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GEOCHEMISTRY OF A SEDIMENTARY SECTION AT THE WĄWELNICA ARCHAEOLOGICAL SITE, SZCZECIN HILLS (WESTERN POMERANIA)

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Abstract. The results of geochemical assays on biogenic sediments filling a fossil lacustrine basin at Wąwelnica, in the Szczecin Hills, within the left-bank part of the Oder River catchment are presented. The data reveal a natural Holocene sedimentation sequence similar to that found for other sites in central Europe. The geochemical record of palaeo-environmental changes, which may be a consequence of human activities in the proximity of the site, is distinctly bipartite. The part of the profile corresponding to the lacustrine sediment accumulation during the Greenlandian occasionally shows an increased mineral content and an elevated catchment erosion index. An incidental presence of Palaeolithic and Mesolithic communities is confirmed by archaeological evidence from a few sites in the Szczecin Hills. More distinct episodes of mineral matter supply and more pronounced changes in geochemical indicators can be inferred as occurring from the onset of the older part of the Atlantic until the Older Subboreal. Most of the flint artefacts discovered along with a collection of vessel fragments in the Mierzyn-Dołuje area are associated with the Neolithic occupation. However, changes in the deposits' geochemistry do not reflect all the settlement stages associated with the consecutive human groups identified by archaeological evidence. Possible reasons include a low sediment accumulation rate having restricted peat mass accretion and prevented the storing of any higher amounts of water. This, along with the climate-change-caused lowering of the water table, could have periodically stopped the accumulation of autochthonous organic matter. In addition, intensified human activities coincided with periods of stable and low water level in the basin. On the other hand, breaks in human activity correspond with moist Holocene stages and local flooding events.

Key words: biogenic accumulation basins, drainless areas, geochemistry, human impact, Holocene, Szczecin Hills

Introduction

The young-glacial relief zone features highly diverse geoecosystems, each with its own specific characteristics and landscapes (Kostrzewski *et al.* 2008). Such a zone is dominated by hills and plains, and complemented by flat and wide river valley floors, as well as numerous biogenic accumulation basins in the form of lakes, kettle holes and peat bogs (Sakowicz 1950/51; Kalinowska 1961; Żurek 1987; Pieńkowski 2008; Fec-Beneda 2011; Kordowski 2013; Choiński, Ptak 2019).

Modern limnology addresses changes in the morphometry of lakes and kettle holes (e.g. their number, surface area, shrinkage rate) (Pieńkowski 2000; Marszelewski, Podgórski 2004). In addition, linkages between terrain relief on the one hand and lakes and wetlands on the other can be analysed in the context of the role individual physiogeographic units play in material (primarily water) circulation (Kowalska 1970; Oldak 1988; Rycharski, Piórkowski 2001; Major 2010). In turn, specific conditions of water supply and drainage affect the water level position and dynamics relative to a biogenic accumulation basin's surface area, and determine the nature of sediment-forming processes (Wicik, Więckowski 1991; Tobolski 2004; Błaszkiewicz 2005). The upland areas in the vicinity of Szczecin are exceptional in this regard, due to the fact that despite the considerable terrain tilt angle, the geological setup does not favour pronounced water

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drainage (Borowiec 1993). As a result, leaching of minerals and their transport by groundwater is controlled by the local infiltration conditions. When migrating through the aeration zone, the precipitation water increases its ionic load and transports it to the groundwater level. Component leaching from the catchment depends on a number of factors: the geological setup and the local geochemical background, terrain relief, changes in vegetation cover, and human activities. As those factors vary temporally and spatially, weathering-caused denudation of soil and rock minerals is a very important component of the biogeochemistry of ecosystems (Kostrzewski, Zwoliński 1992; Johnson *et al.* 1994; Gierszewski 2000). Exceptional in this respect are biogenic deposits that record changes occurring at the accumulation site and in its vicinity (Tobolski 2008; Giguet-Covex *et al.* 2011). Reconstruction of the intensity and nature of past denudation processes relies heavily on techniques of absolute dating, sedimentology and geochemistry (Starkel 1988; Borówka 1992; Okupny *et al.* 2013; Pędziszewska *et al.* 2015; Forysiak *et al.* 2017).

Owing to the strategic location of the study area, which is associated with two large intersecting transport routes (the coastal route along the Baltic Sea coast and the continental one along the Oder River), the environs of Szczecin constituted, as early as in the Neolithic, a vibrant and specifically developing microregion (Matuszewska, Kowalski 2013). However, the geological variability, terrain relief and riverine network pattern resulted in non-uniform colonisation of different zones and physiographic regions of Western Pomerania by settlers. A substantial concentration of archaeological sites from the Stone Age and the Bronze Age is associated with the hydrographic node of the downstream section of the Oder River and its tributaries (Płonia, Ina, Gunica) and the Wolin Island (Jankowska 1995; Wesołowski 1995; Matuszewska 2016). However, in contrast to other areas in Western Poland (Brykczyńska, Więcławek 1983; Latałowa 1992, 1999; Malkiewicz 2017; Sobkowiak-Tabaka *et al.* 2019) or northern and eastern Germany (Kaiser 2001, 2004; Kaiser *et al.* 2001, 2003; Jahns 2001; Terberger *et al.* 2004; Dräger *et al.* 2016; Kobe *et al.* 2019), there are no palaeoecological data on changes resulting from natural succession and human activities in the left-bank part of the lower Oder River catchment.

Research at the Wąwelnica archaeological site provided an incentive to study the geochemistry of the sediment filling of a biogenic accumulation basin in the north-western part of the Szczecin Hills. The study used geochemical indicators recorded in biogenic deposits with the aim of reconstructing: water level changes; relative changes in different denudation types and organic matter origin; as well as the processes involved in, and factors controlling, biogenic sedimentation. The deposit's lithological and geochemical variability reflected changes taking place during 11,700–4,250 yr BP, i.e. in the Greenlandian and Northgrippian levels of the new Holocene stratigraphy (see Walker *et al.* 2018).

Study area

The young-glacial study area (Fig. 1A) near the Szczecin Hills is characterised by morphogenetic processes of a highly variable activity (Kondracki 1950/1951; Kozarski 1965; Piotrowski 1981; Gilewska 1986; Mojski 2005). The young-glacial land relief, formed mostly in the Pleistocene, features, *inter alia*, numerous depressions that at present host lakes or peatland (Jasnowski 1962; Żurek 1987, 1999; Pietrucień 1988; Kochanowska, Rygielski 2001; Pieńkowski 2003). Most of them were not connected to the surface drainage networks, for which reason – for several millennia – they served as local denudation bases (Fig. 1B). However, the contribution of drainless basins does not exceed 5% of the lower Oder River catchment, and the isolated drainless depressions show a predominance of evapotranspiration-affected ones over those absorbing water (Hydrographic division… 2006).

A review of drainless basins in the area of study shows a distinct predominance of those smaller than 0.5 ha; in addition, the group of basins smaller than 5 ha is located at the absolute altitude of up to 50 m above sea level (a.s.l.). Most of those basins larger than 5 ha (making up as little as 9% of the total number of basins) are located in the uppermost part of the Stobno Ridge, at altitudes of 50–100 m a.s.l. (Fig. 2). The Wąwelnica site (latitude 53°27'14"N, longitude 14°23'59"E; altitude 30 m a.s.l.) is located in Western Poland, within the Szczecin Hills and, more precisely, north of the Stobno Hills microregion (Fig. 1B). It occupies an oval 1.08-ha basin with a maximum depth of biogenic sediments of 3.80 m (Fig. 3A). The soils near the Wąwelnica site, which are developed mostly on fine-grained sand and tills, are not particularly variable (Piszczek 1960). The parental rock consists of formations of poor to intermediate permeability in which the water table lies not deeper than 2 m (Fig. 3B). A decidedly much higher variability is typical of the groundwater yield, which depends on the complex geological setup of the glacitectonically piled-up Stobno Hills (Piotrowski 1981). The Wąwelnica site is located east of a former large woodland that is locally water-logged, as shown by the archive map, (Fig. 3C). At present, the woodland in the vicinity of the study site covers an area as small as 0.9 km^2, the surroundings being dominated by meadows and arable fields, with drainage ditches totalling 8 km in length (Fig. 3D).

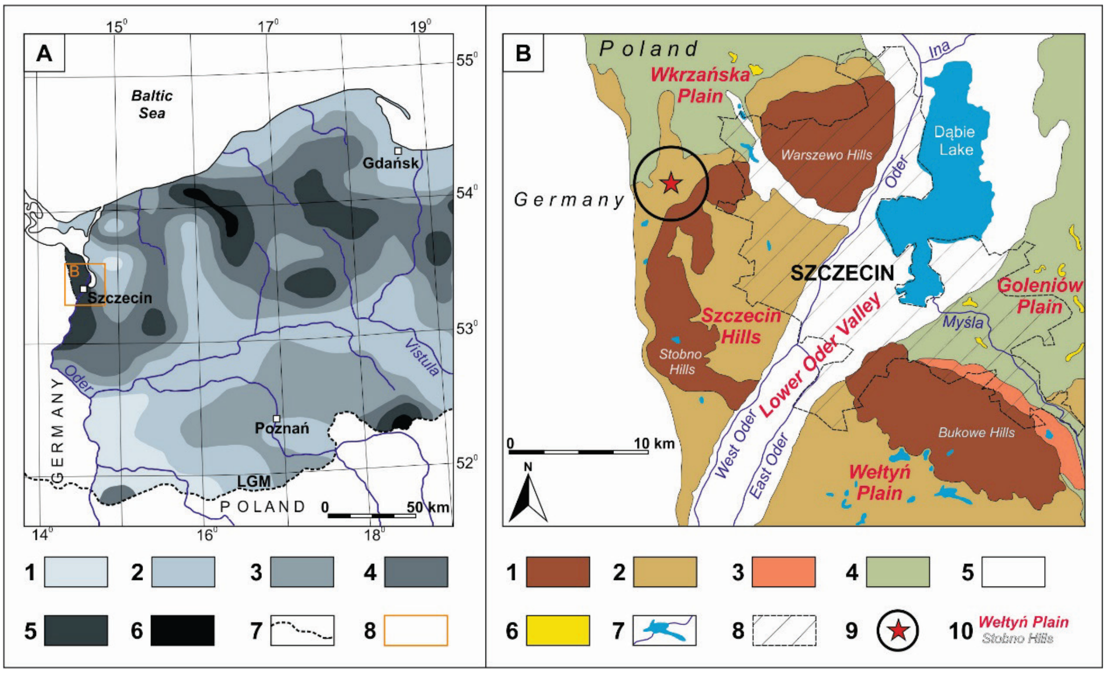

Fig. 1. The Wąwelnica biogenic accumulation basin

A. Location of study area, along with the ratio between the vanished lake surface and the land area after Kalinowska (1961)

1 – below 1%, 2 – 1–3%, 3 – 3–5%, 4 – 5–7%, 5 – 7–9%, 6 – above 9%, 7 – limits of the Last Glacial Maximum after Marks (2005), 8 – area shown in the geomorphological chart in B

B. Geomorphological chart of the Szczecin environs after Gilewska (1986), Borowiec (1993) and Karczewski (2008), modified

1 – morainic plateau with glacitectonic structures, 2 – flat and undulating morainic plateau, 3 – kame terrace, 4 – river valley bottom, 5 – Oder River flood plain levels, 6 – dune hills, 7 – lake and river network, 8 – town, 9 – boundaries of the archaeological study area and location of core WA-2, 10 – boundaries of the mesoregions (bold font) and selected lower order units (standard font)

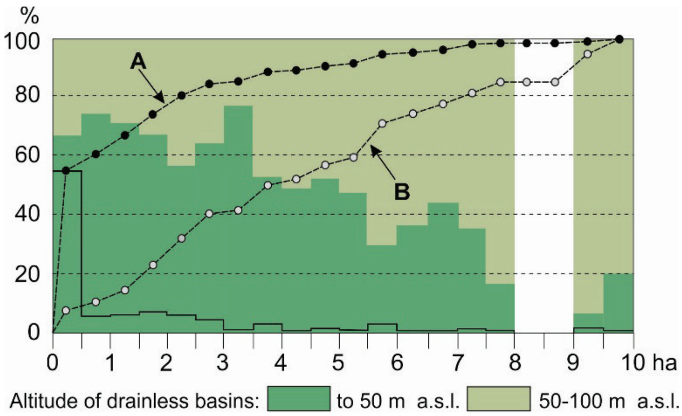

Fig. 2. Frequency of occurrence of drainless basin of specified area

A – in per cent of number of basins; B – in per cent of total area

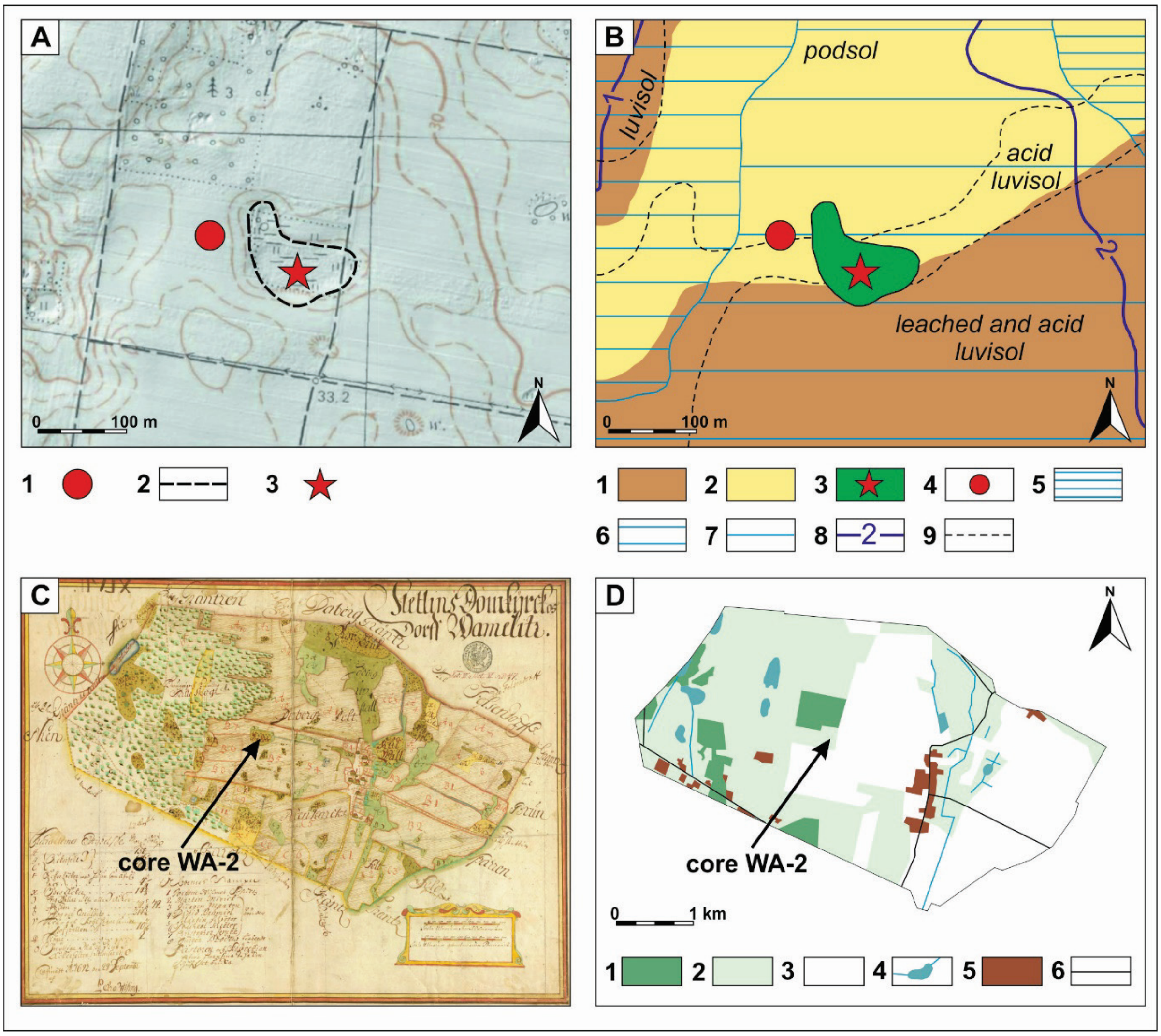

Fig. 3. Location and geographical characteristics of the Wąwelnica study area

A. Archaeological site and biogenic accumulation basin against the background of the LiDAR model

1 – archaeological site with bronze artefacts, 2 – boundaries of the biogenic accumulation basin, 3 – core WA-2 site

B. Map of hydrogeology and soil types (after Geoportal of the West Pomerania voivodeship and Hydrogeological division… 2006, modified)

1 – poorly and moderately permeable soils (mainly sandy clays), 2 – permeable soils (sands of various grain sizes), 3 – peat bog and location of core WA-2, 4 – archaeological site with bronze objects, 5 – groundwater yield > 50 m^3/24h, 6 – groundwater yield 30–50 m^3/24h, 7 – groundwater yield 10–30 m^3/24h, 8 – groundwater level depth (m), 9 – soil type boundaries

C. Part of the Matrikelkarten der Landesaufnahme von Schwedisch-Pommern, Wamiltz, Amt: Distrikt Stettin

D. Recent land-use map (after orthophotomaps from Geoportal of the West Pomerania voivodeship)

1 – woodlands, 2 – meadows and pastures, 3 – arable land, 4 – canals and wetlands, 5 – village buildings, 6 – roads

The Szczecin Hills are controlled by a transitional climate that is strongly affected by the oceanic climate. The region is considered to be the warmest part of Poland, and is characterised by a low temperature amplitude (of 18°C), relatively mild winters with a short duration of snow cover (42 days), and rather cool summers with rainfall higher than that in other parts of Poland (Lorenc 2005). The climatic water budget shows that the surface water and the shallow groundwater in the Szczecin Hills are very intensively used up during the growing season, as the precipitation deficit amounts to as much as 120 mm (Ziernicka-Wojtaszek 2015).

Material and methods

The study is based on analyses of a core (called WA-2) collected at Wąwelnica, on 24–29 May 2015. The 4-metre-long core showed mostly soft organic-rich deposits with pronounced lithological changes along the core length (Fig. 4). The macroscopic lithofacies analysis of the deposit's organic sequences of sediments was conducted using the non-genetic Troels–Smith method for deposit description (see Tobolski 2000). The results are compared with geochemical and sedimentological data. Geochemical assays involving determination of the loss on ignition (LOI), as well as contents of micro- and macroelements, were conducted on every second 5 cm-thick core slice.

Loss on ignition is measured to determine the organic matter (OM) content in a sample (e.g. Bengtsson, Enell 1986). The procedure consisted of two steps. First, crucibles containing about 5 g wet sediment from each core slice were kept for 10 hours at -170°C. Subsequently, the crucibles with the frozen material were placed in the freeze-drier for 24 hours, after which the samples were dried for two hours at 105°C in a Memmert oven and reweighed. In the second step, the crucibles containing about 3 g dried material were placed in the Gallenkamp muffle furnace and combusted at 550°C to constant weight. The percentage OM concentration was calculated from the difference between sample weights before and after combustion.

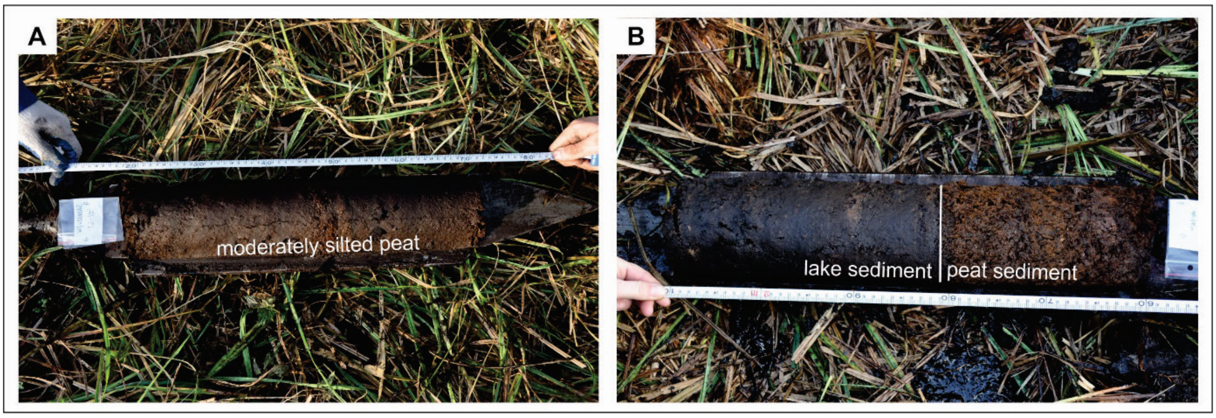

Photo by B. Cedro, 2015

Fig. 4. Upper part of the core WA-2 (A) and the border between coarse detrius gyttja and peat at the central part of core WA-2 (B) from the Wąwelnica biogenic basin

Contents of selected elements (Na, K, Ca, Mg, Fe, Mn, Cu, Zn and Pb) were determined by atomic absorption spectrometry (AAS) using a manual 969 Unicam Solaar apparatus (Borówka 1992). Prior to the instrumental analysis, dried samples of known weight were reconstituted in a mixture of concentrated nitric acid (HNO_3), hydrochloric acid (10% HCl) and perhydrol (H_2O_2) using a Berghof microwave mineraliser. The results expressed in g/l were converted to mg/g or µg/g dry weight (d.w.). Contents of total carbon (TC), total nitrogen (TN) and total sulphur (TS) were determined separately using a VarioMAX analyser (Elementar) at 5-cm resolution. Pre-dried and homogenised samples were weighed in ceramic crucibles and analysed based on the principle of catalytic tube combustion at high temperatures in the presence of oxygen (Binczewska *et al.* 2018). The anthropogenic mercury (Hg) content was determined using a DMA-80 Analyser (Milestone Company). The total mercury content in solid samples is determined based on the principle of thermal decomposition, catalytic conversion, amalgamation and atomic absorption detection (Leipe *et al.* 2013).

The sediment grain size (11 selected samples) was analysed using a MASTERSIZER MICRO ver. 2.19 laser granulometer (Malvern Instruments Ltd.). The test material was dispersed in a liquid in the apparatus. Prior to the study, the organic matter in the sediment was removed by combustion at 550°C. Subsequently, the grain-size metrics: mean grain diameter (M_Z), sorting (σ_I), skewness (Sk_I) and kurtosis (K_G) were determined with Gradistat software, using the Folk and Ward formula (1957).

The geochemical stratigraphy of the core was based on a radiocarbon date set, with eight bulk samples being subjected to dating using the LSC technique according to the standard procedure (Tudyka *et al.* 2015).

The interpretation of data was limited to eight thousand years, and was compared with phases of vegetation changes in the Szczecin Lowland, as described earlier by Jasnowski (1962). The geochemical data were integrated with results of archaeological research carried out so far by analysing two sheets (No. 29-04 and 30-04) of the documentation produced within the framework of the Polish National Record of Archaeological Sites (Pol. *AZP – Archeologiczne Zdjęcie Polski*) programme; the sheets contain also the basic descriptive and spatial information on earlier discoveries (reported by e.g. Czarnecki 1983; Siuchniński 1983), and are complemented by new findings on the settlement community in the vicinity of Wąwelnica. The comparison eventually allowed anthropogenic effects on the natural environment at the study site to be determined. The interpretation rests on a key assumption that lithophilic and biogenic elements were derived from different sources, and that they were accumulating in the deposits under different physico-chemical conditions. The elemental ratios (Fe/Mn, Fe/S, C/N, Cu/Zn, Ca/Fe, Na/K, Ca/Mg, Na+K+Mg/Ca and |r|) were used to classify the deposits and to reconstruct environmental changes in the sedimentary basin and in its catchment (Walanus 2000; Pawłowski *et al*. 2016).

Results

The Wąwelnica site and its immediate vicinity host a substantial number of archaeological sites revealing human settlement and economic activities already in prehistory (Fig. 5A). The Mesolithic artefacts discovered at Wąwelnica were located in a small, dune-like knoll situated between two kettle holes (Galiński 1992, 2016), west of the basin under study. A list of archaeological data from within a 2-km radius of the biogenic accumulation basin under study revealed evidence of the presence of not only Mesolithic, but also Neolithic, Bronze Age and Iron Age communities. The distance between the ancient settlements and the hydrographic networks (rivers and basins) was usually 10–20 and 50–100 m, respectively (Fig. 5B), their distribution showed a distinct preference towards podzolic soils composed of intermediately permeable loose sands. Brown soils, due to the poor permeability of their underlying deposits, were of low preference (Fig. 5C).

In 2014, one of the authors (B. Cedro) found an archaeological hoard at Wąwelnica, in the immediate vicinity of the basin. The deposit, containing mostly various bronze artefacts (vessels, ornaments) and some bone buttons, was tentatively assigned to the Bronze Age period V (about 950–780/740 yr BC). The objects included some items rarely found either in Pomerania or in the neighbouring Mecklenburg and Brandenburg, e.g. bronze vessels (known so far from only 4–5 sites) and an ornamented bronze belt (7 finds dated to the younger Bronze Age; Sprockhoff 1956, map 33). The two openwork arm-pieces found in the hoard have no equivalents known so far, making them unique (Fig. 6).

Based on the geochemical results, four geochemical zones have been distinguished (coded GZI-IV) in the vertical deposit succession (Fig. 7 and 8):

GZI (385–261 cm) represents the phase of mineral-organic and organic lake deposition (OM of 44.5–91%) under reduced conditions (Fe/Mn ratio often >120) and gradual changes in mechanical denudation (Na+K+Mg/Ca ratio – 0.37–7.34). The zone shows three levels of increased contents of Zn (up to 150 μg/g) and one level of an increased Cu content (up to 20 μg/g).

GZII (261–158 cm) is a record of mainly lake sedimentation (OM content of 86–91%), the sedentation onset of the autochtonous, authigenic rock-forming material (the average OM concentration increases to 92%), and associated changes in mechanical denudation and redox conditions (reduced contents of lithogenic elements: Na below 0.18 mg/g, K below 0.2 mg/g, and Mg below 1.60 mg/g; the Fe/S ratio decreased first down to 0.05, to then increase to 0.47; the Ca/Fe ratio range of 5.08–46.5).

GZIII (158–66 cm) provides a record of a dynamic change in the type of biogenic sedentation, as also indicated by the reduced OM concentration (from 92 to 84%) and Na content (from 0.15 to 0.09 mg/g). In contrast, the upper layer of the poorly decomposed peat was deposited under oxidised conditions (the mean Fe/Mn ratio 15.4) and stable, albeit low mechanical denudation (the Na+K+Mg/Ca ratio between 0.2 and 0.25).

GZIV (66–0 cm) represents a phase of change in the mineral-organic matter ratio (the OM concentration reduced from 82.8 to 53%) in the deposit formed in a telmatic environment. The Ca content here increased to 56.8 mg/g. The concurrent increase in the Na/K (to 1.2) and Ca/Mg (to 42) ratios points to a considerably higher temperature and humidity of the environment and an increased chemical denudation. The Fe/Mn ratio (mean 37.4) indicates a change from reduced to oxidised conditions.

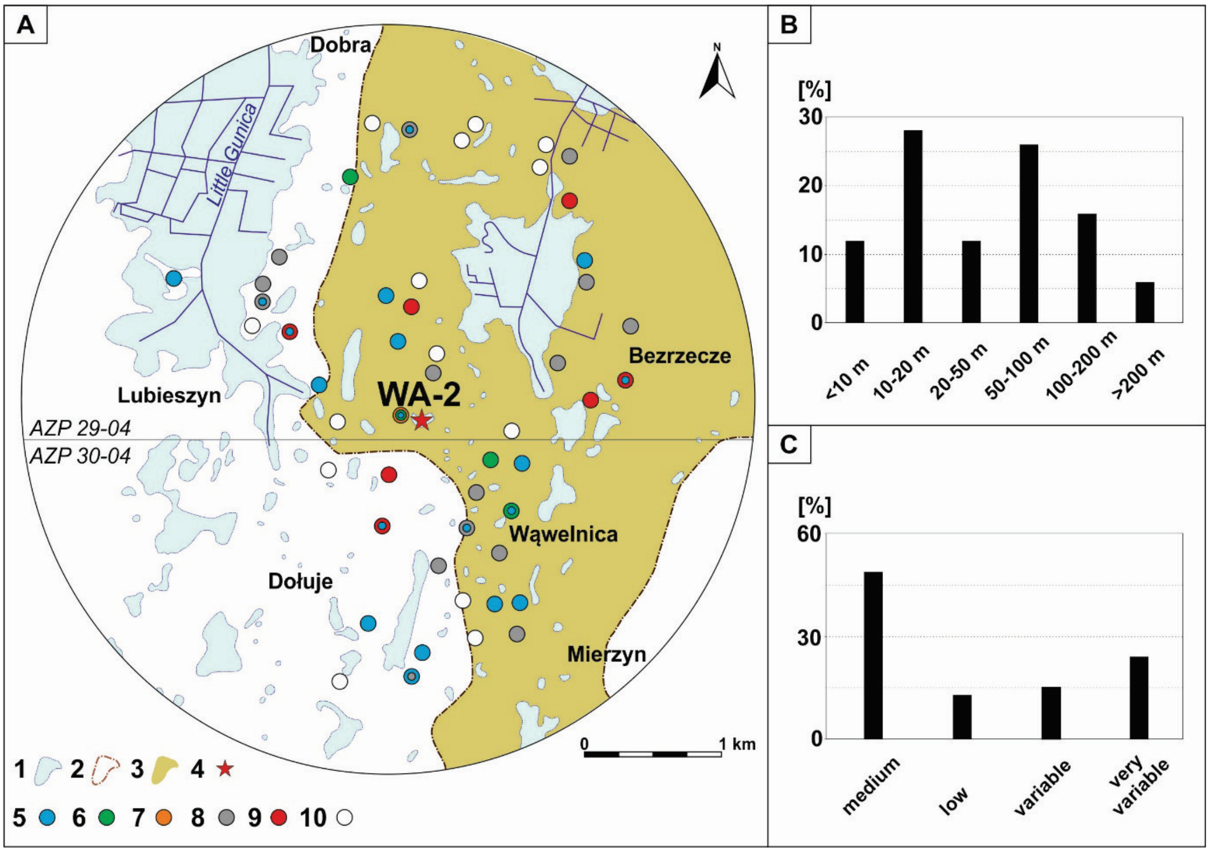

Fig. 5. Map of archaeological sites in the surroundings of the Wąwelnica biogenic accumulation basin

A. Environmental characteristics of study area and sites of human activity

1 – wetlands, 2 – third-order catchment, 3 – boundaries of drainless areas, 4 – core WA-2 site, 5 – Stone Age; 6 – Bronze Age; 7 – Pre-Roman, Roman and Migration Periods, 8 – Prehistory, 9 – Early Middle Ages, 10 – Early Modern Period

B. Distances between human activity sites from the river network and wetlands

C. Frequency of human activity sites relative to soils of different permeability

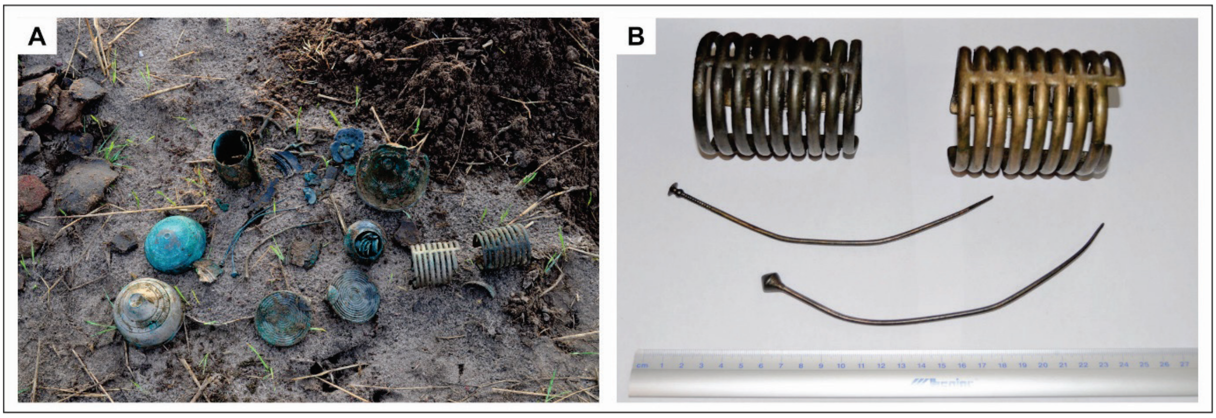

Photo by B. Cedro, 2014

Fig. 6. Bronze artefacts discovered in vicinity of village of Wąwelnica (A) and archeological exhibits at the National Museum in Szczecin (B)

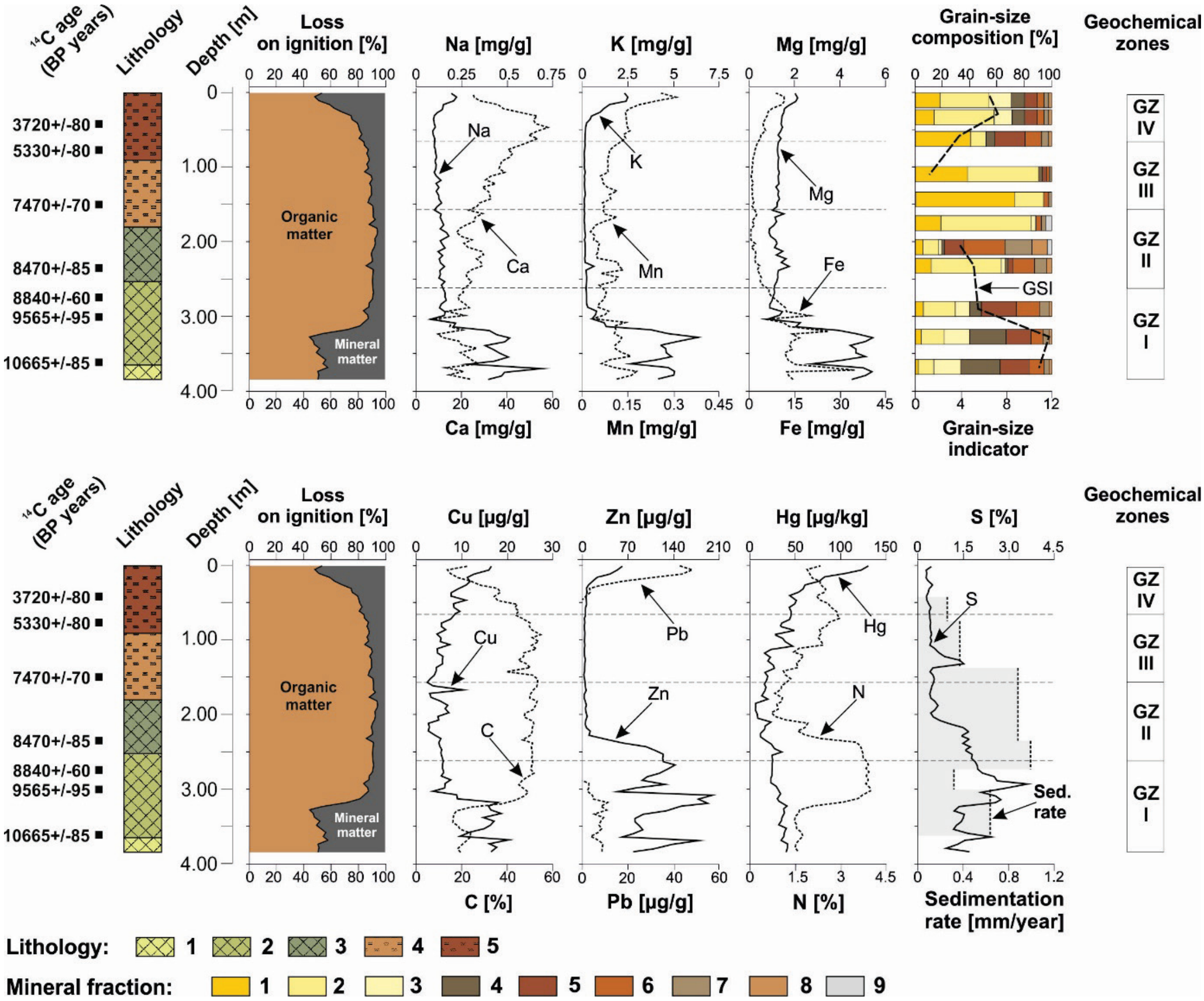

Fig. 7. Chemical characteristics of the Wąwelnica sediments in relation to deposit age, lithology and grain-size composition

1 – fine detritus gyttja with silt admixture, 2 – fine detritus gyttja with silt and sand admixture, 3 – coarse detritus gyttja, 4 – poorly decomposed peat, 5 – highly decomposed peat; grain-size composition: 1 – medium sand, 2 – fine sand; 3 – very fine sand, 4 – very coarse silt, 5 – coarse silt, 6 – medium silt, 7 – fine silt, 8 – very fine silt, 9 – clay; grain-size index (GSI) measured as the ratio of coarse silt to fine silt

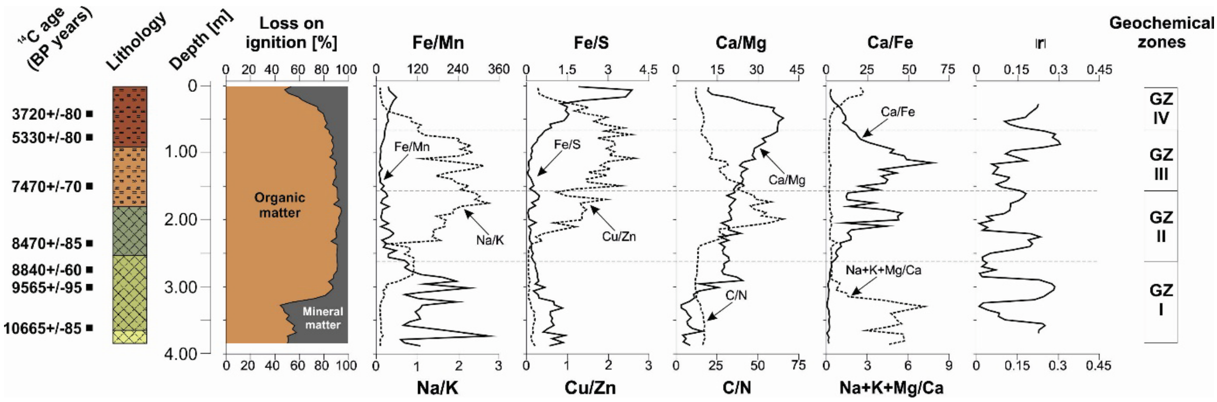

Fig. 8. Profiles of selected geochemical parameters in the Wąwelnica deposits

for lithology see Fig. 7

Discussion: a geochemical record of the natural basin evolution and human impact

Late-glacial stage (3.85–3.32 m; >11,700 cal. BP)

Changes in the lithology of the Wąwelnica accumulation basin reflect a typical sequence of changes in hydrological conditions recorded in drainless basin peat bogs in Western Pomerania. As demonstrated by Jasnowski (1962), peat deposits in the vicinity of Szczecin can be divided into three layers. Clayey (more seldom carbonate) gyttja at the bottom is overlain by fens (mainly sedge-mossy, locally with an admixture of reeds); these were subsequently covered by accumulating transient (mainly sedge-sphagnum moss) peat. A sample from a depth of 3.65–3.67 m (from the fine-detritus gyttja layer in core WA-2) was dated to 10,655±85 yr BP (GdS-4162), which makes it possible to regard the lacustrine deposit as originating at the end of the Late Glacial (Table 1). The formation of glacial lake depressions was associated with the melting of dead ice blocks (Błaszkiewicz 2005), and the abundance of such depressions in the landscape was conducive to establishing short-lived Late Palaeolithic camp-sites (see Kalicki *et al.* 2018).

Table 1

Results of radiocarbon dating of 8 bulk samples from the core WA-2

No.	Sample name	Lab. No.	Radiocarbon age (BP)	Calendar age – 68.2% confidence intervals (cal. BP)	Calendar age – 95.4% confidence intervals (cal. BP)
1	Wąwelnica WA-2/40–42cm	GdS-4186	3720±80	4230–4200 (5.5%) 4160–3965 (58.8%) 3950–3925 (4.0%)	4355–4325 (1.3%) 4300–3840 (95.4%)
2	Wąwelnica WA-2/75–77cm	GdS-4161	5330±80	6265–6250 (3.7%) 6205–6100 (32.8%) 6095–5995 (31.8%)	6285–5935 (95.4%)
3	Wąwelnica WA-2/1.50–1.52m	GdS-4166	7470±70	8360–8280 (36.2%) 8270–8195 (32.1%)	8410–8165 (93.6%) 8080–8050 (1.8%)
4	Wąwelnica WA2/2.35–2.37m	GdS-4177	8470±85	9545–9420 (68.2%)	9605–9570 (1.2%) 9560–9270 (93.3%) 9170–9145 (0.8%)
5	Wąwelnica WA-2/2.75–2.77m	GdS-4173	8840±60	10130–10060 (16.1%) 10045–10020 (4.1%) 10015–9985 (5.7%) 9965–9880 (19.2%) 9875 9765 (23.2%)	10175–9690 (95.4%)
6	Wąwelnica WA-2/3.00–3.02m	GdS-4187	9565±95	11095–10910 (36.4%) 10900–10740 (31.9%)	11190–10650 (93.6%) 10625–10595 (1.8%)
7	Wąwelnica WA-2/3.65–3.67m	GdS-4162	10655±85	12735–12615 (66.5%) 12520–12510 (1.8%)	12755–12575 (77.2%) 12570–12480 (18.2%)

Radiocarbon dates were calibrated by OxCal 4.4 calibration program (Bronk Ramsey 2010) using the new IntCal20 (Reimer *et al.* 2020) calibration curve.

Greenlandian (3.32–1.54 m; 11,700–8236 cal. BP)

The first woodland communities in Western Pomerania were a birch–pine forest, followed by a denser pine–birch forest with elm, associated with climate warming at the beginning of the Holocene (Malkiewicz 2017). This period is recorded in the basin studied with fine-detritus gyttja showing a gradually increasing OM content (from 72 to 90%) and a stable C/N ratio (about 12), which is typical of the limnic sedimentary regime (Ochiai *et al.* 2015) (Figs 7, 8). Distinct variations in the Fe/Mn ratio (122–274) provide evidence that the water level in the basin was related to the groundwater table and, on account of a permeable substrate, responded readily to changes in climate wetness. A similar geochemical stratification, expressed mainly as changes in the contents of Fe, S and Ca, has been reported for numerous European lakes (Słowański 1961; Żurek, Dzięczkowski 1971; Pawlikowski *et al*. 1982; Apolinarska *et al*. 2012; Kobe *et al*. 2019).

The low values of the catchment erosion index (Na+K+Mg/Ca) provide evidence of a relatively low denudation rate during the period of small human groups' activities at the terminal phase of the Late Palaeolithic (Fig. 9). This is also confirmed by the GSI values (the ratio of coarse silt to fine silt), which, at the onset of the Holocene, dropped from 12 to 5.

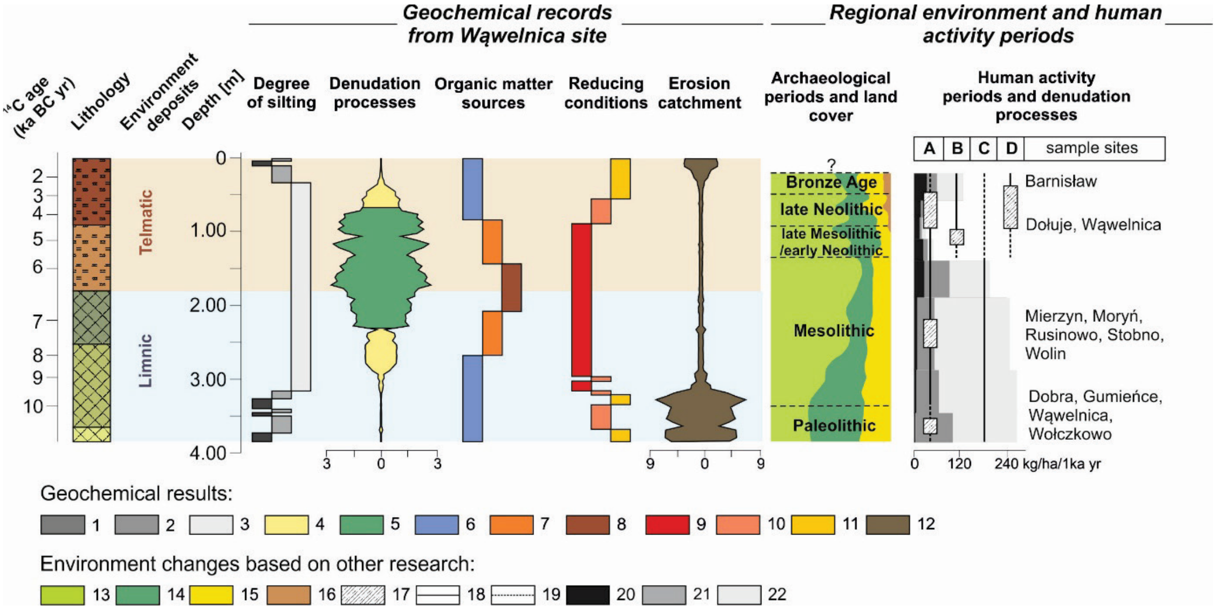

Fig. 9. Palaeoenvironmental changes in study area in relation to intensity and type of regional denudation (after Borówka 1992), sub-regional land cover (after Dietze *et al.* 2018) and human activity periods in Western Pomerania (after Siuchciński 1983; Czarnecki 1983; Kowalski 2007; Matuszewska, Kowalski 2013; Kotrys 2015)

1 – heavily silted deposits, 2 – moderately silted deposits, 3 – unsilted deposits, 4 – domination of mechanical denudation (Na/K ratio <1), 5 – domination of chemical denudation (Na/K ratio >1), 6 – organic matter of planktonic origin (C/N ratio <12), 7 – organic matter of terrestrial and planktonic origin (C/N ratio between 12 and 22), 8 – organic matter of terrestrial origin (C/N ratio >22), 9 – low availability of reactive Fe and higher S contents in organic matter, 10 – Fe reduced to Fe^{2+} and converted to pyrite (Fe/S ratio about 0.87), 11 – very high Fe/S ratios due probably to denudation, 12 – catchment erosion (Na+K+Mg/Ca ratio), 13 – arboreal, 14 – Scots pine, 15 – open land, 16 – human presence, 17 – documented human activity in region 18 – weak human impact, 19 – very weak human impact, 20 – carbonate leaching, 21 – leaching of other substances, 22 – mechanical denudation; types of human activity: A – clearings, B – grazing, C – fire, D – cultivation; for lithology see Fig. 7

Settlement behaviours of communities dwelling at that time in the lower Oder River basin area are aptly illustrated by studies at site 1 in Bolków, i.e. a part of the Wkrzańska Plain adjacent to the Szczecin Hills (Galiński 2013). The Late Palaeolithic peoples of the Ahrensburg Culture were active there during a few occupation episodes at the Late Weichselian/Holocene transition and setted short-lived camp-sites on a small elevation between two lakes. Similarly, data from numerous sites of the Ahrenburg Culture occurring in Western Poland and north-eastern Germany point to a short-term and probably seasonal stay of small human groups in these areas, mainly related to summer reindeer hunts (Sobkowiak-Tabaka 2011; Terberger *et al.* 2004). In terms of social organisation, the communities were small and scattered, for which reason the record of their activities is poor, with a low level of activities directly interfering with the geological structure of the immediate Szczecin vicinity (Fig. 9).

The progressing improvement in climatic conditions in Western Poland during the Boreal resulted in expansion of pine–birch woodlands, which showed an increasing contribution of *Corylus* and *Ulmus* and a persistently low admixture of *Alnus*, *Fraximus*, and *Tilia* (Masojć *et al.* 2007; Madeja 2012; Jurochnik, Nalepka 2013; Malkiewicz 2017). The change in the lithology in the Wąwelnica basin to coarse-detritus gyttja that is assigned to that period provides evidence of a gradual lowering of the water level in the lake (Fig. 7). This is also confirmed by the low mean sediment accumulation rate (between 0.34 and 1.08 mm/yr), which is typical of numerous Early Holocene biogenic accumulation basins (Żurek 1987). The downward trend in the water level during the Preboreal is also characteristic for most of the closed lake basins of NE Germany (Kaiser *et al.* 2012). In this period, the significance of catchment leaching was growing (Na/K ratio increasing from 0.52 to 1.56), accompanied by a simultaneous decline in the total denudation indicator. Those results are in agreement with the stratigraphic variability of denudation intensity and type in the Early Holocene, as demonstrated by Borówka (1992) for other basins in Western Pomerania (Fig. 9).

Northgrippian (1.58–0.41 m; 8236–4250 cal. BP)

A subsequent distinct change in sedimentation conditions occurred in the Atlantic. The broadleaf forests prevalent at the time are evidence of a lowering of the water table, with a simultaneous increase in the amplitude of its periodic variations (Jasnowski 1962; Malkiewicz 2017). Sedimentation of coarse-detritus gyttja initially continued, but the sediment at 1.80 m in the core records a shallowing of the basin and the formation of a low peat bog. The water budget of peat bogs being formed at that time in northern Poland's uplands depended on the intensity of groundwater supply, the groundwater being more frequently free and less seldom confined (Żurek 1969). The Wąwelnica basin became a sedentation site for moderately and poorly decomposed sedge-moss peat under a constant supply of shallow groundwater and surface water. The mineral matter concentration seldom exceeded 10%, the C/N ratio increasing sharply from 13 to 65.6, thus confirming the terrestrial OM origin (Fig. 8). At the onset of the Middle Holocene, a distinct rise in the water level left a signature visible as a poor decomposition (10–20%) of the autochthonous OM and periodic variation in the redox indicators such as the Fe/Mn, Fe/S, and Ca/Fe ratios. In his study on water level changes in Poland, Żurek (1993) refers to the Littorina transgression of the Baltic Sea, the water level rise in the Łeba peat bogs, the formation of a gyttja cover over peats in the lakes Jamno, Sarbsko and Gardno, and an accretion of rush peats in the Szczecin Lagoon area as taking place at that time. In the second half of the Atlantic, the water level in the Wąwelnica peat bog dropped (a decrease in the Fe/Mn ratio from 50 to 8), similarly to what was taking place in other biogenic accumulation basins in Poland (Ralska-Jasiewiczowa, Starkel 1988; Borówka 2007; Pleskot *et al.* 2018), and also in north-eastern Germany (Kaiser *et al.* 2012).

At older stages of the Atlantic, Western Pomerania – similarly to large areas of Europe – was inhabited by Mesolithic hunter-gatherer communities; the fundamentals of their culture were formed at the onset of the Holocene, during climate changes and the evolution of boreal forests (Galiński 2002). Those communities were specialised in hunting forest game and birds and in fishing in inland water bodies. During the Atlantic, as the human population size was growing – and when marine transgressions reduced the habitat of Mesolithic communities – the thus-far small groups managing fairly extensive hunting grounds became structured in clans of up to several tens of individuals (Galiński 2011). Mesolithic camps were usually being set up in dry, sandy areas with direct access to water, such as Wąwelnica, Dobra and Dołuje (Galiński 1992; Kobusiewicz 1999). The close association between the Mesolithic settlement network and the shores of water bodies and the riverine network was demonstrated also by studies in, *inter alia*, the Myślibórz Lakeland (Kotrys 2015), the Łagów Lakeland (Sobkowiak-Tabaka *et al.* 2018), Charzykowy Plain (Bagniewski 1983, 1987) and northern Germany (Groß *et al.* 2018).

Changes in the biogenic sediment chemistry (a decrease in the Na/K ratio from 2.6 to 1; an increase in |r| from 0.01 up to as much as 0.32, with a relatively high but stable catchment erosion index of about 0.25) in the second half of the Atlantic may have been a result of the area being penetrated by communities of the Early Neolithic Danubian Cultural circle (mostly the Linear Pottery Culture), followed by an advance of the Funnel Beaker Culture people (Siuchniński 1983; Jankowska 1995). Settlements of the Danubian (Incised Ware) culture have been being discovered in the Szczecin Hills mainly over the last 20 years (Kowalski 2003; Matuszewska, Kowalski 2013; Dziewanowski 2015). The communities occupied both high-altitude and water-logged areas of various sizes located south and south-east of the Mierzyn–Stobno line. Worth pointing out is a correlation between the Linear Pottery Culture peoples' settlement location and the presence of brown soils and black soils, as well as the use of local resources for flint processing (with a low import from the south of

Poland) as well as the presence of food remains, including cereals, bones of (primarily domesticated) animals, and freshwater fish (Kowalski 2007).

The period between the Atlantic and the Subboreal witnessed a significant change in the nature and intensity of elemental migrations within the basin, brought about most probably by deforestation of the catchment. This resulted in a gradual change in the sediment lithology to a strongly decomposed and muddy (the mineral matter contribution varying within 15–20%) sedge-mossy peat with an average accumulation rate of 0.85 mm/yr. Because of periodic flooding, the OM supply and decomposition began to change as well (the C/N ratio decreased from 20 to 15, while the Fe/Mn ratio increased from 10 to 34). The periodic rise of the groundwater at the turn of the Middle and Late Holocene caused by the demise of woodlands in northern and western Poland and the emergence of extensive open pastures was documented by, *inter alia*, Latałowa (1999) and Lamentowicz *et al.* (2019). During the period analysed, the Stążki peat bog showed the appearance in the sediment of *Arcella discoides*, a species typical of hydrologically unstable environments (Lamentowicz *et al.* 2010). One of the factors deciding on the direction and rate of environmental changes could have been fires. They brought about a disappearance of climax oak forests and the expansion of beech (*Fagus sylvatica*) woodlands. Moreover, marsh birch forests appeared, which should be associated with the emergence of habitats typical of transient peat bogs and soil acidification (Jasnowski 1962; Żurek 1993).

Geomorphological processes in the left-bank part of the Szczecin environs were relatively intense, but stable. This is evidenced by a decrease in the OM contribution from 84 to 80%, with moderate values of the catchment erosion index (Na+K+Mg/Ca ranging within 0.18–0.25). The profile-lowest GSI values could be taken as a signature of relatively intense weathering processes and the mineral matter supply from distant source areas (Fig. 7). Kozarski *et al.* (1969) and Kappler *et al.* (2019) referred to anthropogenic involvement in western-central Poland and in north-eastern Germany, respectively, as resulting in two phases of intensified aeolian erosion during that period. A supply of terrigenous material of a similar magnitude was reported by Miotk-Szpiganowicz (1992) from lacustrine sediment in the Tuchola Forests (Charzykowy Plain). The Late Neolithic picture of the human activity in Western Pomerania distinctly points to a tendency towards a change in the economic orientation from land tilling that had thus far prevailed, to the dominance of pasture-based animal husbandry. The transformations were manifested by a scarcity, and a virtual lack in the Early Bronze Age, of settlements (Siuchniński 1983). The sources from the area of interest are, for all practical purposes, limited to artefacts from graves (Dołuje, Mierzyn) and single stone and flint tools associated with the Late Neolithic Corded Ware Culture. No evidence could be obtained from the initial periods of the Bronze Age. It may be presumed that activities that could have been reflected in the composition of the deposits filling the basin studied might include mid-forest pasture use at the end of the Neolithic and at the onset of the Bronze Age (Siuchniński 1983).

Meghalayan (0.41–0 m; <4250 cal. BP)

Sedimentation of deposits showing a high mineral content (frequently in excess of 40%) that continued until historical times, most probably as a consequence of intense settlement processes in the 13th century and at the turn of the 14th (Rogosz 1991/92). The analysis of grain size distribution and metrics points to an increased intensity of denudation processes responsible for the growing sediment accumulation rate in the basin, and resulting from a higher accessibility of and proximity to source areas (Fig. 7). This phase corresponds with the lithogeochemical record in several other lakes and peatlands from central Europe (see Pawłowski *et al.* 2015; Pleskot *et al.* 2018; Stolz *et al.* 2020).

Conclusions

During the Late Weichselian, similarly to most young-glacial areas of the European Lowland, the Allerød permafrost degradation resulted in the emergence of numerous lake-type basins of various sizes. The smallest basins rapidly filled with deposits originating from denudation, but some small lakes – like the Wąwelnica basin analysed – persisted over several thousand years, usually until the onset of the Atlantic, when the intensified evapotranspiration associated with the development of climax woodlands resulted in the water table being lowered.

As a consequence of natural denudation processes taking place in more topographically complex areas and a sparse vegetation cover at the initial phase of succession, at the end of the Late Glacial and during the Preboreal, the Wąwelnica site experienced an accumulation of gyttja with a considerable admixture of mineral silt. No record of any major effects on the basin produced by the Palaeolithic and Mesolithic human communities could be assigned to that period of time, although the immediate vicinity of the study site contains archaeological evidence of at least seasonal presence of various small human groups at that time.

The initial phases of human activity intensification manifested as an increasing catchment erosion index and as a change in the grain-size distribution of the allochthonous mineral matter in the Neolithic and the Bronze Age in particular. The changes in deposit lithology and geochemistry evidence a progressing degradation of the natural vegetation cover, and consequently a gradually increase in mechanical denudation.

A more precise assessment of the effects of prehistoric human activities documented in the vicinity of Szczecin by numerous archaeological sites dated from the Late Neolithic to the Modern Period requires further multiproxy-based research on sediments deposited in sedimentation basins located in various geomorphological settings, including those in the dune area of the Wkrzańska Plain and morainic uplands, and in the immediate vicinity of the Lower Oder River Valley.

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