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HOW WELL MULTI-INDICATOR PALAEO-ENVIRONMENTAL STUDIES MEET THE NEEDS OF RESEARCH ON SETTLEMENTS, ON THE EXAMPLE OF THE EARLY MEDIEVAL SETTLEMENT COMPLEX IN SZCZECIN: METHODOLOGICAL PROBLEMS AND EVALUATING INTERPRETATION VALUE

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Abstract. The subject of the work is a reconstruction of environmental conditions in the Lower Oder River Valley in the early Middle Ages with use multi-proxy research. This was considered in terms of natural determinants of the development of hydrogenic habitats in the estuary section of a large lowland river, but at the beginning of a headland of natural morainic plateau known as Castle Hill in Szczecin. In a relatively small area, three different types of geochemical landscapes were distinguished that had specific functions in matter cycles, including the water cycle. The article mainly presents the results of geochemical studies for a series of biogenic deposits separated by a series of lacustrine sediments with a large admixture of mineral material. An attempt was also made to determine subfossil animal remains in the sediments.

Key words: geochemistry, natural environment, early medieval period, urban site, human impact, Western Pomerania

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Introduction

Szczecin is an interesting example of urban centre, its favourable geographic location having afforded considerable important economic and cultural importance to the entire West Pomerania region for over a thousand years. The first settlement with early urban features was built around the middle of the 9th century on the site of a tribal settlement dating to the turn of the 8th century (Łosiński 1996). It was situated on present-day Castle Hill and inhabited mainly by merchants, craftsmen and fishermen. Work edited by Kowalska and Dworaczyk (2011) presents detailed results of archaeological research carried out in the early-medieval settlement accompanied by a stronghold, within the so-called Vegetable Market but also discusses the conditions for the development and economic history of the entire settlement complex. Archaeological research conducted to date within the confines of the former Vegetable Market (Kowalska (ed) 2019) confirms that the area between the slope of Castle Hill and the Oder River channel was the main craft and fishing district of early-medieval Szczecin. According to Leciejewicz (1962), for these reasons, this area may have been referred to as a second "hill", despite the barrel soil level here being about three meters below the present sea level.

The results of previous analyses of cultural layers and organic sediments at the settlement complexes have repeatedly confirmed their utility for detailed reconstructing environmental conditions in areas of settlements and human-environment relations (Tobolski (ed) 1998; Latałowa 1999a; Hildebrandt-Radke 2007; Makohonienko, Nalepka 2007; Tobolski, Żurek 2012; Muzolf *et al.* 2013/2015; Kittel *et al.* 2018, 2020, 2021; Czerwiński *et al*. 2019; Wieckowska-Lüth *et al.* 2021; Dörfler *et al.* in press). In the case of archaeological sites in Poland, palaeobotanical analyses was the field of study decidedly most frequently used for this purpose as it provides a lot of information about plants in terms of their use as food, as raw material for crafts or in medicine (Badura *et al.* 2004; Lityńska-Zając, Wasylikowa 2005; Latałowa 2007; Wasylikowa *et al.* 2009; Moskal-del Hoyo 2021), while also allowing sediments to be dated and local and regional changes in vegetation to be reconstructed (Latałowa *et al.* 1998; Milecka 2007; Tobolski 2008; Dobrowolski *et al.* 2013/2015; Badura *et al.* 2022). The remains of aquatic invertebrates are also often used in the study of archaeological sites located around water bodies. These include molluscs, water fleas (Cladocera) and non-biting midges (Chironomids), whose fossils can provide valuable information on environmental conditions (Pawłowski 2017), changes in water level (Płóciennik *et al.* 2020; Kittel *et al.* 2021, in press; Antczak-Orlewska *et al.* 2022) and temperature (Płóciennik *et al.* 2022; Antczak-Orlewska *et al.* in press). The analysis of subfossil remains of water fleas also enables a detailed reconstruction of the stages of eutrophication of lakes attributable to settlement cultures' direct activity (Szeroczyńska 1998) or to their intentional activity in the immediate vicinity of lakes (e.g. fires intended to improve the exploita- tion of natural resources; Sobkowiak-Tabaka *et al.* 2020) from the end of the Palaeolithic (Sobkowiak-Tabaka *et al.* 2022) and the Neolithic (Kittel *et al.* 2021) to historical times (Kittel *et al.* 2014, 2018).

Geochemical methods are relatively less frequently, despite one of the key results of human activity being changes in the chemical composition of individual environmental features (Konecka-Betley, Okołowicz 1998; Zgłobicki, Ziółek 2006; Forysiak *et al.* 2012; Foltyn *et al.* 2018). However, the results of all the aforementioned methods are key in the increasingly frequent attempts to estimate the scale of changes in environmental components of caused by human activity (Latałowa 1999b; Płaza *et al.* 2013/2015; Majorek 2017; Lamentowicz *et al.* 2019; Mroczkowska *et al.* 2021; Słowiński *et al.* 2021; Makohonienko *et al.* in press) and should be used more fully to forecast future environmental changes (Lamentowicz 2007; Słowiński *et al.* 2019).

In the case of geochemical studies of limnic and peat sediments, it is crucial to determine the share of the main sedimentary processes responsible for forming a sediment cover in a biogenic accumulation reservoir. According to Borówka (2007), the most important of these processes are: terrigenic sedimentation (the supply of allochthonous mineral matter, mainly from the catchment), biogenic sedimentation (e.g. the accumulation of amorphous organic matter or the sedimentation and decomposition of diatom shells, molluscs, etc.) and chemogenic sedimentation (the dissolving and precipitation of crystalline and amorphous substances such as calcium carbonate, hydroxides, sulphides or phosphates). All these processes are variable in space and time (Bojakowska, Sokołowska 1997; Apolinarska *et al.* 2012; Kittel *et al.* 2020; Adamek *et al.* 2021; Pleskot *et al.* 2022; Sojka *et al.* 2022), and their intensity can increase markedly depending on the nature and degree of human impact (Kosiński *et al.* 1994; Korzeniowski *et al.* 2020; Cybul, Okupny 2021; Płóciennik *et al.* 2021, 2022). In this respect, strongholds, defensive settlements and urban centres are special; though they contain historically valuable features, they also constitute an irreplaceable testing ground for geoarchaeology, which also includes environmental geochemistry (Wardas-Lasoń *et al.* 2007; Hildebrandt-Radke 2011; Galas, Jaeger 2016; Kittel *et al.* 2018; Twardy *et al.* 2018).

The issues central to interdisciplinary geoarchaeological research include identifying topography and surface geological structure and their impact on the settlement and economic activity of past communities (Rutkowski, Starkel 1989; Hildebrandt-Radke 2011; Kittel 2012; Twardy 2013/2015; Janowski 2021). In addition, climate change and increasing human impact have increased the importance of geomorphology and palaeogeography in recent years, as evidenced by, for example, the amount of research aimed at reconstructing anthropogenic transformations of morphology and lithology that is increasingly being conducted within the borders of urban centres (Troć, Milecka 2008; Kaniecki 2013; Święta-Musznicka, Latałowa 2016; Zwoliński *et al.* 2017; Łajczak, Zarychta 2020; Wierzbicki *et al.* 2021). Bearing in mind the examples of the aforementioned environmental conditions of settlement and the geological record of the activity of former communities, this article presents the results of geoarchaeological research conducted within the boundaries of medieval Szczecin. The article aims to compare the results of palaeozoological and geochemical studies conducted on a series of organic sediments accumulated before and during Szczecin’s initial settlement expansion phase in the early Middle Ages. The results of the palaeogeographic research were considered in the context of the natural conditions of the city's location, allowing existing reconstructions of medieval Szczecin’s hydrological network to be verified. In interpreting of the geochemical research results, the relationship between abiotic elements of the geographical environment and the activity of ancient of human communities proved to be key, and, on the assumption that these relationships are reciprocal, the level of human-induced pollution was assessed. In addition, findings on chemical composition and palaeozoological results were compared against the results of a taxonomic identification of plant remains by Sady-Bugajska (2021) for ten samples from the cultural layers of various buildings dated to the 11th and 12th centuries and from mulch layers between and below wooden structures.

Study area and study object

Physical geographical location of the area

In the geomorphological division of Poland (Gilewska 1986), Szczecin is located within three mesoregions, i.e. the Lower Oder River Valley, Szczecin Heights and Bukowe Hills, which are parts of Szczecin Coastland macroregion of the Southern Baltic Coastlands subprovince in the Central European Lowland province (Fig. 1). A simplified, but still the most complete picture of the shape of the research area’s surface is presented on the geomorphological map of the Myślibórz Lakeland and the Szczecin Lowland by Karczewski (2008). From the point of view of the circulation of matter, the study area’s main macroform is undoubtedly the Oder River valley, which is several kilometers wide and whose lower section separates three large glacigenic units, dividing the Stobno Hills and Warszewo Hills to the west from the Bukowe Hills to the east (Fig. 1B).

The studied organic sediment profiles (SK--1 and SK-3) are from within the Rybaki 15 Street and short distance to the north-east from Vegetable Market and south from Castle Hill in Szczecin (Fig. 2). Although the Szczecin area is among the country’s peatiest (Żurek 1999), detailed palaeogeographic studies have been conducted on biogenic sediments for sites in the vicinity of the city (Jasnowski 1962; Latałowa 1994; Borówka *et al.* 2005; Latałowa, Borówka 2006; Okupny *et al.* 2020). The reason

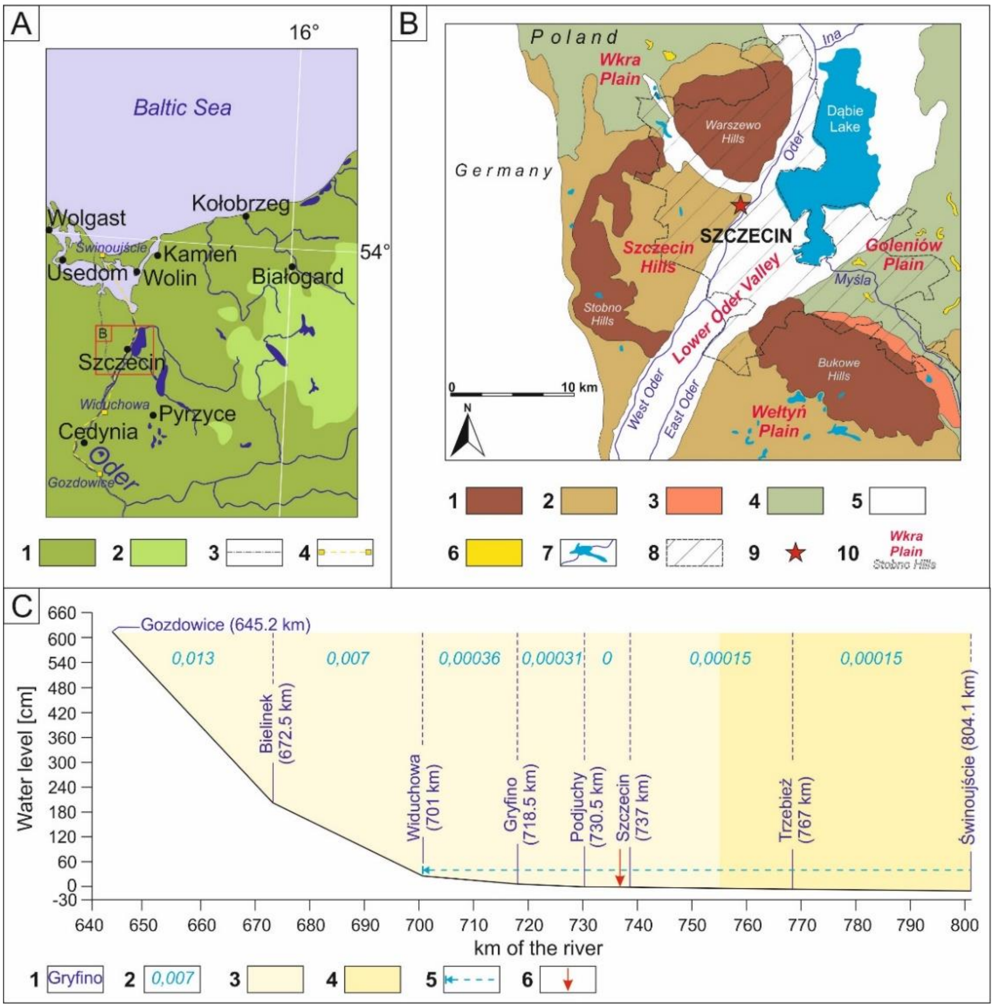

Fig. 1. A: Location of the study area against the other important urban centers in the areas of the Oder estuary in the early Middle Ages after Cnotliwy *et al.* (1983)

1 – altitude below 100 m a.s.l, 2 – altitude between 100–200 m a.s.l., 3 – country border, 4 – line of the hydrological cross--section and selected water-gauges (see Fig. 1C)

B: Location of study area against the division to geomorphology mesoregions after Gilewska (1986) and the geomorphological chart after Karczewski (2008)

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

C: fall the water level on the lower Oder according to the few-year average water on a given water gauge after Wiśniewski *et al.* (2005) against the mechanical denudation ratio after Brański and Banasik (1996) – changed

1 – water gauge, 2 – fall the water (in %), 3 – mechanical denudation ratio < 3 Mg·km^2·year^{-1}, 4 – mechanical denudation ratio between 3–10 Mg·km^2·year^{-1}, 5 – the maximum extent backwater floods, 6 – study cores location

for this is, the influence of the centuries-old human economy, which in the case of Szczecin led to changes in the hydrological network, the intensive management of wetlands and the destruction of the substrate in zones progressively covered by residential, industrial and service buildings (Kochanowska, Rygielski 2001; Duda, Borówka 2007; Rudewicz 2021). Difficulties in finding biogenic sediments of undisturbed chronology in historical city districts have been indicated by, among others, Wasylikowa *et al.* (2009) for Kraków and Latałowa *et al.* (2009) for Gdańsk.

Of the many physical geographical features of the research area in terms of the location of Szczecin, the most frequently mentioned are: its central location within the Szczecin Lowland, the possibility of building a crossing over the Oder River valley with harbours on sandy beaches and terrace outlier, and the possibility

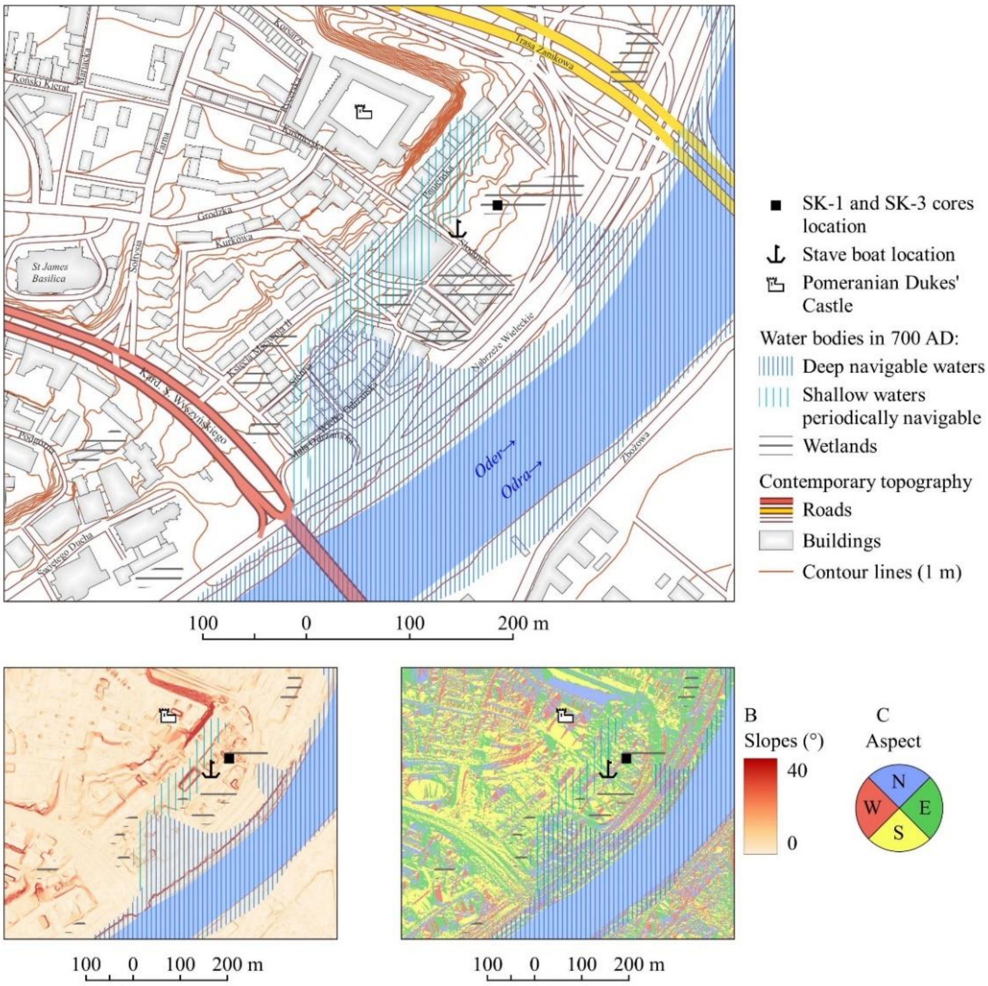

Fig. 2. Location research cores
A – the background of the modern urban central part of the Szczecin, location and stave boat from 9th century (after Łosiński 1996) and reconstruction of wetlands area near Old Town after Borówka and Wolny (2011), B – spatial changes of slope parameters, C – spatial changes of slope aspect

of developing a seaport at the junction of maritime and inland routes (Łosiński 1996; Piotrowski, Hoc 2010). On the other hand, Zaremba and Orlińska (1965) emphasise that Szczecin was established in a place where a natural trail ran that made it easy to cross the wide Oder River valley (avoiding the wide but relatively shallow waters of Lake Dąbie) and at the end of which was a steep plateau edge. Two ravines that descend sharply to the Oder River valley along the modern-day streets Trasa Zamkowa and Wyszyńskiego may also have served defensive functions (Fig. 2). As a result, the relief in the vicinity of early-medieval Szczecin was shaped mainly by the erosional and accumulational activity of river waters, slope processes, the processes sedentation of peat and accumulation of gyttja in wetlands, and anthropogenic activity (Borówka, Wolny 2011). From the point of view of the studied profile, it should be emphasised that the progressive bogging of the bottom of the Oder River valley and the resulting increase in biogenic and fluvial sediments eventually blurred the hypsometric distinctness of the edges separating the valley from the plateau surfaces of the Warszewo Hills and the Stobno Hills. The reason for favourable hydrogeological conditions in the area of the Oder River estuary, which are conducive to accumulation (*sensu lato*) of organic matter, is the very low water level slope (usually 0.00015–0.00036% over a distance of almost 100 km; Fig. 1C). The above-described physical geographic characteristics thus confirm the legitimacy of distinguishing all three geochemical landscapes within the borders of early medieval Szczecin – from autonomous, through transit–
–to subordinate (Perelman 1971).

Outline of chronological cultural and socio-economic site characteristics

The day-to-day living habits of early-medieval Szczecin's inhabitants can be determined based on traces of their living conditions, preserved features of the land development of the inhabited area, and features related to their places of work. The nature of activities undertaken, the quality and technical advancement of the objects, tools, clothing and ornaments produced (as well as the material from which they were made) attest to the dynamic development of this settlement on the Oder (Łosiński 1972; Dworaczyk *et al.* 2003).

In the 9th century, there were changes in the development of the hilltop settlement. The permanent log buildings intersected by a system of wood-paved streets were bounded by wood and earth reinforcements (Leciejewicz 1962; Kowalska, Dworaczyk 2011). The inhabitants of Szczecin engaged in craftworking, continuing to trade both locally and with Scandinavian countries. Long-distance imports of the time were raw materials, mainly low-phosphorus iron ore and slates of quartz crystal, i.e. phyllite and decorative glass products (Łosiński 1997). The increased exchange of goods forced the inhabitants to build a port facilitating transshipments, thereby providing access to the main branch of the river.

In the early 10th century, the riverside wetlands and floodplains were turning by people's economic needs into a regular, stable, densely built-up and settled area, which in the mid-10th century was additionally surrounded by defensive fortifications. The settlement's economic centre was moved from the hill to the riverside areas. There, the log-frame buildings erected were larger than those on Castle Hill. In an environment that made transport difficult, people moved along stabilised platforms or along wood-paved communication routes (Łosiński 1996; Kowalska, Dworaczyk 2011). Fish cathes were transhipped here, and craft workshops specialised in processing glassware from imported semi-finished products to create, for example, items of women's jewellery. Numerous examples of glass beads and rings were found during the archaeological excavations (Kowalska, Dworaczyk 2011). The quality of manufactured iron knives and the technical quality of animal skin processing increased. The exchange of goods with the northerly countries was not abandoned, but the local market was most important. Luxury goods, products made of semi-precious stones and ceramics were imported from long distances (Kowalska, Dworaczyk 2011). Increased activity on the water encouraged the development of outbuilding. There was lively blacksmithing and pottery production whose products were sold by exchange (Leciejewicz, Wieczorkowski 1983).

The buildings of the district along the River Oder and on the hill was a permanent part of Szczecin settlement's landscape by the early 11th century. The inhabitants continued to engage in carpentry, tanning and metalworking for local needs. They used small-scale fishing equipment, but fishing did not exceed local needs of the time. Fishing became more important in the general structure of the inhabitants' activities in the latter 11th century. This is characterized by an increase in the number of fishing instruments, including technologically more advanced fishing nets evidencing the need to involve a larger group of specialized people. This occupation brought more profits, allowing the inhabitants to increase the variety and quality of household items. At that time, the assortment of locally crafted clay and glass vessels and coopering products increased (Kowalska, Dworaczyk 2011). Mass transshipments of grain and agricultural and forestry products were carried out in the port and these wares were exchanged mainly for local products. Thus, trade became one of the dominant sectors of the economy, replacing manufacturing.

From the excavations carried out in 2020 in excavation 1 at Rybaki 15 Street, the youngest level of buildings consisted of remnants of a late medieval tenement house that was rebuilt in subsequent centuries. In the modern century, while the floors were being replaced and basement rooms renovated, the ground under the planned floor was stabilised with thick wooden logs laid as a grate structure that is visible in the profiles of the excavation. Directly under the floor and logframe stabilising structure, there were early medieval layers. In this

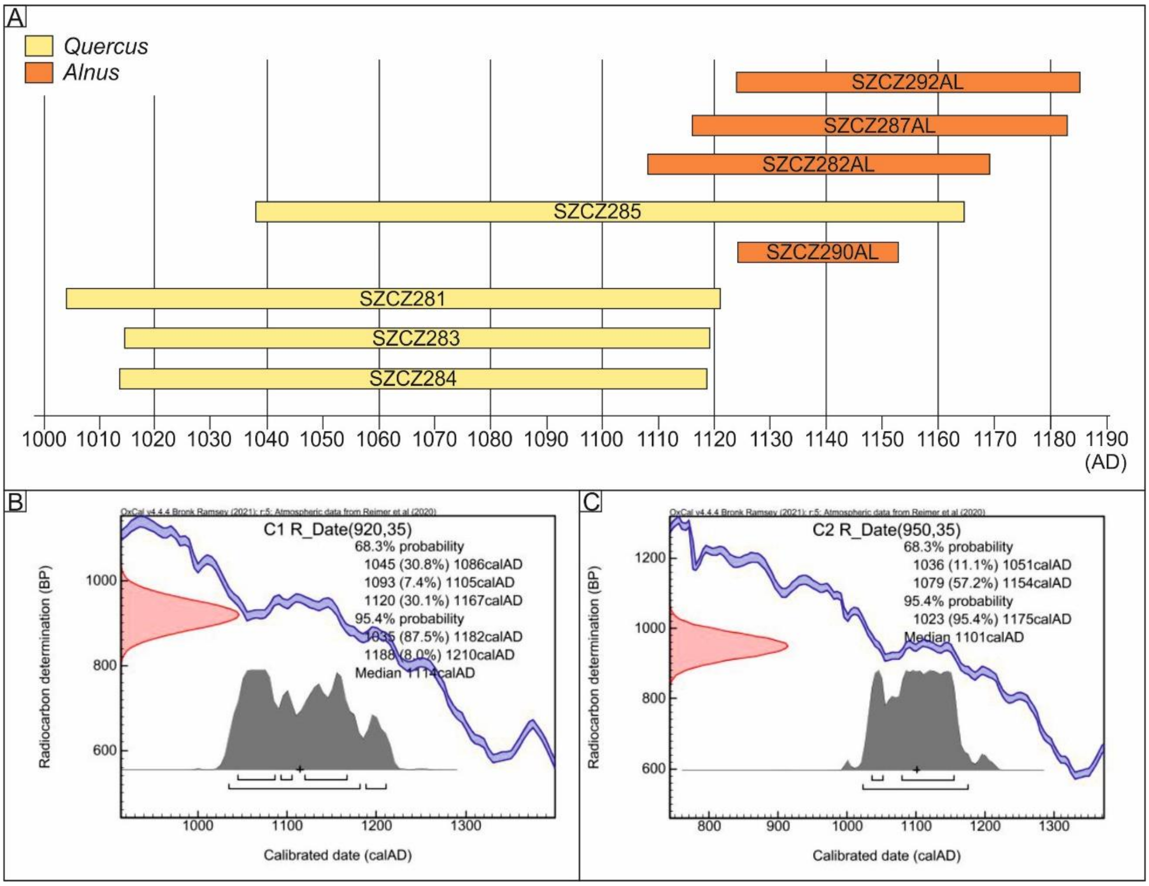

Fig. 3. Dendrochronological dating of growth sequences of charred wood (A) and calibartions plots of the results radiocarbon dating from MKL-5104 (B) and MKL-5105 (C) samples from study area at Podzamcze in Szczecin

excavation, five levels of wooden structures were uncovered. Structures I–III and V were remnants of logframe wooden buildings, while structure IV was preserved too fragmentarily to determine its original purpose. Analyses of movable materials and dendrochronological studies dated the younger structures I and II to the fourth quarter of the 12th century and early 13th, the older level III to the second-third quarter of the 12th century and structures IV–V to the first quarter of the 12th century (Fig. 3A). This is also indirectly confirmed by the radiocarbon dating of wood samples from structures III and IV from excavation 1 (Fig. 3B), as they were built between 1086–1210 cal AD and between 1051–1175 cal AD (Fig. 3C).

Research methods and materials

Palaeozoological analyses and chemical properties of the discussed sediments were performed for the SK-1 and SK-3 profiles collected from archaeological excavation 1 (Fig. 4) at the Street Rybaki 15, within boundaries of Podzamcze settlement zone in Szczecin. An archaeological excavation of 5.4 m×4.0 m and 2.5 m deep was made in 2020 yr. The roof of the excavation lay at 6 m a.s.l., just 80 m west of the modern River Oder channel. The profile marked SK-1 was taken from the north-western corner of excavation 1, which in the report by Nierychlewska and Bartczak (2021) was assigned to the now non-existent building 15 on Rybaki Street (Fig. 4E). This profile was 125 cm thick, because the first mulch sample collected for palaeogeographical analyses was from 125 cm below the level of cellars constituting the remains of tenement houses. In the same place, a borehole was drilled to a depth of 290 cm (marked SK-3) using Eijkelkamp peat probes (Fig. 4E). The Edelman borer proved to be particularly useful in collecting samples from highly cohesive bedrock sediments. Palaeoecological and geochemical analyses are planned for the SK-2 profile profile collected from the southern wall of excavation 1 (Fig. 4F); it includes less homogeneous geological formations, which is typical for urban sites.

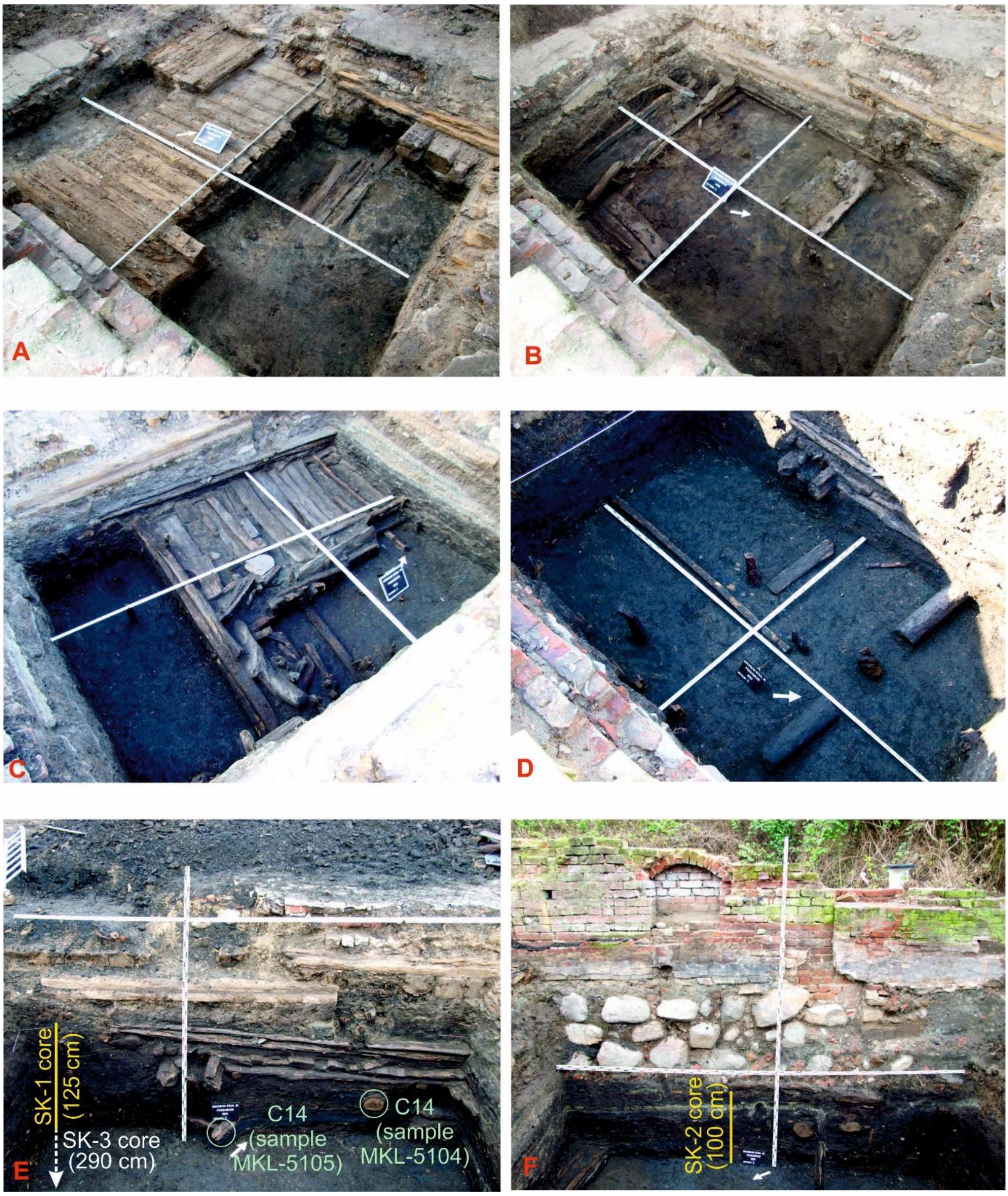

Fig. 4. Podzamcze in Szczecin, site 48 Rybaki Street, archaeological site
A – wooden grate under a brick floor, B – level of wooden structures I and II, C – level of wooden structures III – wooden floor, D – level of wooden structures IV and V, E – the northern part of the excavation (the location of the SK-1 and SK-3 cores for palaeogeographical analysis this article), F – southern part of the excavation (the location of the SK-2 core, not analyzed in this work) (*photo by A. Nierychlewska 2020*)

As a result, for profiles SK-1 and SK-3, a total of 44 samples for palaeogeographical analyses were collected in accordance with generally accepted requirements, i.e. one sample from each genetic sedimentary horizon (Żurek 2010). For this reason, the resolution of the analyses varied, but usually involved 5-cm--long sections of sediments. The exceptions were the analysis of bulk density conducted on 44 samples of volume 2 cm^3 (Chambers *et al.* 2010/11), and the grain-size distribution of the mineral fraction by laser diffraction using a Mastersizer 3000 by Malvern on 12 samples (with the lowest share of organic matter) of mass 1 gram (Płoskonka 2010). The individual samples were described macroscopically in terms of: the share of the main plant remains of size >2 mm; the structure of the sediment; and, for biogenic layers, their degree of decomposition. The percentage ratio of amorphous organic mass to total sample mass was determined as described by Maskimov (1965) based on assessment of the colour and turbidity of water squeezed out by hand, and by hand smear, as defined by Tobolski (2000).

For the analysis of subfossil remains of Chironomidae, samples of 16–32 cm^3 were collected at 5–20-cm intervals. After kerosene flotation (Rolland, Laroque 2007), they were rinsed on a 90-µm sieve and then subjected to the standard procedure described in Brooks *et al.* (2007). Insect remains were selected using a stereoscopic microscope and then dissected on slides (for heads of flies) or secured on paper soaked in a preservative mixture. Identification was based mainly on keys provided by Brooks *et al.* (2007) and Andersen *et al.* (2013).

For the Cladocera analysis, 1-cm^3 samples were taken at 5–20-cm intervals and initially prepared for testing according to Frey's method (1986). They were macerated with 10% HCl, boiled in 10% KOH using a magnetic stirrer, and the resulting residue poured through sieves, washed, and placed in tubes and preserved in formalin. Due to the lack of Cladocera remains, the above procedure was slightly modified. In three successive series of laboratory tests, 2-cm^3 samples were taken and left in distilled water for 24 hours. They were then macerated with 10% HCl and boiled in 10% KOH, but for different times (15, 20 and 30 min), without the use of a magnetic stirrer. The residua obtained from each time series were poured through sieves, washed, and placed in test tubes and preserved in formalin. Unfortunately, no remains of these aquatic invertebrates were found in any of the samples.

As part of the geochemical research, the first stage of the laboratory procedure included lyophilisation of frozen samples using an Alpha 1-1 LD plus lyophiliser from Chrust. Due to the heterogeneous nature and relatively high moisture of the sediments, this process was repeated twice. The percentage shares of total carbon (C), total nitrogen (N) and total sulphur (S) were detemined using a VarioMax CNS apparatus by Elementar using high-temperature combustion of organic samples in ceramic crucibles. The next stage included the mineralisation of samples following the procedures described by Borówka (1990) and Heiri *et al*. (2001). Organic matter was removed by loss on ignition (LOI); sediment samples were calcined for 6 hours in a muffle furnace at 550°C. Then, part of the obtained ash was put into solution 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). Wet mineralisation was carried out in Teflon bombs using a twelve-column ultrasonic mineraliser manufactured by Berghof. In the obtained solutions, the concentration of such elements as sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), iron (Fe), manganese (Mn), cooper (Cu), zink (Zn) and lead (Pb), was determined by atomic absorption spectrometry (AAS) using a Solaar 969 Unicam device and the proportion of phosphorus (P) by injection-flow method using an FIACompact device. The concentrations of most metals were expressed in mg/g dry weight (d.w.) except for Cu, Zn and Pb, which were converted to µg/g d.w. The total mercury (Hg) content (in µg/kg d.w.) was determined using a DMA-90 Analyser (Milestone Company). This toxic metal was determined based on the principle of thermal decomposition, catalytic conversion, amalgamation and atomic absorption detection (Leipe *et al.* 2013). The share of total organic carbon (TOC) was calculated as the difference between mass of inorganic carbon (treated at $CaCO_3$ content) and mass of total carbon (Apolinarska *et al.* 2012). The chemical examination results were used to determine the type and kind of gyttja based on the proposal of Markowski (1980) created based on many years of research on limnic sediments in western Poland. In addition, considering the physical geographical conditions described in the previous section, our interpretation of the chemical composition results for the examined sediments emphasised the functions of individual landscape units in the circulation of matter and water, and the local geochemical background was calculated using first part of "The Geochemical Atlas of the Szczecin Agglomeration" (Lis, Pasieczna 1998).

Results

Lithology and physicochemical properties of sediments

The organic sediments discussed in the paper show a clear tripartite structure. In terms of the share of individual lithogeochemical components and the results of archaeobotanical studies, the thickest part (285 cm) is of biogenic layers whose organic matter content rarely exceeds 60% (Fig. 5). The sediments of limnic genesis with a relatively high bulk density (about 2 g/cm^3) and dominated by terrigenous material are 60% less thick (117.5 cm). However, it should be remembered that the studied organic sediments were heavily compacted by erratic boulders, a road embankment and residential buildings. Over a thousand years of pressure, squeezed out water and changed the sediment structure from plastic to compact, often shale-like. According to Rotnicki's (2009) proposal for calculating the original thickness of organic sediments, the estimated thickness of deposits from Rybaki 15 Street may have been as much as 560 cm, which is nearly 40% thicker than the analysed series of biogenic sediments.

The examined organic sediments quite clearly differ in chemical composition depending on lithology, and the changes in vertical distribution of most of the analysed components allowed three geochemical levels to be distinguished in the SK-1 and SK-3 profiles (Fig. 5). The oldest (GZ I) consists mainly of a biogenic sediments (depth: 415–317.5 cm) with moderately decomposed plant macroremains and relatively high fluctuations in the concentration of most metals (mainly Ca, Mn and P) except Fe and Zn. In the first case, the Ca content decreases from 64.9 to 32.5 mg/g d.w., Mn decreases from 0.58 to 0.21 mg/g d.w. and P increases from 5.6 to 24.3 mg/g d.w. Iron concentration ranges from 3.8 to 6.3 mg/g d.w. and Zn from 95 to 120 μg/g d.w. The share of organic matter in this level does not exceed 72% and the share of $CaCO_3$ is relatively high (18.2–21%). These results are typical for fen peats, which are often enriched with aluminosilicates, opal, vivianite and gypsum (Kwiatkowski 1971; Maciak, Liwski 1996; Rydelek 2011; Okupny *et al.* 2016).

The next geochemical horizon (GZ II), located at a depth of 317.5–240 cm, includes detritus-clay gyttja deposits with two mineral interbeddings (Fig. 5). These deposits have a high proportion of mineral matter (range: 16.3–55%) and the lowest $CaCO_3$ (9.5–17.5%) and TOC (0.7–2.8%) content in the entire profile, and clearly lower concentrations of most elements except Fe, Zn and K. In turn, the rhythmic nature of this horizon is confirmed by the grain-size distribution of the mineral fraction, which forms poorly sorted, alternating layers of silty sand (M_z in the range 3–5 phi) and sand (M_z in the range 2–3 phi). The higher share of clay fraction (in the range 5–8%) is associated with the highest catchment erosion index valuesfor the entire profile (of the order 0.25–0.35, being the quotient of the sum of lithophilic elements: Na, K and Mg to Ca).

The GZ III geochemical horizon, located at a depth of 240–12.5 cm, again includes biogenic sediments with a share of organic matter of 51–64% and the highest average share of $CaCO_3$ in the entire profile, i.e. 20.3% (Fig. 5). In this series, there are five mineral interbeddings in the form of fine- and medium--grained sands (M_z in the range 0.5–2 phi) of moderate sorting (σ_1 of the order 0.8–1.2 phi). In the top of this horizon there is a mulch, i.e. a dark brown anthropogenic layer containing a lot of straw, wood and leather, not exceeding 20 cm thick. This geochemical horizon has the maximum concentrations of such metals as Ca (70.6 mg/g d.w.), Mg (4.45 mg/g d.w.), Mn (0.75 mg/g d.w.) and Cu (36.5 μg/g d.w.). The Na and K concentrations are slightly lower but uniform (2.1–3.13 mg/g d.w. and 2.4–4.3 mg/g d.w., respectively). In the case of mineral interbeddings, the share of all elements decreases slightly except for Fe and Zn, then the share of non-carbonate mineral matter always exceeds 50% and reaches a maximum of 62%. However, according to the classification of Okruszko (1976), these sediments are poorly silted.

Analysis of palaeozoological remains

Only a few remains of Chironomidae larvae were found in the analysed samples. Most were identified as semiterrestrial or wet-soil taxa (*Georthocladius*, *Limnophyes*, *Smittia/Paras-*

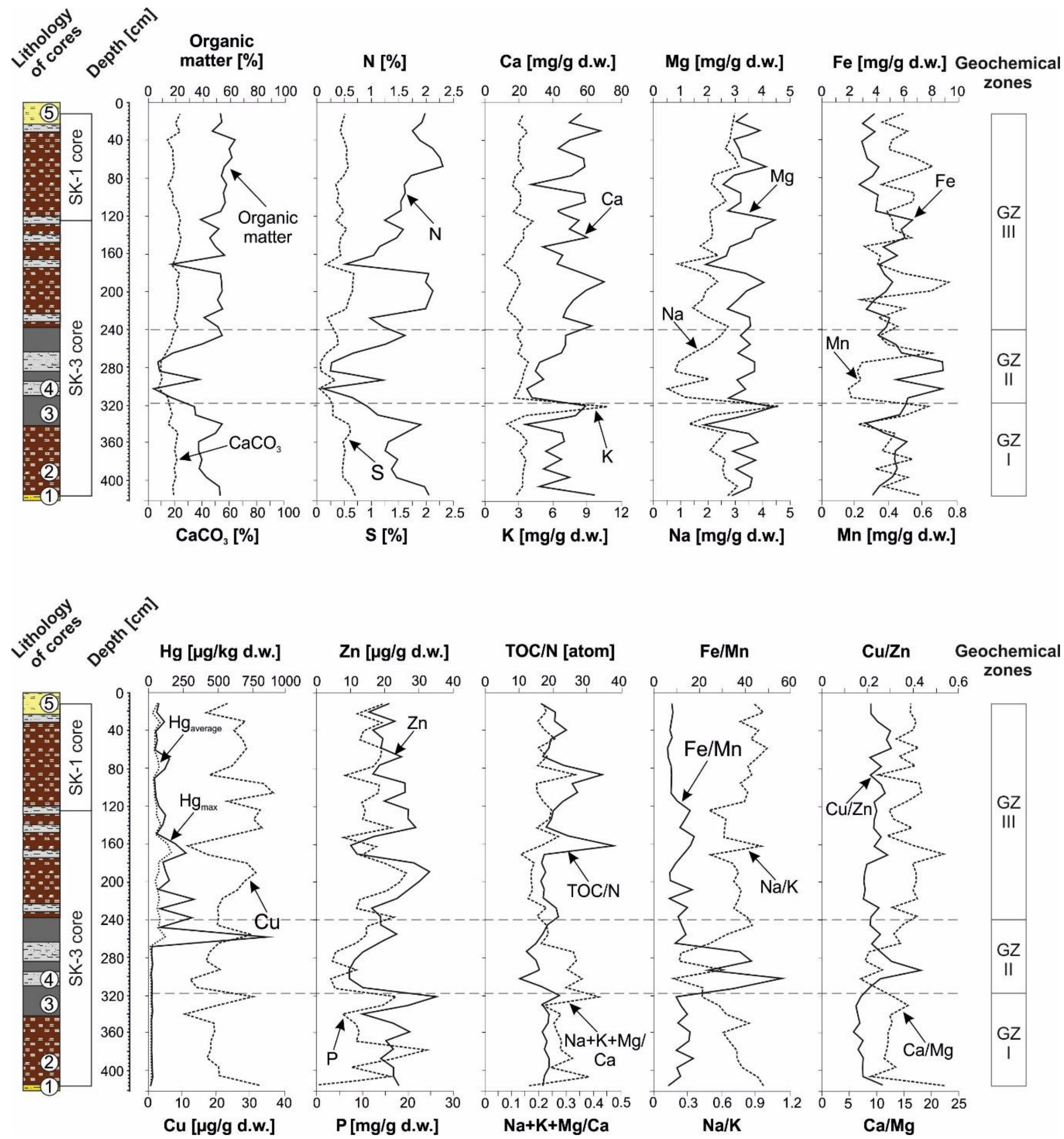

Fig. 5. Geochemical data from SK-1 and SK-3 cores taken from archaeological site 1 at Rybaki 15 Street against the lithology deposits and geochemical zones

Lithology: 1 – mineral bedrock, 2 – biogenic deposits, 3 – detritus-clay gyttja, 4 – clay gyttja interlayered with mineral deposits, 5 – mulch layer

mittia). One *Polypedilum nubeculosum* head found in one detritus-clay gyttja roof sample (GZ II geochemical horizon) may have belonged to a Chironomidae developing in a shallow periodic water surface. The insect remains were relatively abundants heads of drain fly (Psychodidae) larvae, head capules, as well as fragments of pupae and larvae of other flies (Diptera). In addition, a few elytras of the Staphylinidae family and chitinous exoskeletons of Oribatida mites were also identified.

Early medieval evolution of hydrogenic habitats of the Lower Oder River valley in the vicinity of the Podzamcze site in Szczecin

Referring to Perelman's (1971) concept of elementary geochemical landscapes, the research archaeological site is associated with the functioning of subordinated areas, otherwise known as accumulation areas, in the lower Oder River valley. These include depressions of impeded water outflow in which organic matter accumulates. According to Rycharski and Piórkowski (2001), the dynamics and manner of matter circulation are conditioned in this case by geological structure and topography, maybe old forms of land use, which are reflected in the structure of wetland habitats and the chemical composition of biogenic sediments. The chemical compositions of the biogenic sediments from Rybaki 15 Street in Szczecin presented herein record the diversity of many elements of the geographical environment established as the important urban centre functioning in the early Middle Ages in a geomorphological situation typical of the lower Oder River valley.

Despite the high water table, as evidenced by the enrichment of sediments in $CaCO_3$ (the average share in the entire profile is 21.5% with a standard deviation of only 2.3%), high Ca/Mg ratios (usually between 15 and 20) and low Na/K ratios (not exceeding 0.8 for 77% of the samples), the sediments were nevertheless laid down with high availability of oxygen. Changes in the S concentration (in the range of 0.04–0.7%) and Fe/Mn ratio (in the range of 6.43–52.5) show a close relationship with the lithological type of sediments and record changing oxidation-reduction conditions in the periodic moistland (Fig. 5). The chemical composition described above mainly result from changes in the water table at the edge the wide, mire valley. According to Żurek (1993), this habitat type functions in seepage erosion zone or depressions between channels, and the accompanying gley processes are responsible for the accumulation of mineral-organic peat formations. Therefore, the water table at the western slope of the Oder River valley remained below the ground level, thereby hindering the development of a rich organic layers. It is also worth emphasising that the Podzamcze settlement zone in Szczecin lies beyond the area of frequent occurrences of bog iron ores (i.e. precipitation of hydrated iron oxides) in Poland (Ratajczak, Rzepa 2011); thus, the high water table in the hinterland of the wide Oder River valley probably created conditions favourable to their formation. Bog ores may also have occurred in the stagnant waters of other smaller rivers near Szczecin and in the vicinity of Lake Miedwie; this, in conjunction with easy access to wood supplies from nearby forest complexes (i.e. the Bukowa, Goleniowska and Wkrzańska Forests), was conducive to larger-scale metallurgical and blacksmithing production (Rogosz 1983).

The periodic moistland was not a typical habitat for aquatic invertebrates. Their development may be due to the specifics of the accumulation environment (lack of water), whose the conditions were not conducive to conserving organic material or with an existing supply of toxins (such as Hg concentrations; Fig. 5) that hinder the development of aquatic invertebrates. The few semiterrestrial Chironomidae and Oribatida moss mites developed in a terrestrial environment. Boggy sediments provided suitable conditions for hygrophilous Staphylinidae beetles and Psychodidae (Diptera) larvae, which fed on dead organic matter (Koch 1989; Ooesterbroek 2006). The archaeobotanical research shows that peaty and strongly burnt plant fragments were most abundant in the mulch layer and biogenic sediments in the top part of the SK-1 profile. Remains of moss of the genus *Drepanocladus* were identified there, these being found, according to Tobolski (2000), in river valley mires, wet meadows and on the banks of water bodies. The location of the moss sample (southern wall of a building dating to the 11th century), suggests that the voids between the wooden structures were filled with this material to seal and insulate the buildings. The moist nature of the habitat is also confirmed by other fragments of plants found in the wall of the excavation, i.e. *Calla palustris*, *Stellaria uliginosa*, *Calystegia sepium*, *Cyperus fuscus*, *Lycopus europaeus*, *Ranunculus sceleratus* and *Typha* sp. (Sady-Bugajska 2021). However, due to the strong human impact of study area, it can be assumed that some of the remains were redeposited.

The literature review shows that biogenic layers with a 40–60% admixture of organic matter are usually 30–40 cm thick in this type of habitat (Żurek 1993; Jóźwiak, Solovey 2019). However, in the studied profiles, the biogenic sediments are ten times thicker. The reason for this could be: a clearly weaker river current and heavy marshing due to the falling water table in the Oder River valley. According to Borówka and Wolny (2011), these conditions are associated with, among other things, the gradual rise in the sea level and lowering of land in the vicinity of Szczecin (in the range of 1 to 2 mm per year) as a result of isostatic movements of the earth's crust. In addition, the slow-flowing waters in the anastomosing riverbed were superimposed on increased denudation processes and the washing out of mineral material by underground waters seeping from Castle Hill. As a result, in the lower section of the Oder River, limnic-bog sediments rich in mineral admixture accumulated, constantly growing upwards. Research by Jasnowski (1962) and Duda (1999) shows that, in the vicinity of Szczecin, these sediments often exceed 5 m thick (and up to 10 m). Such sediment accumulation conditions in the Lower Oder River valley have probably existed for 4 000 years and record the functioning of an anastomosing river system. According to Duda and Borówka (2007), the intense development of reed vegetation was responsible for stabilising the Oder channel and preventing its horizontal movement. This is also evidenced by the TOC/N index values, which are usually in the 15 to 20 range. With reference to the studies of Meyers and Teranes (2001), it can therefore be assumed that the organic matter in the profiles comes mainly from partially decomposed vascular plants, and to a lesser extent from compounds produced by phytoplankton in the lake. This is also confirmed by the results of archaeobotanical research, and more specifically the dominance of herbaceous plants (accounting for as much as 80% of all identified taxa) – mainly those growing wild on the banks of water bodies and wet meadows. *Nuphar lutea* and *Cladium mariscus* were the only typically aquatic species found among the remains in the profiles (Sady-Bugajska 2021).

Biogenic sediments, which dominate in the studied profiles, also have two to three times higher concentrations of C, N, S, Ca and Na than do series of mineral sediments and detritus-clay gyttja. A relatively uniform, but not very high share of organic matter (around 50–65%) classifies the sediments as poorly silted according to Okruszko (1976). It should be emphasised, however, that this term does not refer to the most common grain size of the mineral fraction, whose supply is associated with slope processes on the eastern slopes of Castle Hill (Fig. 2C). The Na/K ratios close to 1.0 and the more than ten-fold advantage of Ca over Mg prove that the early medieval biogenic sediments accumulated under conditions in which denudation was more chemical than mechanical and relatively high decalcitation of glacial and fluvioglacial formations was building the nearby plateau. The above-mentioned elements occur in similar orders of magnitude in water sediments in other parts of the Lower Oder River valley (Lis, Pasieczna 1998) and in the bottom sediments of Lake Dąbie (Borówka 2001).

The increased chemical denudation of the eastern slopes of Castle Hill may also have been caused by the mosaic system of surface sediments, consisting of fluvioglacial and glacial sand and gravel soils, boulder clays of the moraine plateau, and sand and gravel soils of higher terrace levels of the Oder Lagoon Plain (Malinowski, Watycha 1958). The high degree of soil moisture and the migration of dissolved compounds also depended on the inclination of the slopes, which often exceed 3° (Fig. 2B). However, it should be remembered that, in the examined series of rich organic layers, the relatively small amount of peaty plant remains, in combination with the predominance of highly mineralized fragments with numerous charcoals, nonetheless provide evidence of major water table fluctuations and limited fossilisation of organic matter. It was also a period of clear changes in Cu and Zn concentrations, i.e. sulphophilic metals whose geochemical circulation in a bog environment depends on the possibility of bioaccumulation (Pawłowski *et al.* 2015) and the dynamics of oxidation–reduction conditions (Kittel *et al.* 2020).

Bearing in mind the reasons for the biogenic sediments relatively high enrichment in $CaCO_3$ described above, the role of environmental alkalinity as one of the key ecological determinants of crop cultivation in the early Middle Ages is interesting (Tobolski 2008). Fragments of crop plants accounted for only 3 to 9% of the number of isolated and identified remains of individual samples taken from deposits below the wooden structure, with a relatively rich species composition (including: *Triticum, Secale, Panicum, Hordeum, Humulus, Linum, Cannabis*). According to Rembisz *et al.* (2009), the coexistence of the above-mentioned cereal grains may suggest slash-and-burn agriculture near the settlement. Among herbaceous plant species, however, common weeds of cereal crops dominated – although weed species such as *Galium* sp. that have higher soil requirements were relatively common (Sady-Bugajska 2021). Archaeobotanical materials from medieval Elbląg published by Latałowa *et al.* (1998) show that, calcium-carbonate-rich soils could limit cultivation on the large areas.

In addition, for the studied sediments from the Podzamcze area in Szczecin, $CaCO_3$ and Ca were moderately strongly correlated with P (Pearson correlation coefficient r is 0.6 and 0.63, respectively). According to Woszczyk (2011), this may occur in the conditions of continuously high calcite supersaturation of waters in the accumulation reservoir, and the precipitation of $CaCO_3$ itself is conducive to biogenic phosphorus being removed from waters and binding in sediments. In addition, in the upper series of biogenic layers, chemical denudation in the catchment was recorded to have decreased in intensity twice (depths of 165––160 cm and 100–80 cm in the GZ III geochemical horizon). Rapid drops in Ca concentration (even of the order of 37 mg/g d.w.) are accompanied by a higher share of autochthonous organic matter in sediments (TOC/N values in the range 22–37). These changes also correspond to clear decreases in the concentration of biogenic substances (P and N), thus confirming the definitely lower biological productivity of the habitat (Fig. 5). Comparing the results of the P content in the studied geological formations with other archaeological sites in northern Poland (e.g. Rembisz *et al.* 2009; Święta--Musznicka, Latałowa 2016), it appears that the Podzamcze area in early Szczecin was very heavily used. The highest recorded values of this element in 80% of samples of SK-1 and SK-3 profiles exceeded 10 mg/g d.w., and the maximum concentration slightly exceeded 24 mg/g d.w. These geochemical properties may therefore be the result of the presence of sources of biogenic elements in the research layers in the form of post-consumer remains of animals, as well as the presence of their excrement and of wild and cultivated plants on the surface. Unfortunately, the lack of remains of Cladocera and aquatic Chironomidae prevented a more accurate reconstruction of the accumulation environment's trophic conditions prevailing trophic conditions.

However, the decrease in concentration of biophilic elements (C, N, S and P) was clearest – and the share of non-carbonate mineral matter greatest (even exceeding 80%) – in the GZ II geochemical horizon. This is quite a thick series (about 100 cm) of limnic sediments (probably related to shallow water bodies) composed of fragmented parts of plants and animals (so-called *Limus detrituosus – Ld* in brief) and characterised by low TOC/N values (even below 10) and the lowest average concentrations of most metals except Fe (of the order 4.1––8.9 mg/g d.w.). The section of sediments in question also has the highest and most uniform catchment erosion index values (Na+K+Mg/Ca ranges from 0.25 to 0.35) with a significant deterioration of oxygen conditions in the periodic moistland (the Fe/Mn index reaches maximum values of 42–56). In the bottom of these sediments (320 cm deep), apart from numerous char- coals, the single highest concentrations of P (24.3 mg/g d.w.) and Zn (176 µg/g d.w.) were recorded, these being elements with strong bioaccumulation properties (Kabata-Pendias 1979; Konecka-Betley, Okolowicz 1998). In addition, the decrease in share of organic matter (to barely a few percent) and the value of geochemical indicators such as Na/K and Ca/Mg are probably associated with a initiation of surficial sheet wash processes (maybe as result phase of deforestation areas around Castle Hill). Based on the lowest share of organic carbon in the entire profile (0.3–2.2%), it can be assumed that the erosion troughs that developed at that time intersected the accumulation horizon of the overlying soils. This is also accompanied by a slight decalcification of sediments ($CaCO_3$ drops below 8%), probably due to the supplied mineral matter being washed out by streams of periodic waters. The record of increased mechanical denudation processes is also preceded by Ca and Cu concentrations increasing and then sharply decreasing. This may be due to recirculation of the aforementioned metals being inhibited by changes in the intensity of ground runoff (Borówka 1994) or acidification of the soil cover in the habitat catchment (Sapek *et al.* 1991).

With reference to research results for pottery found in excavation 1 (Nierychlewska, Bartczak 2021) and the existing knowledge on the early development of the settlement, consisting of a stronghold on Castle Hill and a neighbouring settlement on a low terrace of the Oder River (Leciejewicz, Wieczorkowski 1983), the geochemically recorded possible deforestation phase can most likely be attributed to the 8th century AD. This period is clearly recorded in the analysis results regarding the geochemistry (Borówka 1994; Korzeniowski *et al.* 2020), sedimentology (Siedlik, Borówka 2019; Okupny *et al.* 2020) and palynology (Madeja 2012; Jurochnik, Nalepka 2013; Bloom 2015; Okuniewska-Nowaczyk 2021) of limnic sediments of western Poland studied to date. The slash-and-burn economy of the time and the heavy exploitation of wood for construction contributed to rapid deforestation. As a result, the biogenic sediments record, for example, decreased percentage share of tree pollen, changes in the proportions of the pollens of many plants (e.g. *Carpinus betulus*, *Fagus sylvatica* and *Alnus*) and an increased proportion of mineral matter due to the intensification of denudation and erosion processes in individual lake catchments. In this context, enrichment in trace elements and phosphorus of research sediments in relation to the local geochemical background indicates strong human impact. It is the creation at the deforested areas of meadows and the development of ruderal communities that are best illustrated by the results of sedimentological and geochemical analysis (Szal *et al.* 2013/2015).

From the point of view of heavy-metal contamination of the examined sediments, it should be emphasised that the average concentration of Zn is several times higher than that of Cu. Furthermore, these metals show the most dynamic changes in content, sometimes of even 100 μg/g d.w. between two adjacent samples (Fig. 5). In the case of Zn, average concentrations are highest in biogenic layers from the GZ I geochemical horizon (i.e., 113 μg/g d.w.), while average Cu concentrations are highest (25.3 μg/g d.w.) in sediments within the GZ III geochemical horizon. These changes, in conjuntion with the Pb concentration in all tested samples having been below the level of quantification, should be explained by differences in the durability of bonding by deposits and by resistance to corrosion. Regardless of this, the heavy-metal concentrations are several times lower than those found in medieval strata from the Kraków area (see: Wardas *et al.* 2009; Wardas-Lasoń *et al.* 2010; 2013/2015). According to the criteria for classifying water sediments based on selected geochemical indicators by Bojakowska and Sokołowska (1998), in terms of Zn, all samples from Podzamcze in Szczecin exceed the geochemical background but are in the first purity class. For Cu, all tested samples also exceed geochemical background, but only 30% of the number of samples meet the first purity class criterion. The remaining samples, mainly representing biogenic layers from the SK-1 section, are classified as the second purity class. However, these results and the relationship between metals in the migration series differ from those of contemporary water sediments accumulated in the estuary section of the Oder River valley (Piotrowski 2007). In the case of Hg, the maximum concentration found in research sediments are very high, because for 47% of samples they exceed the value of 70 μg/kg d.w. Other results of Hg concentration don't exceed the level of 50 μg/kg d.w. (Fig. 5) and are typical for meadow environments in river valley, also in urban areas of Poland (cf. Bojakowska, Sokołowska 2001; Pasieczna 2012).

In comparison with other biogenic sediments from the Polish Lowland (cf. Borówka 1992; Borówka *et al.* 1999a; Latałowa 1999a; Latałowa, Borówka 2006; Owsianny *et al.* 2011; Apolinarska *et al.* 2012; Okupny *et al.* 2016; Korzeniowski *et al.* 2020; Adamek *et al.* 2021) several times higher Na concentration was documented in the research profiles from Szczecin. For 80% of the tested samples, the concentrations of this metal doesn't fall below 2 mg/g d.w., and the maximum results are in the range of 3–4.5 mg/g d.w. These results are typical of biogenic sediments accumulated in lakes periodically supplied with saline water and increase frequency and height of sea storm surges (Wojciechowski 1987; Rotnicki *et al.* 1999; Tobolski *et al.* 1999; Borówka *et al.* 1999b; Borówka, Wolny 2011; Strzelecka, Wróbel 2021). These observations are confirmed by the results of modern sea level monitoring in the Świnoujście-Widuchowa transect (Fig. 1C), which confirm a stronger response of the water level to the influence of the sea water than to the flood wave of the River Oder (Wiśniewski *et al.* 2005).

On the other hand, the content of sulphur in sediments from Podzamcze in Szczecin is not too high, because these results don't even exceed 1%. In the case of Lakes Sarbsko and Jamno, the content of S in bottom sediments is three times higher. Woszczyk and Betchel (2008) and Bieniek *et al.* (2013) explain this situation intensified processes of bacterial reduction of sulphates in conditions of significant concentration of SO_4^{2-} which are typical for coastal environments. Moreover, in the analysed samples from Szczecin, the ratio of TOC to S variable in a very wide range from 16.8 to 136, which may also indicate significant, periodic changes in water salinity in the estuary section of the Oder River. However, the TOC/S ratios in the research samples never dropped to level around 2.8, which Berner (1984) considers appropriate for the marine environment. Therefore, the changes in Na concentration presented above may also result from the overlapping of the human impacts, which was growing during the Middle Ages, with relatively dynamic hydroclimatic fluctuations in the lower Oder River valley. This is confirmed by numerous fragments of sodium and potassium glasses (e.g. vessels, beads, lumps of clay covered with glassy infiltrates) found in medieval layers in Szczecin (Dekówna 1983).

Conclusions

The first palaeogeographical studies of early medieval organic deposits allowed, on the one hand, a reconstruction of the environmental conditions of the Podzamcze area in Szczecin, and on the other hand, an assessment of human environmental impact in the lower Oder River valley in the initial development phase of one of the most important urban centres of Western Pomerania. Considered in the context of how the local community lived and was organised, chemical compositions are recorded in three separate series of biogenic sediments that accumulated under conditions of supply by shallow groundwater.

The most legible record relates to a deforestation phase on the moraine plateau. Probably in the 8th century AD the destruction of oak and beech forests in the vicinity of the Old Town in Szczecin led to slope processes being activated and increased supply of lithophilic elements to the periodic moistland habitat. This phase was preceded by an increase in concentrations of biogenic substances leached from the catchment's soil cover and eventually led to a short-term inhibition of Ca and Cu recirculation processes. In this case, both the studied habitat's close proximity to steep slopes of moraine Castle Hill and the relatively small area of wetlands and low moor bogs within a low terrace of the Oder River valley turned out to be crucial.

Mentionworthy among the difficulties of the research are the limitations on palaeoecological interpretation imposed by the lack or paucity of species composition of the subfossil remains of Cladocera and Chironomidae. This was the result of unfavourable habitat conditions, which changed due to natural factors (e.g. hydroclimatic conditions, intensity of denudation processes) and depending on how individual parts of the urban centre were used and input to environment toxic metals, mainly Hg. Further research should therefore determine the role that the long-term dry episodes of the medieval climatic anomaly played in water table fluctuations in the Lower Oder River valley.

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