

# Factors influencing temporal changes in chemical composition of biogenic deposits in the middle Tążyna River Valley (Kuyavian Lakeland, central Poland)

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## Abstract

The present paper discusses the influence of geochemical properties on biogenic deposits in the Wilkostowo mire near Toruń, central Poland. The analysed core has allowed the documentation of environmental changes between the older part of the Atlantic Period and the present day (probably interrupted at the turn of the Meso- and Neoholocene). In order to reconstruct the main stages in the sedimentation of biogenic deposits, we have used stratigraphic variability of selected litho-geochemical elements (organic matter, calcium carbonate, biogenic and terrigenous silica, macro- and micro-elements: Na, K, Mg, Ca, Fe, Mn, Cu, Zn, Pb, Cr and Ni). The main litho-geochemical component is CaCO<sub>3</sub>; its content ranges from 4.1 per cent to 92 per cent. The variability of CaCO<sub>3</sub> content reflects mainly changes in hydrological and geomorphological conditions within the catchment area. The effects of prehistoric anthropogenic activities in the catchment of the River Tążyna, e.g., the use of saline water for economic purposes, are recorded in a change from calcareous gyttja into detritus-calcareous gyttja sedimentation and an increased content of lithophilous elements (Na, K, Mg and Ni) in the sediments. Principal component analysis (PCA) has enabled the distinction the most important factors that affected the chemical composition of sediments at the Wilkostowo site, i.e., mechanical and chemical denudation processes in the catchment, changes in redox conditions, bioaccumulation of selected elements and human activity. Sediments of the Wilkostowo mire are located in the direct vicinity of an archaeological site, where traces of intensive settlement dating back to the Neolithic have been documented. The settlement phase is recorded both in lithology and geochemical properties of biogenic deposits which fill the reservoir formed at the bottom of the Parchania Canal Valley.

**Keywords:** lake sediments, peat, geochemistry, human activity, central Europe

## 1. Introduction

Biogenic sediments constitute a kind of natural archive that makes it possible to track environmental changes that took place in antiquity (Cohen, 2003; Zolitschka et al., 2003; Chambers & Charman, 2004). Such changes are driven not only by a range of natural processes but also by human influence (Kalis et al., 2003; Rösch & Lechterbeck, 2016). Geochemical analysis is one of the research methods used for studying biogenic sediments. Gorham & Swaine (1965), Mackereth (1965) and Jones & Bowers (1978) all listed some of the factors that have an impact on the chemical composition of sediments that fill reservoirs of biogenic accumulation, namely the geological structure and lithology in the catchment of a basin, the source of the supply and the catchment of lake waters, the intensity of photosynthetic processes, the intensity of  $\text{CaCO}_3$  precipitation, the morphology of lake basins, the water balance of the lake, a change in the rate of denudation processes and changes in the vegetation cover, as well as land use in the catchment area. Due to increased human impact on the environment and also contamination of this with toxic substances (e.g., trace elements), the chemical composition of the biogenic sediments has become a matter of interest to many researchers (e.g., Birch et al., 1996; Tylmann, 2005; Fiałkiewicz-Kozielec et al., 2011; Pawłowski et al., 2015; Martínez Cortizas et al., 2016).

The aim of the present study was to investigate the distribution of litho-geochemical elements in the sediment of the peatbog at Wilkostowo (central Poland), the development of which took place in the Mesoholocene in relation to the creation of a lake in the River Tążyna Valley. The factors which might have an impact on the distribution of elements in limnic and peat deposits were recognised. In the context of increased human impact and environmental changes, the geochemical research corresponds with the results of a study of relief transformation in the mid-section catchment areas of the River Tążyna, which occurred during the Mesozoic and Neoholocene.

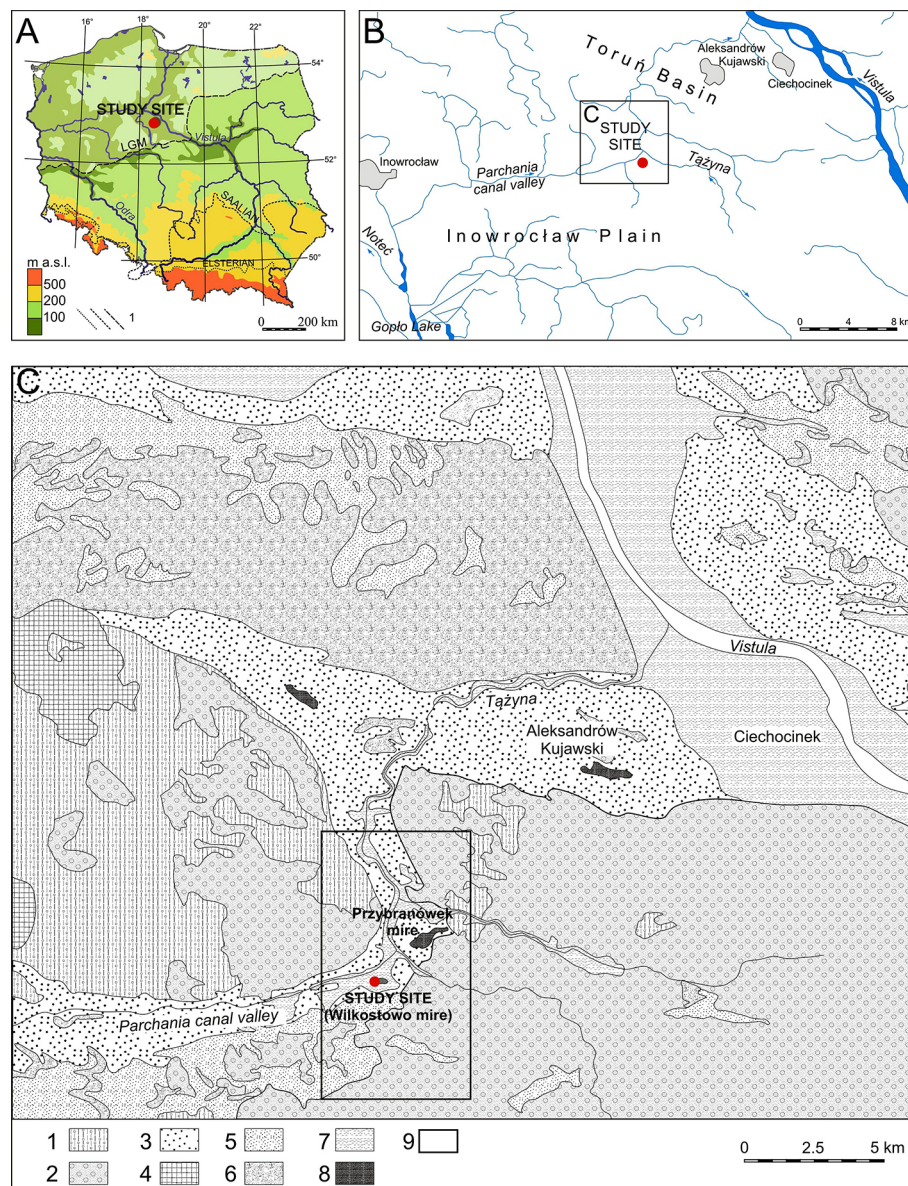
## 2. Regional setting

The study area is situated in the eastern part of the Kuyavian (Kujawy) Lakeland in the northwestern portion of the Inowrocław Plain (Krygowski, 1961) (Fig. 1A-B). From a geological point of view (Stupnicka, 1989), this area belongs to the Kuyavian-Pomeranian (central Polish) anticlinorium. Salt anticlines are located in the vicinity of Inowrocław,

around 20 km west of the study area. Czerwiński (1996) and Hulisz (2007) recorded the frequent presence of salinity of waters and soils of the Kuyavian Lakeland. The use of saline springs hypothetically played a very important role in local stability of prehistoric occupation of the middle Tążyna River Valley. In relation to the discussed area, these springs were located within several hours' walk.

Altitudes in the study area range from 102.9 m a.s.l. in places where dunes covered the moraine plateaus to less than 70 m to the north of the study site, at the bottom of the Tążyna River Valley. The relief of the research area is relatively poorly undulated; the reason for that is that it was situated within the area of the last glacial cover. It consists of forms of glaciogenic (moraine plateaus), glaciofluvial and fluvial (glaciofluvial plains and the Tążyna and Parchania Canal valleys) and aeolian origin (aeolian plains and dunes). The glaciofluvial sands and gravels contain less than 10 per cent of  $\text{CaCO}_3$ . Biogenic deposits are of great importance for the surface composition of the research area – they occur in the form of several patches of bogs and shallow, temporary reservoirs. A general description of the geological and geomorphological setting of the Tążyna River Valley and neighbouring areas was presented by Andrzejewski (1995), Weckwerth (2010) and Andrzejewski & Weckwerth (2010). A set of closed depressions within the sandur came into existence as part of thermokarst-forming processes during the late Weichselian; however, depressions formed at the bottom of the Parchania Canal Valley had a different origin. While the formation of the lake basin at Przybranówek took place before the Allerød interstadial (Rzepecki et al., 2015), the palaeolake at Wilkostowo formed during the Mesoholocene when thermokarst-forming processes in the Polish Lowland had already ceased (compare e.g., Goździk, 1995; Błaszczewicz, 2007). As has been revealed by works performed on the fossil base of the swamps, the depressions are relatively narrow and elongated and their origin can be linked to some sections of riverbeds (Fig. 1C). The peatbog at Wilkostowo is of irregular shape, its longitudinal axis being 210–220 m in length, the latitudinal 100–150 m. It occupies an area of nearly 3 hectares and is situated 300 m away from the centre of the Neolithic Age settlement.

The archaeological site at Wilkostowo was explored between 1999 and 2011 and the surveyed outcrops amounted to a total area of 10,120.5 m<sup>2</sup>. As a result of the excavation works, a total of 50,203 pottery fragments related to Trichterbecher culture (TRB) were recovered with a total weight of 433,669 g. Moreover, 16,624 lumps of daub (weight:



**Fig. 1.** **A** – Position of the Wilkostowo mire in Poland: 1 – Extent of ice sheets (after Marks, 2005); **B** – Position of the Wilkostowo mire against the river network of the Inowrocław Plain and neighbouring areas; **C** – Geological map of the area surrounding Wilkostowo (simplified after Niewiarowski et al., 1976).

Weichselian, Poznań Phase: 1 – boulder clay; 2 – Ice Age sands and gravels; 3 – glaciofluvial sands (sandur); 4 – glaciolacustrine lake silts; Late Weichselian/Holocene: 5 – aeolian sands; 6 – aeolian sands in dunes; 7 – fluvial silts and sands; 8 – peats and humic muds; 9 – range of hydrological sketch map (see Fig. 2).

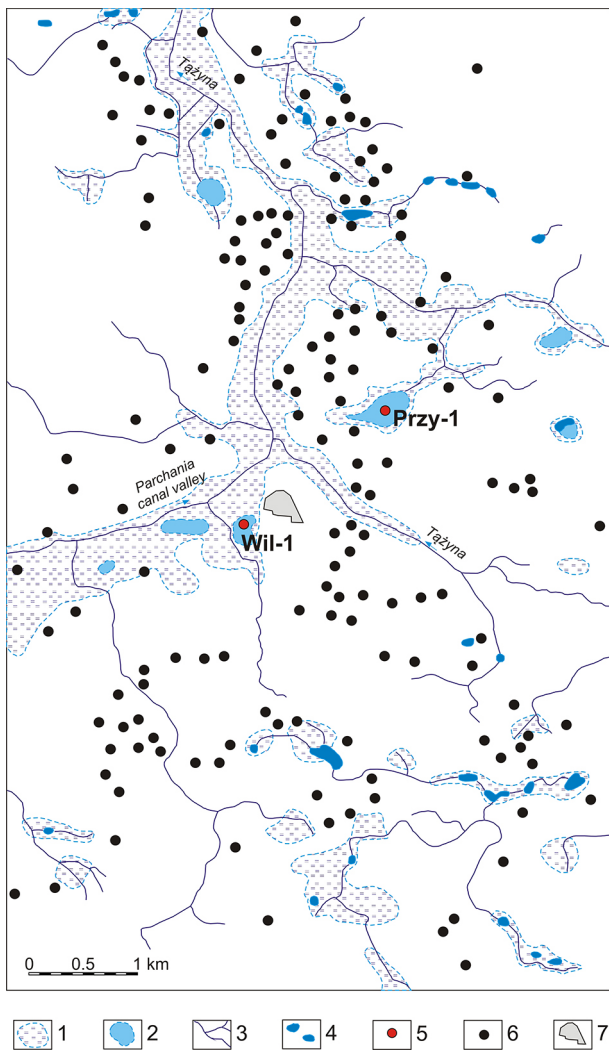
106,685 g), 1,150 flint artifacts, 467 stone artifacts and 4,071 fragments of animal bones were collected. These rich materials were connected with the existence of 12–15 houses, which probably were inhabited by *c.* 60–85 people. It is worth noting that the site, most likely, existed in the period of 3,523–3,449 BC (Rzepecki, 2015). Generally, the occupation of the TRB culture was not located in wet floors of river valleys or on closed depressions that were too wet. However, an important charac-

teristic of many TRB cultural sites is their location in a zone near the very edge of former swamps, mires and floodplains – at a distance of between 100 and 200 m from flowing water (Fig. 2).

### 3. Material and methods

One sediment core for palaeobotanical and geochemical studies was collected from the Wilkos-





**Fig. 2.** Results of analysis of settlement dispersion of the TRB culture in relation to hydrological network.

1 - wetlands functioning in prehistory, 2 - outlines of lakes functioning in prehistory, 3 - river network, 4 - water bodies functioning today, 5 - location of the Wil-1 and Przy-1 cores, 6 - sites of TRB culture, 7 - range of the archaeological site at Wilkostowo.

towo peatbog, where the thickest biogenic deposits were found (up to 220 cm), in the deepest reservoir lying in the southern part of the Parchania Canal floodplain (Fig. 1C). The core Wil-1 (52°48'27" N; 18°36'9" E), obtained with the use of the Instorf sampler, was divided in the laboratory into 2-cm-long sections, which yielded a total of 110 sediment samples. The basic litho-geochemical data for these samples were defined in accordance with the guidelines by Heiri et al. (2001) and Tobolski (2005) concerning the following: organic matter - OM (the loss on ignition method in a muffle furnace at 550°C for 4 hours), calcium carbonate - CaCO<sub>3</sub> (the volumetric method using the Scheibler apparatus) as

well as biogenic opal (SiO<sub>2biog</sub>) and terrigenous silica (SiO<sub>2ter</sub>). In the intermediate stage which preceded the determination of SiO<sub>2biog</sub> content, clean ash, obtained from raw ash by removing the components soluble in HCl, underwent assay. The residue after acid treatment (SiO<sub>2tot</sub>) was separated by extraction of opal (SiO<sub>2biog</sub>) with KOH (Tobolski, 2005). The content of SiO<sub>2ter</sub> was calculated as SiO<sub>2ter</sub> (per cent) = SiO<sub>2tot</sub> - SiO<sub>2biog</sub>. The determined ratios of these components were used for the classification of sediments recorded, following the procedure proposed by Markowski (1980). In addition, the pH values of sediments were recorded (the potentiometric method - the sample is dissolved in distilled water) and the degree of peat decomposition (H) was estimated according to the scale published by von Post in 1924 (Aaby, 1986; Drzymulska, 2016). Furthermore, a detailed geochemical examination of 55 samples was performed (in order to determine the content of micro- and macro-elements). The ash after ignition, free of OM, was wet digested in a microwave digestion system, using concentrated HNO<sub>3</sub>, 10 per cent HCl and H<sub>2</sub>O<sub>2</sub>. The resulting solution was used to determine the concentration of the elements vital for palaeogeography: Na, K, Ca, Mg, Fe, Mn and trace elements (Ni, Cu, Cr, Pb and Zn), by the Atomic Absorption Spectrometry technique.

A stratigraphically constrained cluster analysis (using the method of incremental sum of squares) was applied to distinguish geochemical zones. This frequently used method is thought to be one of the best agglomeration techniques (Mangiamelli et al., 1996). In order to determine the variability of factors controlling the chemical composition of the deposits we used principal component analysis (PCA), which is one of the basic ordination techniques applied to data in palaeolimnology (Legendre & Birks, 2012; Minyuk et al., 2014). This analysis was performed on a correlation matrix of major and trace elements (with the exception of Pb) and OM, CaCO<sub>3</sub>, pH, SiO<sub>2biog</sub> and SiO<sub>2ter</sub>. To assign the same weight to all measurements, each variable in the original data set was standardised by subtracting its mean and dividing it by its standard deviation:  $a_{ij} = (x_{ij} - \bar{x}_j) / \sigma_j$ , where  $a_{ij}$  is the value after standardisation,  $x_{ij}$  is the value before standardization,  $\bar{x}_j$  is the mean value of geochemical properties and  $\sigma_j$  is the standard deviation. According to Xue et al. (2011) standardisation may amplify the noise associated with minor variables that may carry a relatively larger analytical error. The variability in conditions of sedimentation was estimated on the basis of the correlations of results of different measurements as was done by Walanus (2000). In the case of the Wil-1 core, the

**Table 1.** Results of radiocarbon dating from the Wilkostowo mire (Wil-1 core).

Sample no.	Depth (cm)	<sup>14</sup> C age (a BP)	Calibrated age (95.40% probability) cal. a BP	Deposit
MKL - 1224	215-210	9860±100	9141	detritus-calcareous gyttja
MKL - 1278	141-137	6950±90	5673	calcareous gyttja
MKL - 1279	95-92	6020±90	4796	detritus-calcareous gyttja

[f] marker was calculated for 15 variables (geochemical properties) as a moving mean. The calculations were run using PAST version 2.17c software (Hammer et al., 2001).

The chronology of the accumulation of biogenic-carbonate deposits is based on the radiocarbon dating of the series of the deposit with a high content of organic remains. The radiocarbon dating, using the scintillation technique, was carried out in the Laboratory of Absolute Dating at Skała near Kraków, Poland (MKL signature). The age was calculated for three samples (Table 1). Conventional radiocarbon dates were calibrated using OxCal 4.2.2 (Bronk Ramsey, 2009) and the IntCal13 calibration curve (Reimer et al., 2013). The attempt to perform a palynological analysis of the sediment core sampled at Wilkostowo showed its limited suitability for a palaeobotanical reconstruction (M. Obremska, pers. comm., 2014).

## 4. Results and discussion

### 4.1. Relationship between chemical composition and lithology

The concentration of most litho-geochemical components from the Wil-1 core corresponds to a range of lithologies (Fig. 3). Exceptions are contents of Cu, Pb and Mn. The Ca content reveals the strongest link to lithology. This element occurs mostly in the form of calcite in lake deposits (Jones & Bowser, 1978; Schnurrenberger et al., 2003). Because of this, the highest values of Ca concentration were recorded within the lacustrine chalk and carbonate gyttja (nearly 30 times higher than in other sediment types) (Fig. 4A). However, a negative correlation between the content of CaCO<sub>3</sub> and Fe (Fig. 4B) records sedimentation processes typical of the deepest parts of a lake. Intensive photosynthetic activity of plankton leads to rapid exhaustion of CO<sub>2</sub> dissolved in lake water and its simultaneous oxygenation. Under such conditions, a reduction and dissolution of Fe compounds is observed, together with precipitation of sparingly soluble carbonates, which gradually sink to the bottom of the reser-

voir. The CaCO<sub>3</sub> content ranges from 4.1 per cent in the herbaceous peat to 92 per cent in the lacustrine chalk. The high CaCO<sub>3</sub> content in sediments studied indicates the long-term persistence of high water supersaturation with respect to calcite in the reservoir. Yet, data for carbonate deposits reveal a very low content of other components (mainly SiO<sub>2</sub><sup>biog</sup>, K, Fe and Zn).

Biogenic silica in sediments of the Wilkostowo reservoir indicates two periods of development (Fig. 3). In the middle part of the lacustrine sedimentary sequence (between 125 and 100 cm) the maximum concentration of SiO<sub>2</sub><sup>biog</sup> attains about 22 per cent. In the top part of the section, SiO<sub>2</sub><sup>biog</sup> increases to 24 per cent. Culminations of SiO<sub>2</sub><sup>biog</sup> correspond to a decrease of CaCO<sub>3</sub> content and an increase of OM (Fig. 5A-B). No correlation between the content of SiO<sub>2</sub><sup>biog</sup> and SiO<sub>2</sub><sup>ter</sup> attests to a higher diatom productivity in periods of decreased denudation in the catchment (Fig. 5C). Such a situation allows to exclude an important role of accessibility of orthosilicate (H<sub>4</sub>SiO<sub>4</sub>) for the development of diatoms in lakes (Woszczyk, 2011). The influence of changes in intensity of CaCO<sub>3</sub> precipitation of on different degrees of dilution of other components was also found by Nowaczyk (2008) in lake deposits at the locality of Osłonki and by Apolinarska et al. (2012) in sediments taken from Lake Skrzynka.

The vertical variability of the Mn content was fundamentally different from other elements analysed (Fig. 3). The largest concentrations of this element were found in the lower and middle parts of the Wil-1 section. Within the part dominated by lacustrine chalk a sharp decline of Mn concentration was found. Manganese was in the first place in the group of the migrating elements (at a depth of 186-164 and 126-112 cm), which may indicate the superiority of the power of the river or surface water. River water is either rich in Mn<sup>2+</sup> ions or acts as a transport medium for its colloidal suspension (Kabata-Pendias, 2011).

The vertical profiles of the Cu, Cr and Ni content are characterised by considerable irregularity. Changes in concentrations of these elements neither correspond to the lithological type of sediments nor correlate with the content of other components (Ta-

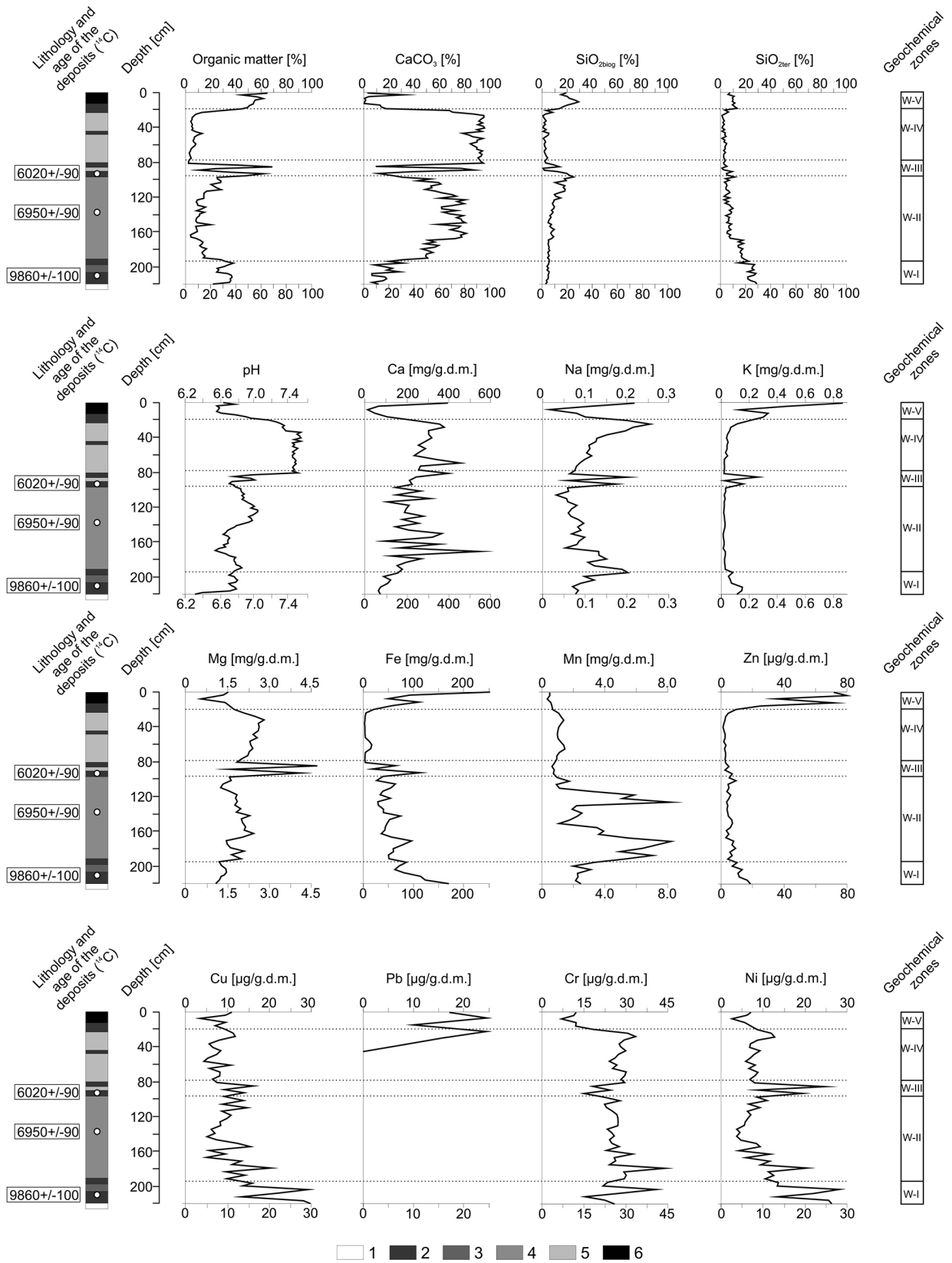


Fig. 3. Geochemical diagram and geochemical zones in sediments of the Wil-1 core.

1 - mineral (sands) deposits, 2 - detritus-calcareous gyttja, 3 - clay-calcareous gyttja, 4 - calcareous gyttja, 5 - lacustrine chalk, 6 - highly decomposed herbaceous peat.

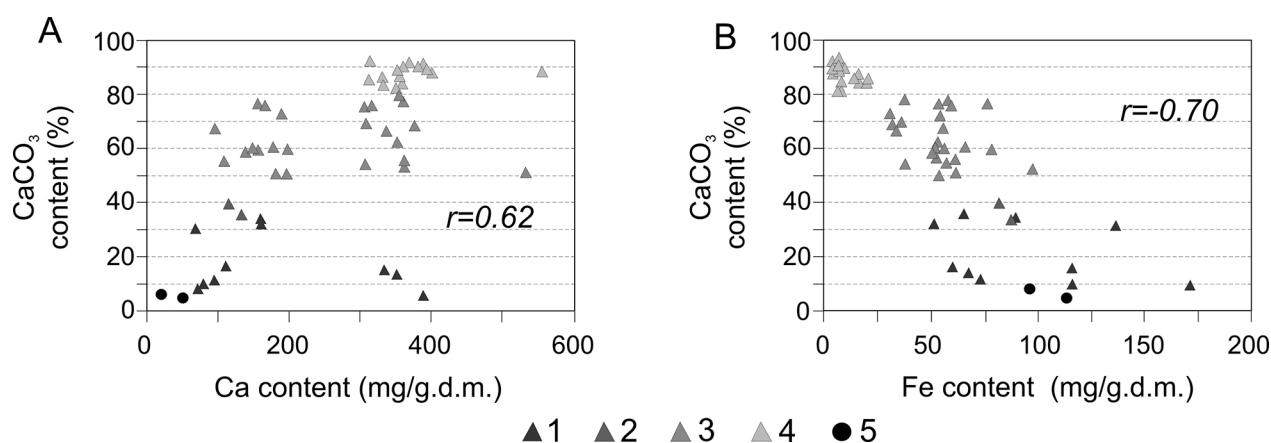


Fig. 4. Relationship between  $\text{CaCO}_3$  and Ca content (A) and  $\text{CaCO}_3$  and Fe content (B) within lake and peat deposits of the Wil-1 core.

1 - detritus-calcareous gyttja, 2 - clay-calcareous gyttja, 3 - calcareous gyttja, 4 - lacustrine chalk, 5 - highly decomposed herbaceous peat.

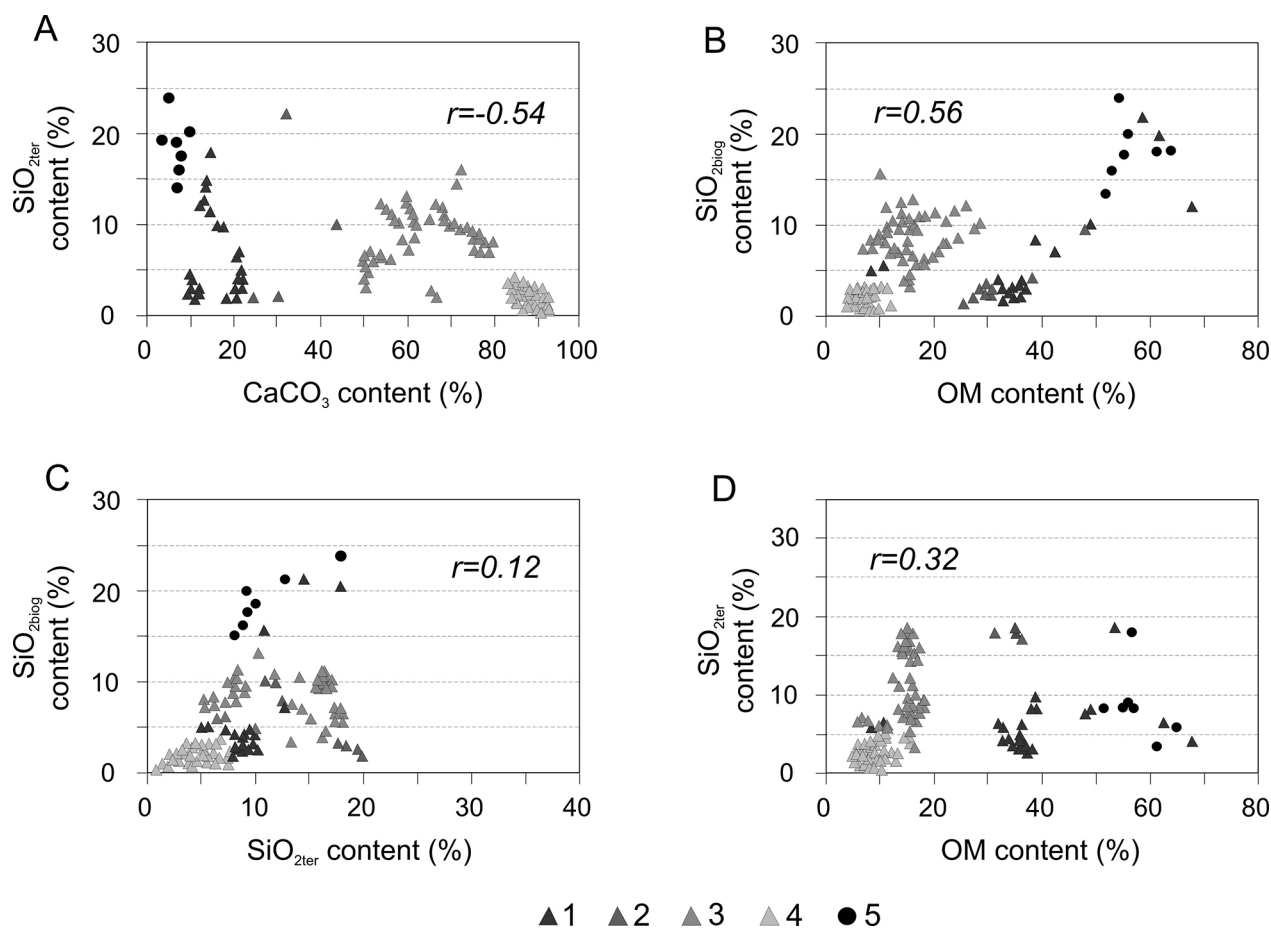


Fig. 5. Relationship between selected litho-geochemical elements:  $\text{SiO}_{2\text{ter}}$  and  $\text{CaCO}_3$  (A),  $\text{SiO}_{2\text{biog}}$  and OM (B),  $\text{SiO}_{2\text{biog}}$  and  $\text{SiO}_{2\text{ter}}$  (C) and  $\text{SiO}_{2\text{ter}}$  and OM (D) within lake and peat deposits of the Wil-1 core; for lithology see Fig. 4.

ble 2). There is no sign of enrichment of these elements in the top part of the profile either, which was the case for other litho-geochemical components analysed (Fig. 3). The concentrations of trace

elements in sediments of the Wil-1 core are clearly higher than the deposits in other reservoirs of biogenic accumulation in Poland (Bojakowska & Lech, 2008).



**Table 2.** Correlation matrix ( $r$ ) and coefficient of determination ( $R^2$ ) > 0.5 between contents of selected metals in deposits of the Wil-1 core.

r/R <sup>2</sup>	Na	K	Ca	Mg	Fe	Mn	Cu	Zn	Cr	Ni
Na	1									
K	0.41	1						0.69	0.50	
Ca	0.29	-0.11	1							
Mg	0.36	-0.13	0.52	1						
Fe	0.17	0.69	-0.31	-0.36	1					
Mn	-0.12	-0.39	-0.17	-0.24	0.07	1				
Cu	0.07	0.05	-0.23	-0.31	0.35	0.21	1			
Zn	0.05	0.83	-0.35	-0.38	0.62	-0.22	0.07	1		
Cr	-0.16	-0.71	0.28	0.11	-0.41	0.42	0.26	-0.66	1	
Ni	0.19	0.09	-0.19	-0.03	0.29	0.09	0.09	-0.01	0.13	1

Wilkostowo Wil-1 core (n=55)

## 4.2. Geochemical stratification of the Wil-1 log

The vertical variation in chemical composition of sediments depends on their lithological structure and the conditions of their sedimentation. As a result of a hierarchical cluster analysis, five developmental phases (including three natural and two anthropogenic) of the reservoir of biogenic accumulation at Wilkostowo were determined.

Phase 1 (W-I zone; 220 – 196 cm) took place in the older Atlantic period (9141 cal. a BP); it had a natural character and included detritus-calcareous gyttja with a small interbedding of clay-calcareous gyttja. An increased content of such elements as: Na, K or Ni, confirms the natural and high mechanical denudation of the catchment area during deposition in the lake. The above-mentioned elements may be strongly absorbed by clay minerals, which cause the possibility of complex absorption being characterised by much higher contents of particular elements while forming the sedimentary cover than in an aqueous solution (Woszczyk & Spsychalski, 2007). In this period the increased content of Zn, an element susceptible to intensive bioaccumulation by certain plant species, was quite common. It was most likely caused by widespread plant communities with significant or even dominant presence of *Betula*, which at the time was developing in the vicinity of the palaeolake (Rzepecki et al., 2015). *Betula* displays a bioaccumulative tendency towards Zn, which was noted by Fortescue (1980) and Reimann et al. (2007). Generally, in the older Atlantic Period *Pinus sylvestris* still played an important part in building forest communities. However, communities of *Quercus*, *Alnus*, *Fraxinus excelsior* and *Corylus* were gaining increasing foothold (Ralska-Jasiewiczowa et al., 1998; Nalepka, 2008).

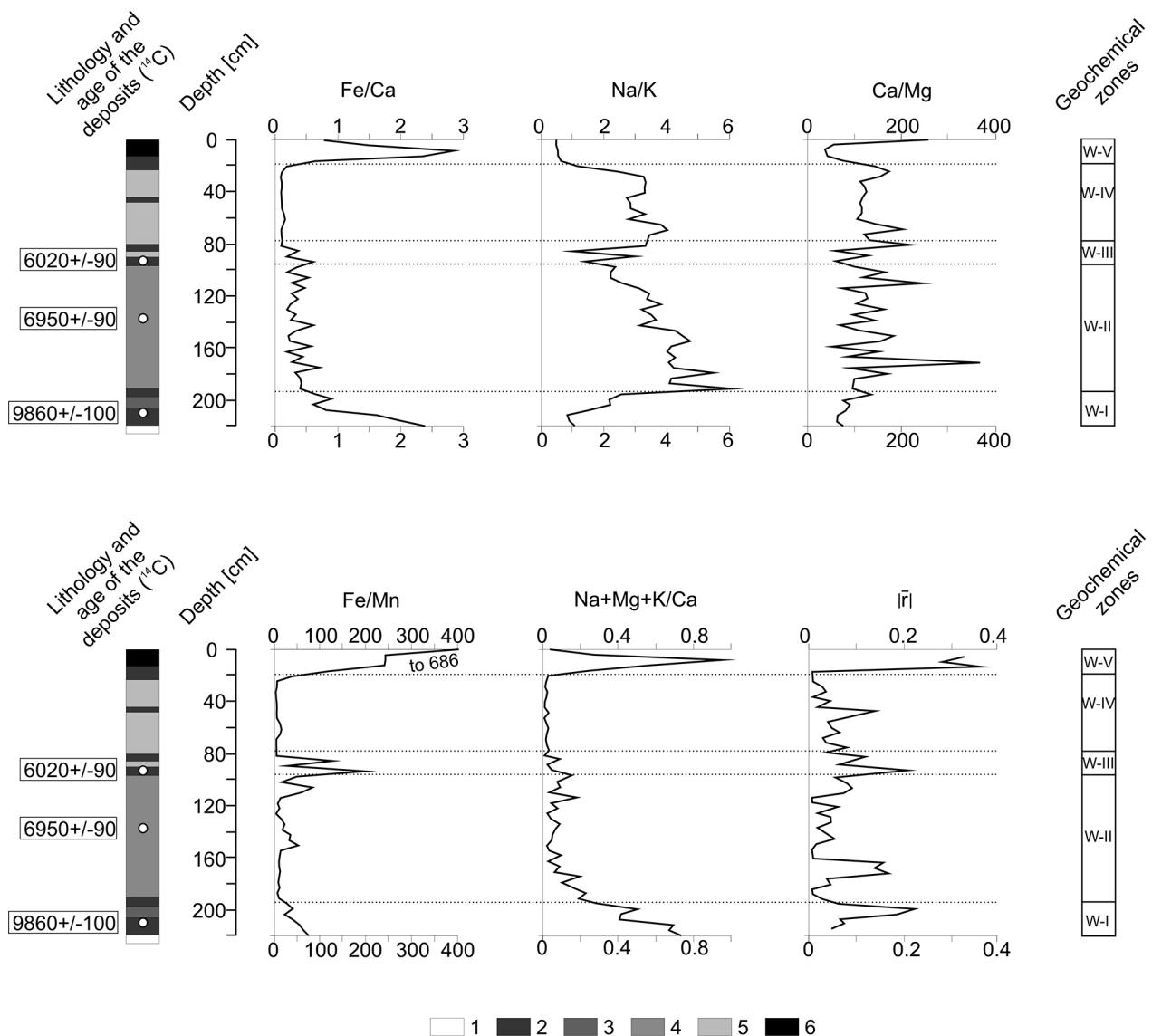
The recorded variability of the content of macro- and micro-elements attributed to the next – natural stage of the development of the reservoir (W-II zone; 196 – 100 cm). It shows a gradual change in the nature of denudation in the environment of the lake – from mechanical to chemical (six-fold predominance of Na over K concentration and over 300 hundred-fold of Ca over Mg content). The rapid increase in CaCO<sub>3</sub> content (up to nearly 80 per cent) results from the presence of calcium bicarbonate in lake waters and the biogenic decalcification of the lake waters caused by a high biomass of aquatic macrophytic nature. Good oxygenation of waters during sedimentation of these deposits at Wilkostowo is defined by a low value of Fe/Mn (mean value does not exceed 30) and a low OM content (mean value does not exceed 15 per cent), which is caused by rapid decomposition of organic remains.

Sedimentation of calcareous gyttja was interrupted by an increased supply of OM and lithophilous elements (first anthropogenic zone: W-III; 100 – 80 cm). A similar situation (i.e., a sharp decline in CaCO<sub>3</sub>, SiO<sub>2ter</sub> and SiO<sub>2biog</sub> at the expense of OM content) takes place at a depth of 88 to 84 cm (Fig. 3). The Na/K, Ca/Mg and Fe/Mn ratios display considerable variability (Fig. 6). The chemical composition of these layers is a record of increased erosion processes in the catchment of the lake, an increase in water eutrophication, a change in the nature of the denudation from chemical to mechanical and the restriction of the leaching of soils in the catchment of the lake. An analysis of the chemical composition of the sediments, whose deposition occurred during the late Meso- and Neoholocene (4976 cal. a BP) shows that an explicit mark of man-made impact is preceded by an increase and then a decrease in the content of elements such as Ca and Cu. This may be due to the inhibited recirculation caused by the



increased intensity of the groundwater outflow and acidification of soils in the catchment of the lake. The high variability of depositional conditions can be seen as an abrupt change of the curve, which presents a threefold increase of the  $[\bar{r}]$  marker. The high degree of decomposition ( $H_9 - H_{10}$ ) of organic remains in the W-III zone may be associated with sedimentary hiatus in the Atlantic period. It is possible that these changes were the results of a fire. Therefore, the processes of prehistoric human impact, recorded in the chemical composition of sediments that are classified as belonging to zone W-III, may probably be attributed to the TRB culture. The location of TRB settlements near an area of relatively "sandy soils" is confirmed in the middle Tąży-

na River Valley (Domańska et al., 2013). Across the entire Tążyna River Valley, the TRB settlers were particularly interested in the mixed climax forest environments, and this was also the case for Wilkostowo. Mixed deciduous forests, composed of *Quercus*, *Tilia*, *Ulmus*, *Fraxinus excelsior* and *Corylus* in various combinations, were dominant in the Kuyavian landscape and the neighbouring areas during the Atlantic (Ralska-Jasiewiczowa et al., 1998; Nalepka, 2005, 2008; Karasiewicz et al., 2014). A core fragment from the nearby peatbog of Przybranówek, which can be identified as belonging to the Atlantic Period, shows low thickness of biogenic sediments, which indicates slow accumulation and suggests a possible hiatus in the processes of



**Fig. 6.** Vertical differences in selected geochemical parameters and geochemical zones within the deposits of the Wil-1 core; for lithology see Fig. 3.

biogenic sedimentation. It was probably the reason for the lack of markers of anthropopression in the pollen samples (especially of cultivated plants) associated with Neolithic settlement groups. The sediments from the Przy-1 core contained only a minor presence of carbon dust, a low amount of *Pteridium aquilinum* spores, a single grain of *Utrica* pollen as well as a small amount of pollen classified as ruderalis (Rzepecki et al., 2015). In the charred level of palynological diagrams for the Osłonki site at the turn of the Meso- and Neoholocene pollen was also absent or degraded (Bogucki et al., 2012). Palaeobotanical research at the Gościąż site has allowed correlation of the settlement phase attributed to TRB population with rapid fluctuation of the AP curve (arboreal and shrub pollen) and the percentage maxima of the whole group of cultural indicator forms (Ralska-Jasiewiczowa & Van Geel, 1998).

It is possible that an important factor influencing the chemical composition of the sediments in the two layers of detritus-calcareous gyttja described above, was increased lake water salinity – as a result of the increased productivity of saline water sources located in the vicinity of Inowrocław. The level of salinity of the lake water is an important factor for the circulation of Fe, Mn, Al, Mg and CaCO<sub>3</sub>. In line with the views of Liss (1976), an increase in the salinity of the lake water during that period can be proved by the twofold increase in Fe and Mg in relation to the geochemical background. As that author thinks, the intense sedimentation of the above-elements, during higher salinity levels, was due to the process of coagulation of solid particles suspended in water under increased ionic strength conditions. However, both Fe and Mg – because of strong correlation with e.g., SiO<sub>2ter</sub> – are counted among the lithophilous elements and those could have been passively transported to the lake at Wilkostowo. On the other hand, Schettler et al. (2006) and Woszczyk (2016) underlined that Mg played an important role as inhibitor of CaCO<sub>3</sub> precipitation in saline waters. This is confirmed by a decrease of CaCO<sub>3</sub> content in the sediments obtained at Wilkostowo where, at the depths mentioned, the share of this component in the volume of the sample falls almost sixfold. The highest values of Mg in the whole section may have resulted from the economic exploitation of carnallite (hydrated potassium and magnesium chloride; KMgCl<sub>3</sub>×6H<sub>2</sub>O), which often accompanies deposits of halite (rock salt) in Kuyavian (Poborski et al., 1956). The Na content in this geochemical zone does not exceed 0.25 mg/g.d.m., which is the maximum value characteristic of many sites of lacustrine sediments and peat in the Polish Lowland that are well documented in the specialised literature (Łacka et

al., 1998; Apolinarska et al., 2012; Karasiewicz et al., 2014). The possibility of using local sources of salt (halite) by inhabitants is confirmed by the investigation of mineralogical pottery done by Pawlikowski (2015).

The next natural phase in basin development (W-IV zone; 80 – 24 cm) includes the lacustrine chalk with a thickness of about 60 cm with small interbeddings of detritus-calcareous gyttja at a depth of 48–46 cm. The high level of Ca and Na in relation to Mg and K in the lacustrine chalk, respectively, are indicative of persistent lake alimentation by groundwater enriched with products of the chemical denudation of glacial and glaciofluvial deposits. This phase of lake development probably corresponds to the humid period 5150±400 cal. a BP, which was identified in lakes of northern Poland (Michczyńska et al., 2013). At the turn of the Atlantic and Subboreal periods, mesophilous deciduous mixed forests continued to be the predominant vegetation type but reduction of the forested areas is recorded in the sediments of Przybranówek mire (Rzepecki et al., 2015). An analysis of the cores from the Holocene carbonate sediments deposited in lakes and peatbogs of northern Poland allows to distinguish the key differences in the period of their deposition and their chemical composition (Łacka et al., 1998; Rutkowski et al., 2007; Apolinarska et al., 2012; Mazurek et al., 2014). Those may have been determined by the sites being situated either in the highland or a valley as well as local geological and morphological conditions that determine the type of water supply. The lowest values of the ratio Fe/Mn (average – about 7) indicate that lacustrine chalk accumulated under more oxidising conditions, probably linked to an ascending water supply to the lake. The three periods of a small increase in erosion rate in the catchment of the lake recorded in this layer coincide with intervals of a slight rise in eutrophication of the lake waters and a decrease in the intensity of CaCO<sub>3</sub> precipitation. The largest increase of the correlation between different measurement results [f] is the record of a greater variability of the conditions of sedimentation in detritus-calcareous gyttja (Fig. 6). Most likely, these periods can be attributed to human activity during the Bronze and Iron ages.

The sedimentation of detritus-calcareous gyttja and the highly decomposed (H<sub>8</sub> by von Post scale) herbaceous peat (second anthropogenic zone: W-V; 24 – 0 cm) are indicative of the process of overgrowth of the lake. The maximum content of Zn and Fe in the entire vertical section proves the existence of strongly reducing conditions in the reservoir. An increased concentration of elements such

as K, Na or Pb results from processes of mechanical denudation within the catchment area of the sedimentary basin described. These elements are amongst the most important inorganic constituents in peat deposits and their increased content may be the result of delivery from allochthonous mineral matter, independently of the natural development of the mire (Rydelek, 2013). The highest concentrations of Pb were discovered at depths at which the content of mineral matter falls, and therefore a supply of this metal into the study site area is associated with atmospheric migration of particles. The average concentration of trace elements (Zn and Pb) in the upper part of the Wil-1 core is similar to the Holocene overbank deposits in the Tażyna River Valley (Szymańda, 2008). In comparison with the soils of the Kuyavian Lakeland (e.g., Cieśla et al., 1994; Dąbkowska-Naskręt et al., 2006) the peat deposits studied here contain less Cr, Cu, Ni and Pb, and contain only more Zn.

#### 4.3. Causes of geochemical variation of sediments at Wilkostowo

Using Kaiser's criterion, those factors that have a value greater than 1 (principal component) were distinguished (Fig. 7). The first four are significant (PC1, PC2, PC3 and PC4), which explains a total of 82.2 per cent of the variance.

The first component (PC1) is strongly positively correlated ( $r > 0.6$ ) with OM,  $\text{SiO}_{2\text{ter}}$ , K, Fe and Zn (Fig. 8A). The co-existence of these elements can be regarded as a universal phenomenon that results from the absorption of metals by clay minerals, organic matter and hydrated iron oxides, the co-existence of elements in rocks of the earth's crust, precip-

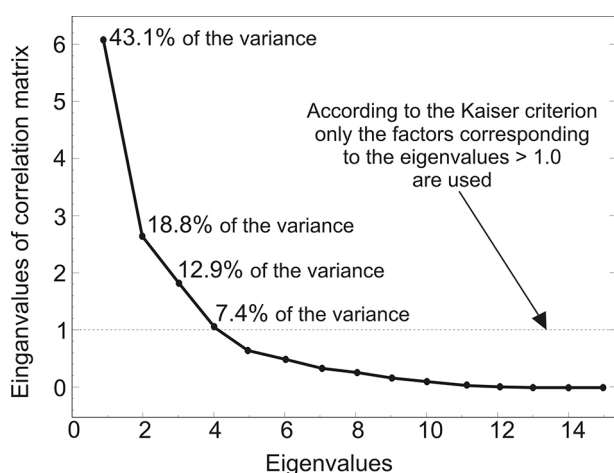
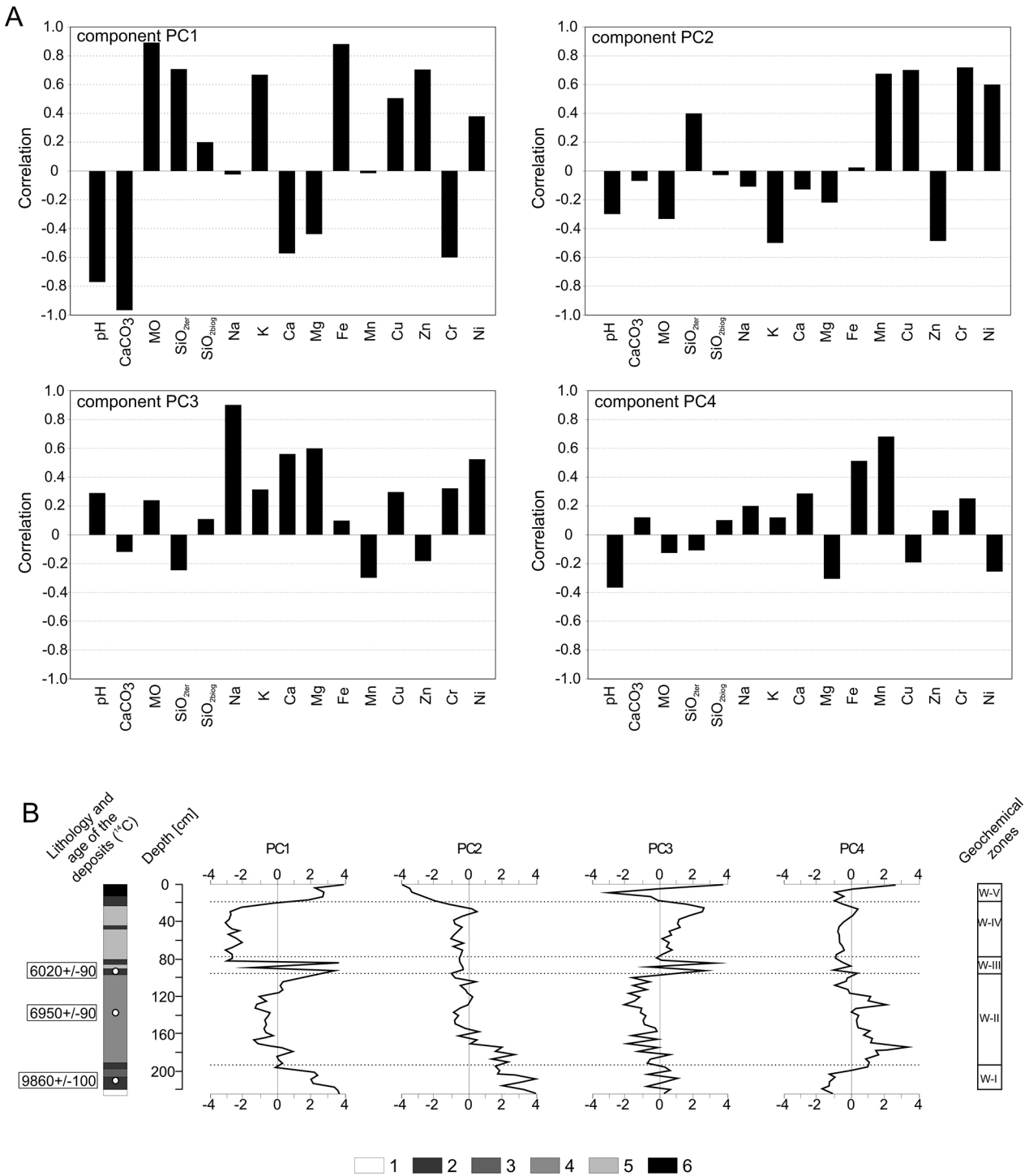


Fig. 7. Eigenvalues of correlation matrix for a set of results of chemical analysis for deposits of the Wil-1 core.

itation of sulphide metal with limited oxygenation and weak decomposition of organic matter (Woszczyk & Spychalski, 2007). The curves of  $\text{SiO}_{2\text{biog}}$  and OM content in the Wil-1 core sediments may reflect real changes in intensity of biological processes in the lake reservoir at Wilkostowo, which are hinted at by the positive correlation between  $\text{SiO}_{2\text{ter}}$  and  $\text{SiO}_{2\text{biog}}$  and the OM (Fig. 5B, D). The clay minerals and Fe oxides played a major role in the process of retention of solids dissolved in the lake's water in the reservoir at Wilkostowo. The K content, which is part of the aluminosilicate, is a measure of the relative concentration of clay minerals in biogenic deposits (Last, 2001; Rydelek, 2013). Moreover, the PC1 component negatively correlates with the pH and  $\text{CaCO}_3$  content (Fig. 8A). The high value of the average content of  $\text{CaCO}_3$  (56.9 per cent) is explained by low biological productivity of lakes with highly alkaline waters. According to this interpretation, deposits with a reduced  $\text{CaCO}_3$  content record a decreased alkalinity of the lake water and a weaker binding of phosphorous in the sediments (Dittrich & Koschel, 2002). Such conditions favour the development of diatom populations and  $\text{SiO}_{2\text{biog}}$  deposition (Woszczyk, 2011). The enrichment of metals such as K, Fe and Ni (geochemical zone: W-III) may indicate an increased intensity of human activity in the catchment of the lake (i.e., the use of saline waters for economic purposes or aeolian processes during the Neolithic). At this level the content of PC1 was highest (Fig. 8B). The remaining part of the log contains levels of PC1 values of high vertical variability with marked spikes in places where the OM content (detritus-calcareous gyttja and highly decomposed herbaceous peat) is higher and drops in places where calcareous gyttja and lacustrine chalk are present.

The second component (PC2) is positively correlated with  $\text{SiO}_{2\text{ter}}$ , Mn, Cu, Cr and Ni contents (Fig. 8A). The highest values of PC2, indicative of a rich presence of trace elements and  $\text{SiO}_{2\text{ter}}$  were identified as belonging to the initial phase of the development of the reservoir (Fig. 8B). The remainder of the log shows this variable as a limited vertical variability, with the exception of the highly decomposed herbaceous peat. Generally, the sections rich in  $\text{SiO}_{2\text{ter}}$  and Mn, may indicate some episodic activation of fluvial processes, a supply of mineral matter by aeolian processes – spurred by man – in the areas cleared of vegetation that are parts of the sandur level. Because of low slope inclination in the area, the influence of slope processes on the delivery of the elements to the Wilkostowo reservoir appears less likely. The Holocene aeolian processes, which were in part synchronous with TRB cultural



**Fig. 8.** Correlation of geochemical variables with four first principal components for a set of results of chemical analysis (A) and plots of principal components PC1-PC4 (B) from deposits of the Wil-1 core; for lithology see Fig. 3.

development, were reconstructed on the grounds of several examples from the neighbouring Toruń Basin (Jankowski, 2002). However, other possible processes of geochemical cycle of Mn in the lake include: precipitation of manganese carbonate in terms of abundant organic matter, no free O<sub>2</sub> and excess CO<sub>2</sub> in a deposit-forming environment, and

impact of diagenetic migration to vertical and spatial distribution of Mn compounds (Davison et al., 1982; Granina et al., 2004).

Trace elements such as Cu, Cr and Ni migrate passively. They are absorbed by mineral matter and exhibit sulphophile ability (Landner & Reuther, 2004). No statistically significant correlations of



Cu with the other components could be a result of a very different stability organometallic Cu compounds. This stability depends on conditions within the deposits, the degree of decomposition and humification of OM and pH of the deposit-forming environment (Woszczyk & Spychalski, 2007). Distribution of trace elements in lake sediments is strongly dependent on the type of geological formation on which the lake is developed and the sedimentation zone of the lake (Poepperl et al., 2001).

The third component (PC3) explains mainly the variation of Na, Mg and Ca (Fig. 8A). The PC3 component exhibits significant cross-sample fluctuations, especially at a depth of 2.2 to 0.8 m (Fig. 8B). The maximum values of this parameter correspond with the highest PC1 values and can be found in sediments containing more OM (detritus-calcareous gyttja and highly decomposed herbaceous peat). The highest content of Na, Mg and Ca was documented in carbonate sediments. These elements are the main components of lacustrine chalk or calcareous gyttja and could have been supplied to the biogenic reservoirs as a result of chemical denudation processes (Stumm, 2003). The increasing importance of leaching processes of Na, Mg and Ca from the catchment can result from changes in vegetation and increased water permeability in soils.

The fourth component (PC4) is strongly positively correlated ( $r > 0.5$ ) with those of Fe and Mn (Fig. 8A). In the bottom part, the PC4 values show high vertical variability (Fig. 8B). The maxima correspond with low PC1 level and can be associated with sediments with the highest concentration of Mn. On the other hand, in the lacustrine chalk sediment the PC4 component displays low cross-sample fluctuation, similar to PC1 and PC2. The concentration of Fe in the studied detritus-calcareous gyttja and peat is much higher than in the other lake deposits, showing the deterioration of redox conditions. In contrast, ferrous oxide was an important part of the process of binding with substances dissolved in water as well as in the migration of numerous elements. K, Na and Cu were quickly captured by surfactants and reached the reservoir in suspension. Also, Fe was grouped in factor explaining the chemical composition in the biogenic sediments of Lake Sarbsko (Woszczyk & Spychalski, 2007). The Fe and Mn concentrations in bottom deposits depend on the average contents of these elements in the rocks forming the catchment, the intensity of mechanical denudation, the oxidation-reduction conditions in the soils of the catchment, the presence or absence of sulfur, precipitation of Mn and Fe carbonates in terms of the abundance of OM

and the impact of diagenesis migration (Emerson, 1978; Davison et al., 1982; Dean, 1999).

## 5. Conclusions

A thick (up to 220 cm) layer of biogenic sediments was studied in the mid-section catchment areas of the River Tążyna, as a source of knowledge of the environment since the Mesoholocene. Sediments of the Wil-1 core are characterised by a high stratigraphic geochemical variability expressed both as the content of the main litho-geochemical components as well as the content of elements. The geochemical features of the biogenic deposits are typical of calcareous gyttja and lacustrine chalk. The limnic sediments were deposited as an effect of intensive chemical denudation processes. The geochemical properties of the peat were formed by the deterioration of redox conditions, intensified erosion of the catchment, metal pollution and acidification.

The results from our geochemical survey have made it possible to reconstruct the main stages in the evolution of the lake basin at Wilkostowo. The main factors influencing the chemical composition of the sediments studied include: the geological structure and lithology in the catchment of the reservoir, the water supply type and the water balance of the basin as well as changes in variation pattern of intensity and type of denudation in the catchment area. The curves of the factor values in the Wil-1 log display a connection between the change in the content of a number of metals (Ca, Mg, Na and Fe) and the lithological alteration. The bottom part of the log shows a high vertical variability in levels of all factors, while the phases of the most intensive growth or decrease can be seen in levels of a Meso- and Neoholocene date.

The effects of the prehistoric anthropogenic activities in the catchment area of the mid-section of the River Tążyna are detectable in changes in sedimentation of biogenic calcareous gyttja into detritus-calcareous gyttja.

The increased human activity of the middle Tążyna River Valley in the Neolithic Age manifested itself by an increase in content of lithophilous elements (Na, K, Mg and Ni) in the sediments, an increase in the value of the erosion rate in the catchment of the lake, an increased eutrophication of the lake, a change in the nature of the processes of denudation, a decrease in the intensity of leaching  $\text{CaCO}_3$  from the catchment area and a reduction in the pH of the soil cover. The greater admixture of  $\text{SiO}_{2\text{ter}}$  in the limnic deposits can be attributed to aeolian processes.

The top position occupied by Mg and Fe amongst migrating elements, together with a lowered CaCO<sub>3</sub> content in sediments deposited during the Neolithic, suggests the use of saline waters for economic purposes.

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