical composition to sediment lithology, the profiles from sites in extensive basin depressions stand out for their clear predominance of mixed lithogeochemical facies with increased concentrations of lithophilic elements such as K, Mg and Na (Fig. 5). According to the description of Okupny and Pawłowski (2021), the distinguished series of lithogeochemical facies should be associated with increasing flood activity during a clear transformation in vegetation cover at the end of the Late Glacial. Taking into account the way the slope and channel system are interconnected in the Koło Basin (Turkowska *et al.* 2000) and the Sieradz Valley (Maksymiuk 1980; Krzemiński 1989), the supply of lithophilic elements to hydrogenic habitats in the area of Koźmin and the Widawka's confluence with the Warta River may result from an increased amount of suspended matter, which is the main sorbent of ions dissolved in water.

There is no doubt that the environmental conditions described above were particularly important in the Late Glacial, as the stable water conditions enabled the uninterrupted functioning of biogenic accumulation basins. Indeed, environmental conditions were changing significantly at that time (Fig. 1C), mainly in terms of: the development of a mosaic of tundra, steppe and forest–

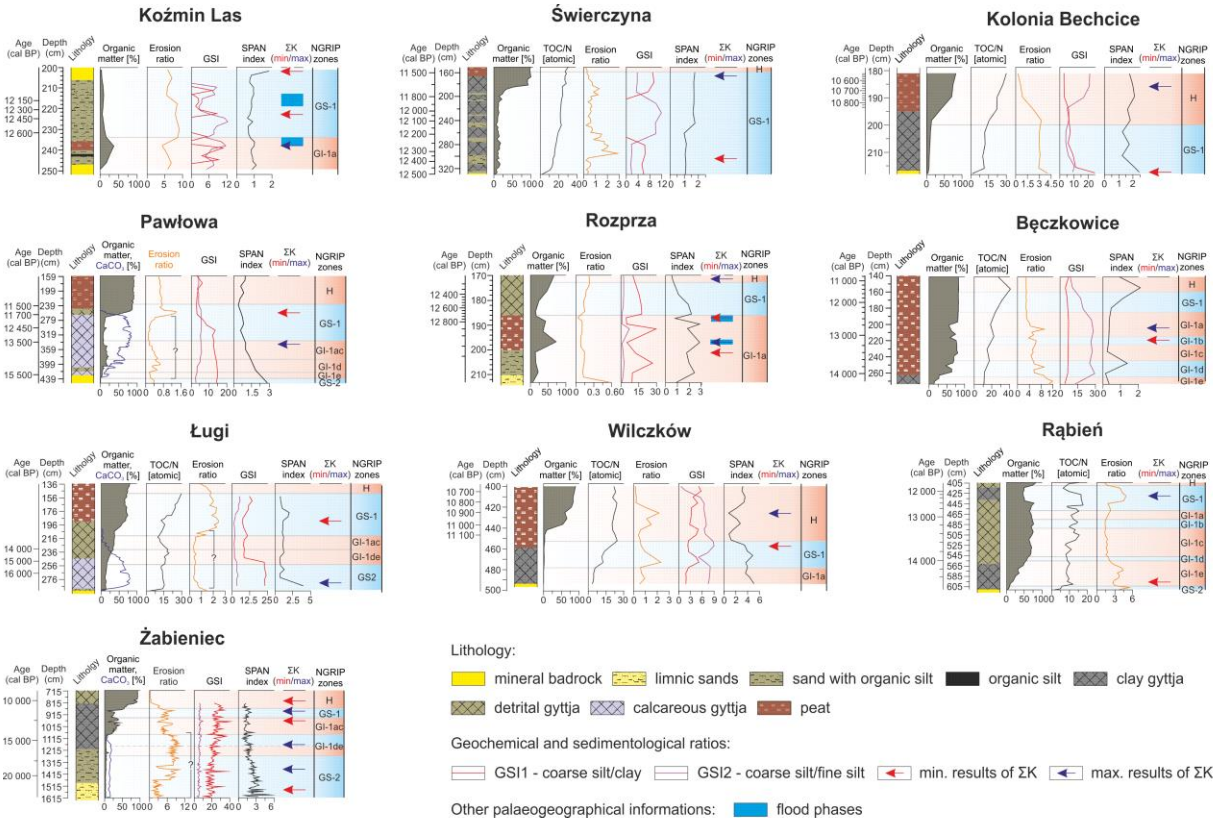

Fig. 7. Stratigraphic results of selected geochemical and sedimentological indicators for the Late Glacial sections of biogenic sediments from the best developed in terms of age of peatlands in the central Poland based on the references cited in the Table 1. NGRIP zones after Björck *et al.* (1998)

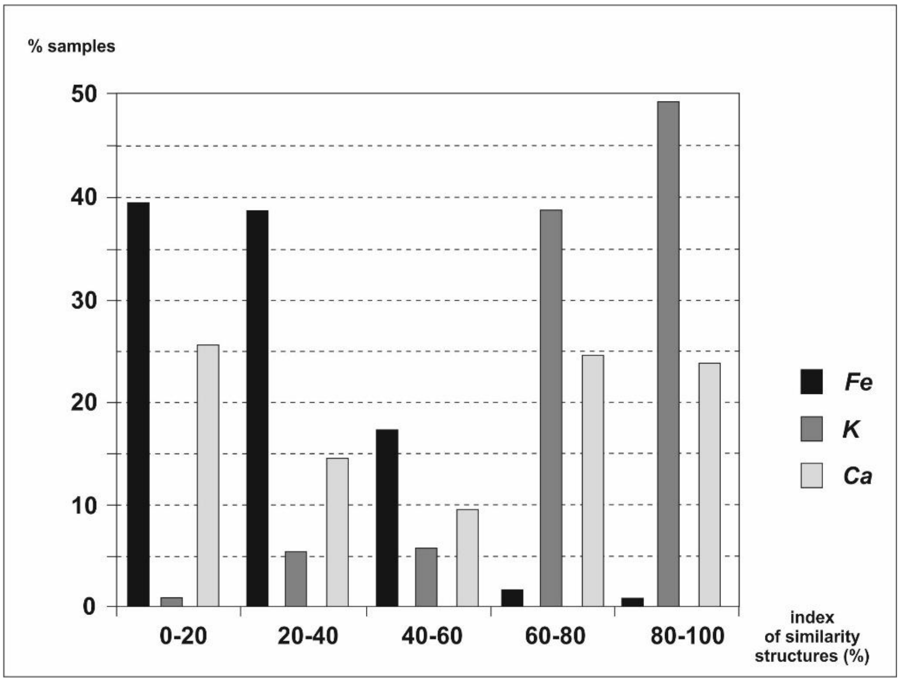

Fig. 8. Index of similarity structures for concentrations of selected elements for biogenic sediments in the central Poland (n=1537)

–tundra patches (Wasylikowa 1964; Latałowa 2004); varying concentrations of river water flows in narrower gorge sections (Turkowska 1988, 1997; Starkel 1997), the intensification of aeolian processes (Kaczmarska 1973; Manikowska 1995; Konecka-Betley *et al.* 1996); and the degradation or change in character of permafrost (Goździk 1995; Błaszkiewicz 2007). As a result, it is in the age range of 15,500–11,500 cal BP that the accumulation of organic matter of aquatic origin usually occurs in the studied reservoirs (the TOC/N index does not exceed 20; Fig. 7), but with the interbedding of allochthonous mineral material supplied as a result of flooding (Forysiak 2012; Płóciennik *et al.* 2016; Okupny, Pawłowski 2021), slope processes (Klatkowa 1964) or wind activity (Forysiak *et al.* 2012a; Płaza *et al.* 2013/2015).

It is worth noting that Maksymiuk (1980) also mentions the proportion of the catchment area composed of silts and alluvial soils among the factors determining the feeding of lowland rivers. These sediments are permanently saturated with water, so in geochemical landscapes in which they accumulate, the water table is shallow (Wicik 1992a; Rycharski, Piórkowski 2001). Such conditions have resulted in significant swamping in the central part of the Widawka River catchment (Żurek, Okupny 2015; Fig. 2), and due to that area's location on one of Poland's main aeolian transport routes, the genetically diverse peatlands were supplied with allochthonous mineral material in the Late Glacial. Even more interesting are the conclusions of Goździk and Konecka-Betley (1992) regarding very low concentrations of lithophilic elements, especially Mg and K, in the Late Glacial biogenic sediments filling small reservoirs in the Krasówka River valley. The phase of limnic accumulation documented by the above-mentioned authors is associated with increased water flow and magnesium and potassium salts being removed from the reservoir with simultaneous rapid precipitation of Al, Fe, Ca and Na.

This interpretation is also confirmed by a comparison of the similarity index of the structure of geochemical data between the studied valley mire profiles (Fig. 8). This indicator was proposed for use in geochemical research by Pawłowski *et al.* (2014), and its greatest advantage is its ability to compare results between measurement series of different lengths. The strongly differentiated structure of results for only three metals (Fe, K and Ca) should be taken to have been caused by the spatial variation in the water cycle, taking into account the genesis of individual types of reservoirs in which biogenic accumulation took place. According to Krzemiński (1989), in terms of the mineral matter cycle in the postglacial valley landscape, the amplitude of fluctuations of the local erosion base and the nature of concave forms and the related type of supply were main. The numerical predominance of samples with high structure similarity index values for K concentration (Fig. 8) is evidence of the development of deposition processes in reservoirs typical for valley forms strongly shaped by surface waters. However, the large dispersion of results of the same measure for Ca concentration with the simultaneous predominance of samples with the lowest index values for Fe concentration attests to periodic changes in the water table in the hydrogenic valley habitats of the region. This can be explained by Ca enrichment of the layers after dehydration (Mendyk *et al.* 2016) or post-sedimentary iron reduction and overprinting the initial iron mineral deposited (Pleskot *et al.* 2018).

Conclusions

The geochemical landscapes of the research area are predominantly of the transit type, which results from the polygenic nature of the relief shaped by a number of morphogenetic factors that change in time and space. The key role in the matter cycle in the postglacial period was played by the plateau's central location relative to the vast depressions and river valleys surrounding it. As a result, exogenous relief-forming factors were responsible for the supply of allochthonous mineral matter, including lithophilic elements, to the genetically diverse biogenic accumulation reservoirs to the west, north and east of the first-order watershed. In addition, the reservoir sediments with a predominance of $CaCO_3$ that have been documented at sites mainly record the intensive dissolution of rocks building the highest parts of individual catchments and the transport of Ca^{2+} and HCO_{3-} ions through groundwater or river waters. They accumulated in various periods of the Late Glacial and Holocene, and therefore the frequent generalisation of permafrost degradation unblocking underground water circulation at the scale of the entire region is overrated.

Although doubts exist as to the methodological soundness of dividing the biogenic sediments according to their admixtures of mineral matter, the degree of silting of the studied lake and peat formations is slightly higher than in other regions of Poland. The shares of mineral matter were lowest in the deposits of oligotrophic mires as well as transitional and eutrophic mires on high terraces in the middle and lower sections of the rivers. The share of mineral admixture is typically highest at sites in river valley bottoms and in interdune depressions. In addition, due to the specific supply conditions of the biogenic accumulation reservoirs, the ash content and chemical composition results are partly related to certain biogenic sediments.

The highest ash content of the examined sediments is also associated with strong silting and the supply of allochthonous material in the initial developmental phase of mires in central Poland. This is confirmed by the catchment erosion index values, whose changes in the postglacial period were conditioned not only by the sum of the content of supplied lithophilic elements, but also by the concentration of calcium leached from the substrate. For this reason, the reconstruction of relative changes in the intensity of denudation processes in catchments of reservoirs with a predominance of ground recharge and accumulation of carbonate sediments is somewhat more complicated and difficult to interpret. Irrespective of this, the intensity of denudation and the nature of the transported material on a regional scale were conditioned by the presence of autonomous landscapes in the axis of the study area located above 180 m a.s.l.; these landscapes were surrounded on three sides by extensive depressions up to 120 m a.s.l. with a predominance of accumulation landscapes and a radial arrangement of valleys of numerous watercourses flowing into the Warta, Pilica and Bzura Rivers, which together with the periglacial plains have been classified as transit geochemical landscapes.

The dominant group of Late Glacial sediments in the biogenic accumulation reservoirs in central Poland is of mineral lithogeochemical facies with increased K concentration. On the one hand, this is a record of the stable water conditions necessary for the accumulation of mainly clay gyttja, which was nonetheless accompanied by increased mechanical denudation and increase allochthonous mineral matter supply due to periodically greater flood frequency or greater intensity of slope or aeolian processes. The documented denudation processes correspond primarily to lithological changes in the reservoir sediments and changes in some geochemical and sedimentological indices, and their frequency across the entire region clearly increases in the period from 15,600 to 12,000 cal BP. However, local differences in when conditions for biogenic accumulation and for individual lithogeochemical component cycles changed are due to the physical geographic features of individual catchments and their diversity of geochemical background values.

The key determinant of the frequency of lithogeochemical changes in the facies in the initial phase of river valley mire development was results of slopes at individual parts of the catchment. In the upper sections of rivers flowing through highly differentiated hill-type landscape units, the passive but high-intensity supply of lithophilic elements was interrupted by short periods of calcium ions leaching from the substrate and plant detritus supply accompanied by changes in the grain size parameters of terrigenous material. The exceptions in this regard are the research sites in the Koło Basin, which is drained by the middle Warta River, where the chemical composition of sediments accumulated in the Late Glacial is highly variable even over short distances. This diversity records the influence of any factors on the circulation of water and substances in a landscape unit that, though vast, is also the least hypsometrically diverse in central Poland. An increased frequency of changes in the distinguished lithogeochemical facies, with a general trend towards increased shares of organic matter in the sediments, also coincides with the end of the Younger Dryas and the beginning of the Holocene. In this case, significant changes in the leaching of individual components from the substrate and their delivery to biogenic accumulation reservoirs occurred not only in the upper sections of river valleys, but also in the gorge sections of rivers in the peripheral parts of the study area.

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