Journal of Elementology ISSN 1644-2296

Gruszczyński T., Małecki J.J., Ziułkiewicz M. 2017. *Reconstruction of paleohydrogeological conditions in the late Holocene based on the study of calcareous tufa in the spring mire of the Wolbórka River drainage basin (central Poland).* J. Elem., 22(3): 1049-1065. DOI: 10.5601/jelem.2016.21.4.1284

ORIGINAL PAPER

RECONSTRUCTION OF PALEOHYDROGEOLOGICAL CONDITIONS IN THE LATE HOLOCENE BASED ON THE STUDY OF CALCAREOUS TUFA IN THE SPRING MIRE OF THE WOLBÓRKA RIVER DRAINAGE BASIN (CENTRAL POLAND)

Tomasz Gruszczyński[1], Jerzy J. Małecki[1], Maciej Ziułkiewicz[2]

[1]Institute of Hydrogeology and Engineering Geology
University of Warsaw
[2]Laboratory of Geology
University of Łódź

Abstract

The article presents the results of research on spring mire cupolas of the Wolbórka River, a left tributary of the Pilica River. The sedimentary sequence overlies fluvial sands and includes three series of calcareous tufa separated by peat layers. ^{14}C dating indicates that the sedimentation in the spring mire area began in the late Atlantic (AT) and ended at the end of the Subboreal period (SB2). Analysis of lithological features of the sediments has allowed the reconstruction of environmental conditions and their impact on the functioning of the groundwater outflow zone in the late Holocene. The mutual relationship between the peat layers and successive series of calcareous tufa records the changes in humidity conditions resulting from periodic changes in climatic conditions. The sediments of the spring mire cupolas, which are composed mostly of calcite, also contain gypsum and pyrite. The ratio of gypsum to pyrite has proven to be a useful tool for reconstructing humidity condictions. It has become the basis for demonstrating that calcareous tufas are sediments of dry periods, and the deposition of cupola sediments depended on the hydrodynamic regime and flow rate of the springs. The main factor contributing to the deposition of calcite was the equilibration of the groundwater solution with the partial pressure of carbon dioxide in the atmosphere, at low flow dynamics.

Keywords: spring mire cupola, calcareous tufa, humidity conditions reconstruction.

prof. dr hab. Jerzy J. Małecki, University of Warsaw, Żwirki i Wigury 93, 02-089 Warszawa, e-mail: jerzy.malecki@uw.edu.pl

INTRODUCTION

In the Holocene, the climatic conditions in the area of today's Poland were subjected to marked changes relating to both the amount of precipitation and thermal conditions of the air. Previous studies were mainly aimed at the reconstruction of climatic conditions, based on analysis of a set of features of Holocene alluvial, limnic, aeolian and biogenic deposits. This paper lies in the mainstream of this studies; however, it differs slightly from the classical palaeoclimate reconstruction. The authors have assumed that the climate transformation affected the recharge rate of the multi-aquifer system, and, consequently, its hydrodynamic and hydrochemical state was also subjected to transformation in time. The work is an attempt to reconstruct the direction of these changes, nevertheless it is a qualitative analysis. An opportunity to carry out such analysis arose from the presence of hydrogenic sediments forming the documented spring mire cupolas at the village of Wardzyń (central Poland). At the end of the Atlantic period and in the Subboreal period, alternating peat and calcareous tufa sediments were formed, and their origin is closely associated with the zone of groundwater discharge to the surface.

INVESTIGATED SITE

Groundwater outflows near Wardzyń (19°38′20″E, 51°38′18″N) are located within the spring mire zone of the Wolbórka River, a left tributary of the Pilica River, in an area where the Romanowskie Hills adjoin the Wolbórka valley near a first-order watershed (Figure 1). They form a set of outflows arranged along an erosional edge. Near the springs there are cupolas composed of peat and calcareous tufa. Area of investigated cupola is about 15 000 m^2 and there are 20 active springs in surroundings of this cupola. Surface of the cupola is covered with alder forest.

Groundwater in the study area occurs in Cenozoic and Mesozoic multi-aquifer formations. The intricate origin of Quaternary deposits and the variable energy of sedimentary environment have resulted in the heterogeneity of this multi-aquifer formation.

The lower part of the Quaternary multi-aquifer formation, represented by South Polish Glaciation deposits, is dominated by poorly permeable sediments (ice-dammed lake deposits and glacial tills). These deposits along with the Neogene cover of weathering loams represent the dividing aquitard. Below there are Mesozoic water-bearing deposits of the Łódź Trough. Analysis of the hydraulic head distribution in the Quaternary and Upper Cretaceous aquifers indicates that the pressures in the deeper aquifer are significantly lower and it cannot considered to represent a potential recharge zone of the springs under study (Figure 1).

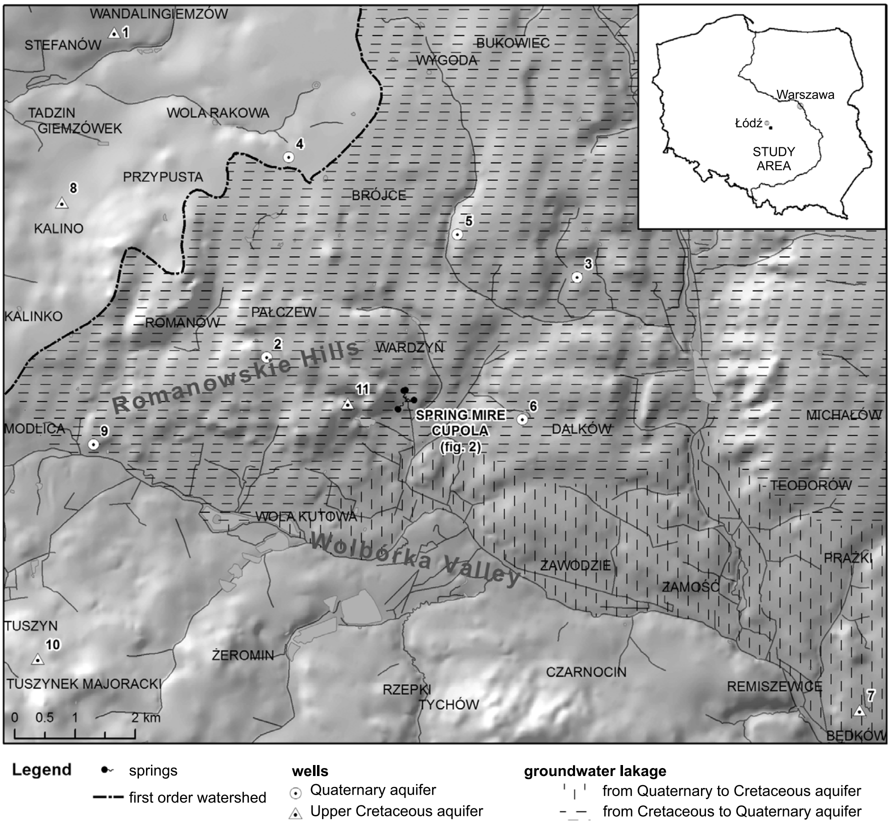

Fig. 1. Location of the study area

The springs of the Wardzyń region are both descending and ascending in nature. The discharge rates in the range of 10.5-16.5 l s^{-1} substantiate their classification into the group of stable springs with the highest yield in the Łódź region, i.e. into Meinzer's discharge class IV (Ziułkiewicz et al. 2012).

MATERIAL AND METHODS

The main goal of the study on spring mire sediments in the Wardzyń region was to find out the structure of spring mire cupolas, continuity of individual interbeds and spatial relationships between the calcareous tufas and peats. Another objective was to determine the origin of the tufas. To achieve these goals, mapping of the spring mire cupolas was carried out, including 23 soundings with an Eijkelkamp Instorf sampler. In order to determine the sequence of events, organic deposits of the cupola were dated. The dating was performed on six samples from two cores, weighing about

50 g. Age determinations were made by the ^{14}C method at the Laboratory of Absolute Dating in Skała, according to the scintillation technique. For the qualitative and quantitative analysis of crystalline mineral phases, 12 samples of calcareous tufa were collected from two cores for XRD determinations. The analyses were performed at a laboratory of Warsaw University, using an X'Pert PRO MPD instrument and the Bragg-Brentano method (Figure 2). Soundings number 22 and 23 of the most deep and complete profile were chosen for ^{14}C and XRD analysis,.

Hydrogeological investigations included measurements of the spring discharges, *in situ* physico-chemical properties of groundwater (temperature, pH, Eh, SEC and CO_2) and analyses of chemical composition (Na, K, Ca, Mg, Cl, HCO_3, SO_4) in a laboratory of University of Łódz . Groundwater samples were collected from five piezometers and from 10 active drilled wells (six from the Quaternary aquifer and four from the Upper Cretaceous aquifer). Elevation of the groundwater table was also measured in the wells. The research was carried out in the period of 2011-2013 at 1–2-month intervals.

Geochemical modelling was made using the *PHREEQC-2 v. 2.0.53* software (Parkhurst 1995). The calculations and simulations were used to identify processes favouring calcite deposition, taking into account the carbonate equilibrium.

RESULTS

The structure of the cupola and its heterogenity

The sequence of spring mire sediments begins with calcareous tufa immediately overlying fluvial sands (Figure 3). It is the oldest series of calcareous tufa (series A) deposited probably at the end of the Atlantic period. Sediments of series A occur only in the axis of the erosional incision. Above, there is a layer of strongly decomposed peat with a considerable amount of calcium carbonate and sandy material. Locally, these deposits interfinger laterally with mineral deposits represented by silts.

The calcareous tufas above the oldest peat layer are concentrated in a narrow, meridionally elongated zone whose trend corresponds to the axis of the erosional incision in the bedrock. These are calcareous tufas with high amounts of plant remains. The greatest thickness (over 1m in places) of these deposits is observed in their southern and central parts. Three calcareous tufa series can be locally distinguished (series B, C and D) with interbedding peat layers. In the northern part, there are several-centimetre-thick intercalations of calcium carbonate within the peats. In the marginal areas of the calcareous tufa and at the top, these sediments show the character of rhythmite. The calcareous tufas are overlain by a layer of rush-wood peat, strongly decomposed at the top.

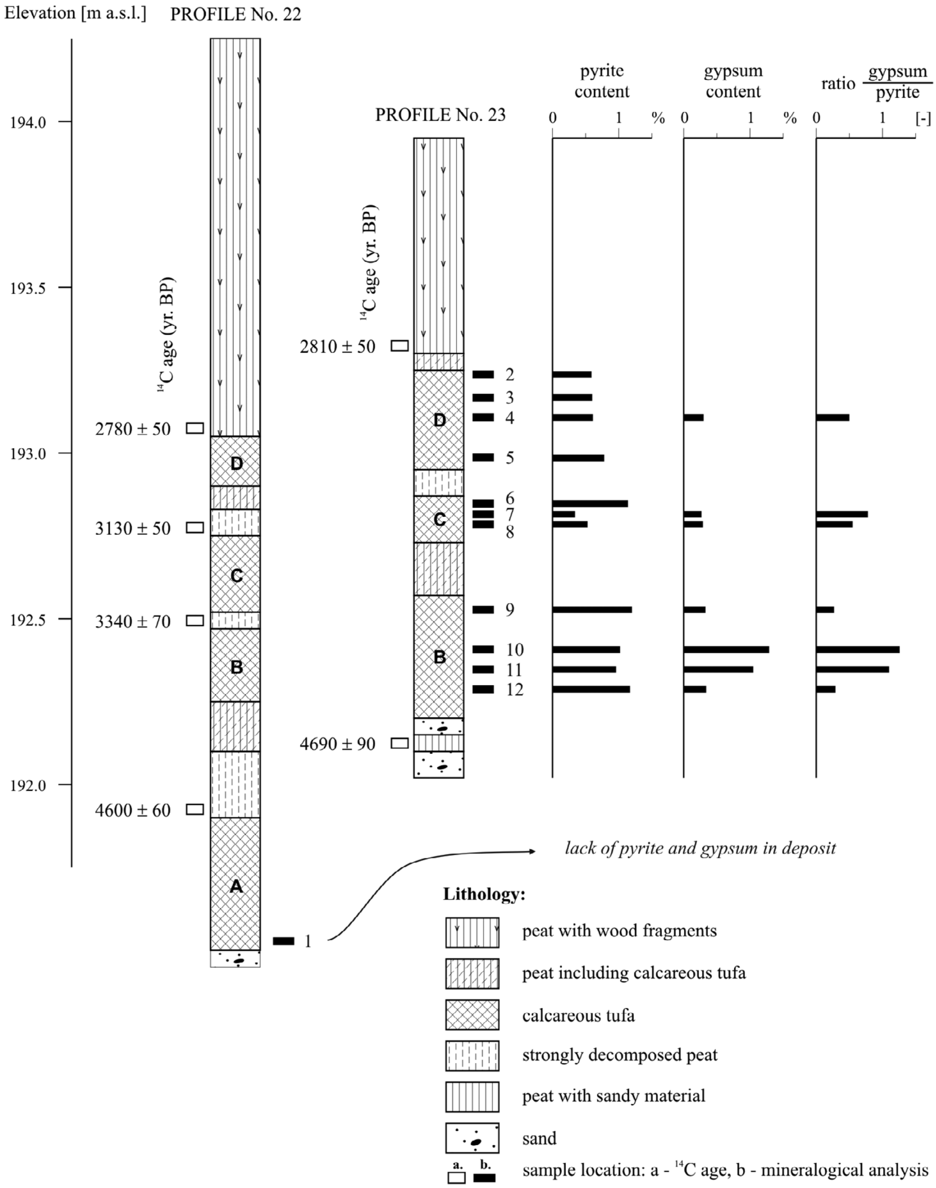

Fig. 2. Mineral composition of the calcareous tufa, and ^{14}C age of the peats

Mineral composition of the calcareous tufas

X-ray diffraction (XRD) determinations performed for 12 calcareous tufa samples show that calcite is the dominant crystalline phase in the sediment. and its content in all samples exceeds 95%. In addition, all samples contain quartz (Table 1), whose share does not exceed 1.5%. Some of the samples

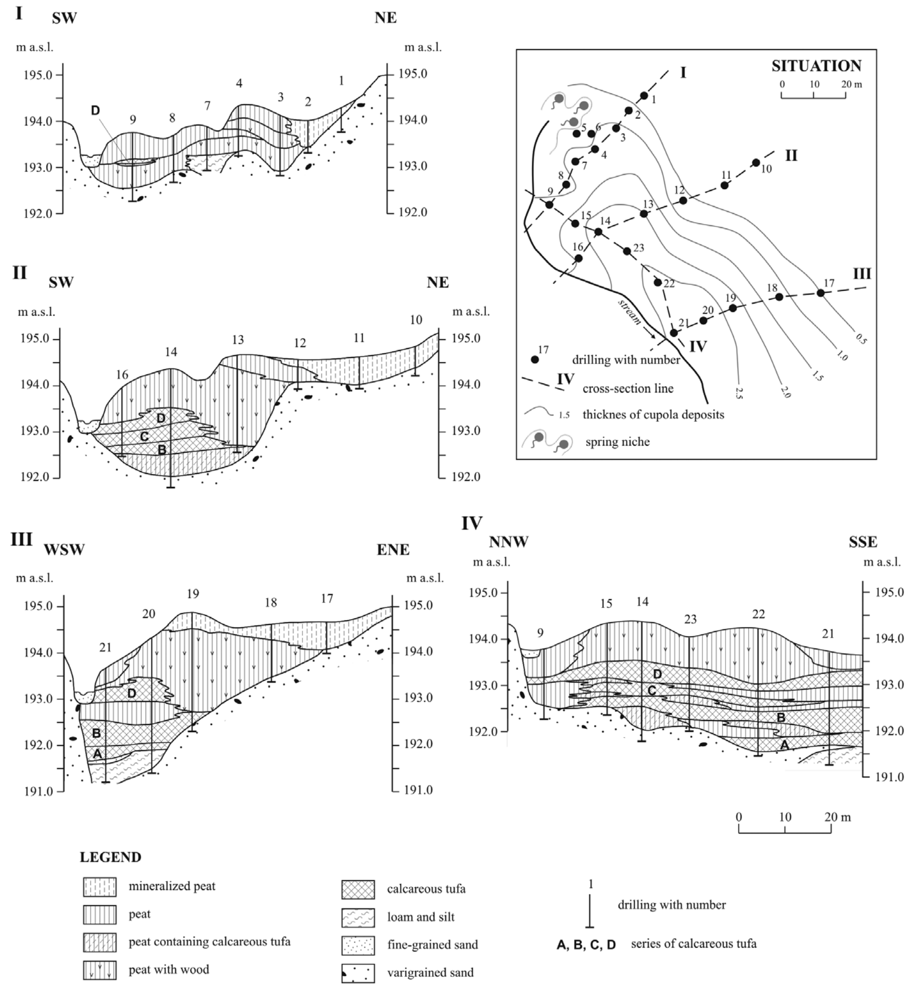

Fig. 3. Geological cross-sections through the cupola

also contain trace amounts of plagioclases. Silicates and aluminosilicates represent allochthonous detrital material introduced into the sediment as a result of fluvial and/or aeolian transport. Sulphur minerals may have formed *in situ*, e.g. pyrite (up to 1.5%), which is a common constituent of the calcareous tufa, and gypsum in some samples. Pyrite was probably formed first due to the precipitation of iron sulphide under reducing conditions that resulted from the accumulation of organic matter gradually transformed into peat within the cupola. In a low-temperature environment, in the outflow zone, pyrite may have been precipitated directly from the solution.

Results of experiments (Schoonen, Barnes 1991) show that amorphous iron sulphide can precipitate from the solution under such conditions, due to the reaction of Fe^{2+} ions and hydrogen sulphide. Subsequently, this compo-

Table 1

XRD qualitative analysis of the calcareous tufa from Wardzyń

Sample	Profile	Depth (m)	Deposit series	Mineral assemblage				
				calcite	pyrite	gypsum	quartz	anorthite
2	23	0,71	D	x	x		x	x
3		0,79		x	x		x	x
4		0,85		x	x	x	x	x
5		0,97		x	x		x	x
6		1,11	C	x	x		x	
7		1,13		x	x	x	x	
8		1,15		x	x	x	x	x
9		1,43	B	x	x	x	x	x
10		1,55		x	x	x	x	
11		1,61		x	x	x	x	
12		1,67		x	x	x	x	
1	22	2,75	A	x			x	x

und can recrystallize into mackinawite, greigite and ultimately into one of the polymorphic forms of FeS_2 – pyrite or marcasite – as a result of sulphidation. Marcasite is a less stable form and precipitates in acid environments ($pH < 5$). In contrast, the formation of pyrite is favoured by $pH >6$. Pyrite is absent only in the oldest calcareous tufa (A). This series rests directly upon sands and had been already deposited before the deposition of the oldest peat layer. It can be assumed that oxidizing conditions prevailed in the outflow zone at that time, which did not favour the precipitation of sulphides from the solution.

Gypsum was found in some calcareous tufa samples representing series B, C and D, but its highest content (locally in excess of 1% of crystalline phases) appeared in the series B sediment. In the areas where gypsum was present, the sediments tended to contain less pyrite, which manifested itself in values of the gypsum to pyrite content ratio (Figure 2). Neither gypsum nor pyrite has been found in a sample collected from series A, which may indicate that gypsum was formed as a secondary mineral due to the oxidation of pyrite in the presence of calcite. This means that the redox conditions within the cupola were periodically changing into oxidizing ones. Significantly, the highest gypsum content was observed in deeper parts of the section (series B), and the gypsum content decreases within the individual series of calcareous tufas toward their top and base. This indicates that sulphur minerals are not evidence of contemporary processes, and their quantitative relashionships in the sediment are a record of changes in the redox conditions at the time when the cupolas were being formed.

The successive series of calcareous tufa were deposited on peat. Initially, the sedimentary conditions were reducing, which favoured the formation of sulphides. A change in humidity conditions led to a gradual lowering of the groundwater table in the outflow zone, and to periodic overdrying of the sediments. Under such conditions, atmospheric oxygen was supplied to the sediment more easily and consequently sulphides were oxidized to gypsum. At the final stage of the calcareous tufa layer formation, the conditions were gradually becoming more humid, which resulted in limiting the availability of atmospheric oxygen and hampering the process of pyrite oxidation. This is manifested by a decrease in the content of gypsum in sediment or in its lack in the top parts of the calcareous tufa in series B, C and D.

Timing of cupolas formation

Peat samples for age determination were collected from the central part of the cupola because of the evidenced relationship between the peat and calcareous tufa deposits in the section. In the zone beneath the calcareous tufa of series B (Figure 2, sections Nos. 22 and 23), mineral-organic sediments and a layer of strongly decomposed peat were drilled, which are suitable for ^{14}C dating. Additional dating was made on peat interbeds in the calcareous tufas and on a peat sample from the top of the carbonate series. The results show that the sedimentation of these deposits within the cupola started relatively late, at the end of the Atlantic period.

The oldest carbonate series was deposited before 4,600 ±60 years BP. After that date, peat deposits with sand admixture were initially accumulated, followed by peats passing gradually into calcareous tufas of series B. At about 3,400 years BP, the sedimentary conditions changed again, as evidenced by the peat layer separating series B and C. The calcareous tufa of series C was deposited between 3,340 ±70 BP and 3,130 ±50 BP, and is covered by a layer of strongly decomposed peats. The youngest carbonate series (D) was deposited between 3,130 ±50 BP and 2,780 ±50 BP. The age of the basal peat layer above the calcareous tufas indicates that the environmental conditions changed in the spring mire area early in the older part of the Subatlantic period, which facilitated sedimentation of rush-wood peat.

The dating results indicate that the calcareous tufas might have been formed in a relatively short time interval of the latemost Atlantic and the Subboreal. However, it is not certain whether the sedimentary series under study is a complete and continuous record of this time interval.

It cannot be precluded that we deal with a record of ephemeral events of shorter durations. With the current stage of knowledge, this issue cannot be resolved unequivocally. However, there is no doubt that the sedimentary conditions during the formation of the sequence were varying, favouring either the deposition of calcareous tufas or peat layers. This is manifested by the presence of peat interbeds or rhythmite-type sediments between the consecutive calcareous tufa layers. The dating of the calcareous tufa deposition indicates that these are young deposits, especially when compared with similar deposits from cupolas in northern Poland, i.e. in areas of late-glacial relief (DOBROWOLSKI et al. 1999, 2002, 2011, 2012, MAZUREK et al. 2014).

Chemical composition of groundwater

Interpretation of the chemical composition of groundwater was carried out separately for the groundwater of the Cretaceous aquifer system and the Quaternary aquifer system. The results show that both the Cretaceous and Quaternary groundwater have composition typical of the hypergenesis zone (Table 2). It is fresh water with dry residue below 500 mg dm^{-3}, HCO_3-Ca and HCO_3-SO_4-Ca in type (Figure 4). The mineralization of the water drained by the springs was greater than of that taken from the wells.

Differences between the Quaternary and Upper Cretaceous aquifer systems are marked as regards the ionic composition. The Quaternary groundwater shows a higher proportion of sulphates and (to a lesser extent) of

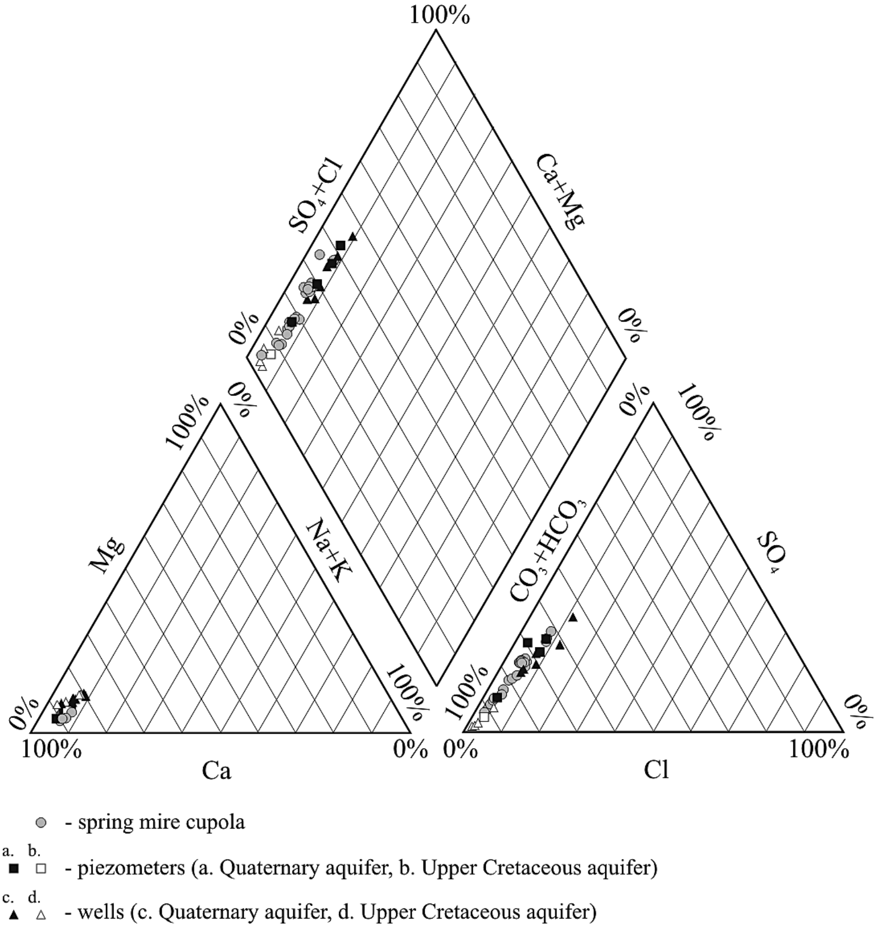

Fig. 4. The groundwater ionic composition

Table 2

Selected hydrochemical parameters of groundwater in the Wardzyń region, the highest mean values are in bold (n = 25)

Hydrochemical parameter min.-max. mean	Spring waters	Unconfined groundwater	Confined groundwater from Quaternary aquifer	Confined groundwater from upper cretaceous aquifer
Temperature (°C)	8.8 – 9.9 9.3	9.4 – 12.6 **10.4**	9.7 – 9.9 9.8	9.2 – 10.9 9.8
Dry residue (g dm^{-3})	0.35 – 0.46 **0.40**	0.20 – 0.24 0.22	0.17 – 0.33 0.26	0.20 – 0.39 0.26
pH	6.89 – 7.97 7.50	6.00 – 7.58 **7.57**	7.20 – 7.49 7.33	7.20 – 7.78 7.40
Redox potential (mV)	+61 – +157 **+109**	-118 – +108 +27	-97 – +89 -30	-151 – -47 -87
Oxidizability (mgO_2 dm^{-3})	1.9 – 6.6 3.4	1.8 – 4.1 2.6	2.0 – 3.6 2.7	2.6 – 7.0 **4.5**
Total hardness (mg$CaCO_3$ dm^{-3})	231 – 291 258	180 – 270 233	223 – 428 **313**	220 – 390 262
Colour (mg Pt dm^{-3})	2.0 – 8.0 5.2	6.0 – 10.0 7.5	6.0 – 10.0 8.3	6.0 – 12.0 **8.8**

magnesium ions. An equilibrium model has been developed for each of the analysed solution.

The results indicate that today both the Upper Cretaceous and Quaternary groundwaters are close to the state of equilibrium with respect to calcite. Moreover, values of the calculated equilibrium partial pressure of carbon dioxide in both these formations are similar and comprised in the range of p CO_2 -1.5 to -2.5 (Figure 5), which is typical for the soil zone (Małecki, Szostakiewicz 2006, Małecki et al. 2016). Carbon dioxide originates from the soil zone, where meteoric water reaches balance with respect to the gas. As a result, calcium carbonate that is present in the Quaternary deposits of the vadose zone can be dissolved. In the deeper parts, due to the absence of endogenous sources of carbon dioxide, dissolution of calcite practically does not occur (Małecki, Matyjasik 2002).

DISCUSSION

Schematic model of the multi-aquifer system in the spring area

The model construction was created by separating the multi-aquifer system contoured by the boundary surface which corresponds to the boundaries

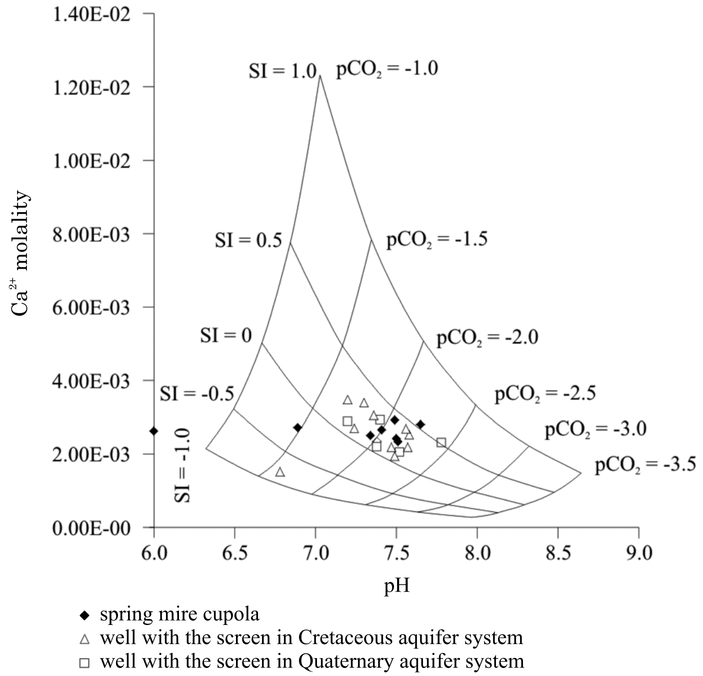

Fig. 5. Groundwater pH vs. Ca^{2+} concentration with theoretical equilibrium curves of calcite saturation index and partial CO_2 pressure (PHREEQC calculation results)

of the recharge area of the springs (Figure 6). The boundary surface of the system thus defined relates to the specified system outputs and inputs that will apply to both the water flow (recharge and drainage of the system) and the potential ability for supplying and removing calcium carbonate. In hydrodynamic terms, part of the boundary surface corresponding to the course of underground watersheds and flow paths contouring the recharge area of the springs can be regarded as closed (no flow boundary). Potential system inputs and outputs can therefore be associated only with its upper and lower boundary surface. Regarding the upper boundary surface, effective infiltration and saturation of groundwater with carbon dioxide (necessary for dissolution of carbonates in the rock mass) can be considered as the potential system input. The system output should be linked with the zones of groundwater discharge to the surface and with possible removal of the dissolved calcium carbonate (chemical denudation).

Thus, the conditions favouring the carbonate sedimentation must have resulted from the transformation of one of the system inputs related to the infiltration recharge (I) or to the intensity of percolation from the deeper aquifers (II) or to the system output (groundwater drainage in the spring mire zone (III) – Figure 6.

It can be assumed that the time variability of system inputs and outputs is a consequence of the time-varying climatic conditions during the Subbore-

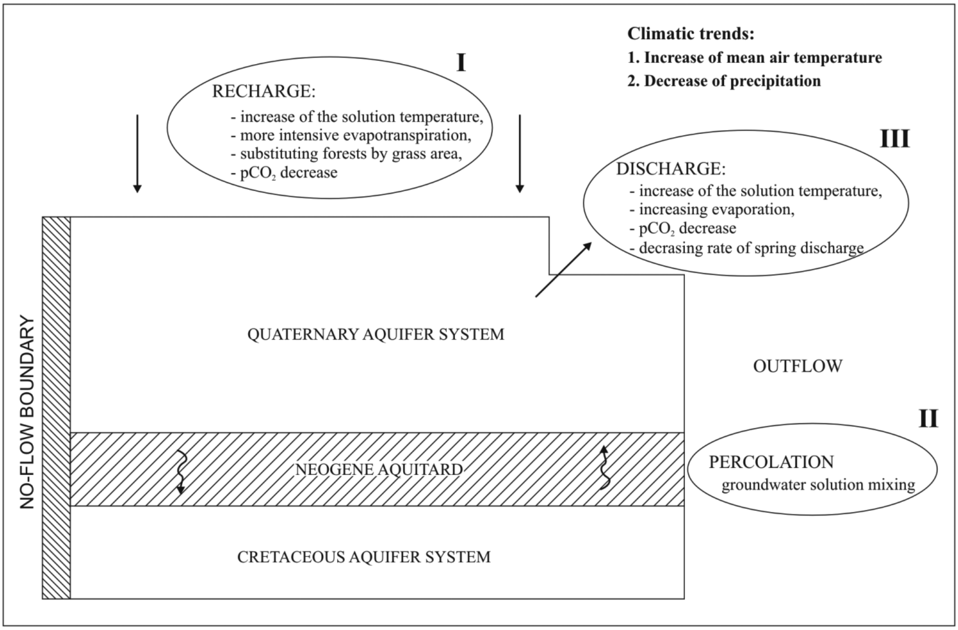

Fig. 6. Schematic model of the multi-aquifer system in the cupola area

al and early Subatlantic periods. In the period of time under consideration, climate changes took place over the territory of today's Poland, inresulting in an increase in the average air temperature and a decrease in total precipitation (Starkel et al. 2013). It is therefore necessary to consider how these changes could have affected the system inputs and outputs, and consequently the conditions of calcareous tufa formation.

Changes in the input system (I) associated with changes in the effective infiltration rate

In the case of decrease in total precipitation, accompanied by an increase in thermal conditions of the air and associated losses due to evaporation, a decrease in effective infiltration took place. Concurrently, weather factors were not conducive to dissolution of carbonates. This resulted partly from an increase in thermal conditions of the solution (decrease in the solubility of calcite with increasing temperature). Thus, it seems that the formation of calcareous tufas in the spring mire zone could result from the transformation of environmental conditions in the system input in its upper part.

Assessment of the system input (II) on the lower boundary surface, i.e. water percolation from the deeper aquifers

The concept that the formation of calcareous tufa is related to the mobilization of water influx from the Upper Cretaceous aquifer seems interesting, especially because the groundwater in this area occurs within carbonate rocks. However, the problem does not arise from the source of calcium carbonate that is present also in Quaternary deposits, but from the ability of its dissolution, which primarily results from the quantity of carbon dioxide dissolved in the water.

The analysed multi-aquifer system is in the hypergenesis zone, and the main source of carbon dioxide is the soil and the plant root zone. Carbon dioxide enters the groundwater along with infiltration water and, until equilibrium is attained, water can dissolve calcium carbonate occurring in sediments. When the equilibrium state is attained, further dissolution of carbon dioxide is not possible. This principle is confirmed also in the case of the system under consideration, as indicated by the lack of significant differences in the chemical composition of the groundwater in the Cretaceous and Quaternary aquifers. Origin of the carbon dioxide from the Cretaceous formations in the studied calcareous tufa is also contradicted by the current hydrodynamic state of the system presented above. Groundwater leakage from the Quaternary system to the Cretaceous system, but not in the opposite direction, is observed in surroundings of the cupola.

For the assessment of changes in the system output (III) in the spring mire zone, the climate change has also been considered as a major factor determining the precipitation of carbonates. As discussed earlier, a warm and dry climate entailed a decrease in the intensity of effective infiltration. In the system output, this resulted in a reduction of spring discharges, even leading to their periodic drying. The drop in the discharge rate entailed prolongation of the residence time of water in the outflow zone, which in turn allowed the solution to equilibrate with the partial pressure of carbon dioxide in the atmosphere. In consequence, the solution became supersaturated with respect to calcium carbonate, which precipitated. The precipitation was obviously also favoured by an increase in the evaporation rate in a warm and dry climate, as well as by the reduction of calcite solubility as the solution temperature increased.

Reconstruction of palaeohydrogeological conditions of the spring mire cupolas formation

The present-day groundwater discharges in the Wardzyń area are related to the contact zone between the moraine upland and the valley depression of a complex origin. The springs form a cluster at the mouths of dry valleys crossing the upland area, near the features identified as spring mire cupolas. Nowadays, the cupolas are no longer the environment of active sedimentation and are being gradually destroyed by erosional processes. The formation of the cupolas should be linked primarily with the Subboreal period, and their sediments are a record of environmental changes during the Holocene. The cupolas are represented by hydrogenic, biogenic (peat) and chemical sediments (calcareous tufa). These sediments can be related to a groundwater environment, and more precisely with the zone of discharge of these waters to the ground surface. The collected results material allow us to make an attempt to reconstruct environmental changes that were controlled primarily by varying climatic conditions.

The oldest sediments of the spring mire cupola are represented by calcareous tufa of series A, which is older than 4,600 years, and its formation can be dated to the end of the Atlantic period (Figure 2.) Carbonate sediments of this series overlie directly fluvial sands of various grain sizes, filling an erosional incision on the continuation of a modern dry valley. It can be assumed that the fluvial sediments provide a record of hydrodynamic conditions in the early Holocene. High total atmospheric precipitation in the Atlantic period resulted in a higher infiltration recharge rate in the multi-aquifer system as compared to the present-day level. In consequence, active groundwater outflow zones in the form of surface watercourses were displaced toward the upland area. This is confirmed by the course of the recently abandoned valleys and by the sediments that fill them.

At that time, the environmental conditions did not favour the formation of spring mire sediments in the area currently occupied by the cupolas. High dynamics of the river flow made the valley to be filled predominantly with detrital material. At the end of the Atlantic period, there was a dramatic change in climate conditions. Total atmospheric precipitation decreased, which was accompanied by an increase in the air thermal conditions (Dobrowolski et al. 2002). This entailed a decrease in the infiltration rate, which must have resulted in the lowering of the groundwater table level. Watercourses that followed the valley depressions in the upland area died out successively. Nevertheless, at the foot of the upland, the groundwater table can be found at a shallow depth close to the ground surface and, at least temporarily, the springs or soligenic swamps exist in this area.

Because of the low flow dynamics, the chemical composition of groundwater drained by the springs was balanced with the atmospheric partial pressure of carbon dioxide within a short distance from the outflow zone. As a result, the solution becomes supersaturated with respect to calcite that begins to precipitate *inter alia* on the surface of plants, forming the oldest calcareous tufa horizon. A significant contribution to this process is made by the increased evaporation, which is also favoured by the southern exposure of the slope. At that time, oxidizing conditions dominated in the outflow zone, as indicated by the total absence of pyrite and the products of its oxidation in the sediments.

About 4,600 years BP, the climate became more humid again (Starkel et al. 2013). The effective infiltration rate increased, causing a rise in the groundwater level in the shallow aquifer. The groundwater discharge rate increased in the neighbourhood of the cupolas. As a result, the contact time of the solution with the atmospheric air became shorter and the solution could not be equilibrated with the partial pressure of carbon dioxide immediately in the outflow zone. This gave rise to the environment favouring the development of plant successions, and the oldest peat layer was formed under anaerobic conditions. Partial rejuvenation of river valleys in the upland area also took place at that time, as evidenced by a a high content of terrigenous material in the peats.

Another change in climate humidity was gradual and oscillatory. Flow rates in the outflow zone changed over time, alternately favouring peat accumulation and calcium carbonate precipitation. Initially, deposition of sediments that show a nature of rhythmite took place. The sediments eventually turned into calcareous tufa of series B. The formation of this level of calcareous tufa can be correlated with the cessation of peat deposition in the North Podlasie Lowland and in the Świętokrzyskie Mountains, which took place about 4,000 years BP (Oświt 1973, Żurek et al. 2002). This was also a time when a decrease in the share of pollen of humid habitat plants was reported in the Łódź region (Krąpiec 2001). The accumulation of organic matter meant that, with a higher water level, reducing conditions prevailed in the outflow zone. This is evidenced by a high content of pyrite in the sediment. Periodically, the flow stopped and atmospheric oxygen was supplied to the sediment as a result of a decline in the groundwater level, which favoured the oxidation of pyrite into gypsum.

Another humid period occurred at about 3,400 years BP (Starkel et al. 2013). This is recorded within the cupolas in the peat layer overlying the calcareous tufa of series B (Figure 2). These deposits can be correlated with the oldest period of heavy floods marked in alluvial sediments in the territory of Poland. After a period of increased frequency of extreme atmospheric precipitation events, there was another dry period. Within the cupolas, the calcareous tufa horizon of series C was being formed at that time (Figure 2). As in the case of series B, redox conditions of the environment in the outflow zone favoured the formation of pyrite. Outflows of groundwater are ephemeral at that time, and the temporary lowering of the groundwater table promoted the oxidation of pyrite into gypsum. The absence of gypsum in the top part of the calcareous tufa of series C indicates a gradual increase in climate humidity. Around 3,200 years BP, the total precipitation values were already so high that conditions favourable for the deposition of the next peat layer appeared. This layer can be also correlated with a period of heavy floods, recorded in alluvial sediments of Poland (Dobrowolski 2011).

A subsequent decrease in climate humidity favoured the formation of the youngest calcareous tufa horizon (series D) – Figure 2. The conditions facilitating calcium carbonate precipitation dominated from approximately 3,100 to about 2,800 years BP. However, at that time, despite a remarkable reduction in the discharge rate in the outflow zone, such frequent drying events as in the older calcareous tufa horizons were no longer observed. Despite the widespread presence of pyrite, gypsum occurs only occasionally and in small amounts in the sediment.

In the Subatlantic period, conditions favouring the formation of calcareous tufa disappeared. The cupola region was covered by an alder forest, and the rush-wood peat was being formed. Currently, the cupolas are no longer an environment of active hydrogenic sedimentation. The lowering of the local erosional base due to drainage engineering operations results in the destruction of the cupolas by erosion caused by flowing waters, while the top parts of the peat are subjected to mineralization.

CONCLUSIONS

The mutual relationships of peat layers and successive series of calcareous tufa documents the changes in humidity conditions resulting from periodic climate changes. The analysis of material gathered for this study shows that the sedimentation within the cupola depended directly on the flow dynamics in the outflow zone, and resulted from the hydrodynamic state of the multi-aquifer system in the neighbourhood of the springs. The features of chemical sediments within the cupola, especially their mineral composition and quantitative relationships between sulphur minerals, indicate an ephemeral nature of the springs in the past. The index proposed in the article, specifying the mutual quantitative relation between gypsum and pyrite in the sediment, has proven to be a useful tool to reconstruct humidity conditions. The peat, which accompanies the calcareous tufa, has allowed dating of the sediment by the radiocarbon method and reconstructing the chronology of events. All this makes that the spring mire cupola is an excellent research object for both palaeoclimate and palaeohydrogeologic reconstructions of late Holocene events.

The authors are aware that the results presented in this article are preliminary and therefore the research will be continued. Especially interesting data can be achieved from the planned studies on the isotopic composition of groundwater. Nevertheless, the material collected so far, according to the authors, has justified the formulation of the above conclusions at this stage of work.

REFERENCES

Dobrowolski R., Alexandrowicz S.W., Bałaga K., Burakiewicz T., Pazdur A. 1999. *Studies of tufa within spring cupola peatbogs in eastern Poland*. In: *Geochronology of the upper quaternary in Poland in the light of radiocarbon and luminescence dating*. A. Pazdur (ed.) Wrocław, 179-197. (in Polish)

Dobrowolski R., Durakiewicz T., Pazur A. 2002. *Calcareous tufas in the soligenous mires of eastern Poland as an indicator of the Holocene climatic changes*. Acta Geol. Pol., 52(1): 63-73. https://geojournals.pgi.gov.pl/agp/article/view/10065/8595

Dobrowolski R. 2011. *Problems with classification of deposits of spring-fed fens*. Stud. Lim.

Tel., 5(1): 3-12. (in Polish) http://www.paleolim.amu.edu.pl//SLETT/slett 05 1/slett 05_1_pp_03-12.pdf

Dobrowolski R., Pidek I.A., Alexandrowicz W.P., Hałas S., Pazdur A., Piotrowska N., Buczek A., Urban D., Melke J. 2012. *Interdisciplinary studies of spring mire deposits from Radzików (South Podlasie Lowland, East Poland) and their significance for palaeoenvironmental reconstructions*. Geochronometria, 39(1): 10-29. DOI: 10.2478/s13386-011-0052-3

Krąpiec M. 2001. *Holocene dendrochronological standards for subfossil oaks from the area of Southern Poland*. SQ, 18: 47-63. http://www.studia.quaternaria.pan.pl/toc/vol_18/005.html

Oświt J. 1973 *Conditions of mires development in lower Biebrza Valley versus hydrological condition)*. Rocz. Nauk Rol., Ser. D, Monografie, 143: 1-80. (in Polish)

Parkhurst D.L. 1995. *User's guide to PHREEQC--A computer program for speciation, reaction -path, advective-transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations*. Report 95-4227: 143 p.

Małecki J., Matyjasik M. 2002. *Vadose zone – challenges in hydrochemistry*. Acta Geol. Pol., 52(4): 449-458. https://geojournals.pgi.gov.pl/agp/article/view/10047/8577

Małecki J., Szostakiewicz M. 2006. *The role of evapotranspiration in the formation of the chemical composition of shallow groundwater (the Polish Tatras*). Acta Geol. Pol., 56(4): 485-492. https://geojournals.pgi.gov.pl/agp/article/view/10247/8769

Małecki J., Kadzikiewicz-Schoeneich M., Szostakiewicz-Hołownia M. 2016. *Concentration and mobility of copper and zinc in the hypergenic zone of a highly urbanized area*. Environ Earth Sci., 75: 1-13. DOI: 10.1007/s12665-015-4789-5

Mazurek M., Dobrowolski R., Osadowski Z. 2014. *Geochemistry of deposits from spring-fed fens in West Pomerania (Poland) and its significance for palaeoenvironmental reconstruction*. Quatern. Geomorphol., 20(4): 323-342. DOI: 10.4000/geomorphologie.10765.

Schoonen, M.A.A., Barnes, H.L. 1991. *Reactions forming pyrite and marcasite from solution: II. Via FeS precursors below 100°C*. Geochim. Cosmochim. Acta, 55: 1505-1514. DOI: 10.1016/0016-7037(91)90123-M

Starkel L., Michczyńska D., Krąpiec M., Margilewski W., Nalepka D., Pazdur A. 2013. *Progress in the Holocene chrono-climatostratigraphy of Polish territory*. Geochronometria, 40(1): 1-21. DOI: 10.2478/s13386-012-0024-2

Ziułkiewicz M., Okupny D., Forysiak J., Fortuniak A. 2012. *Conditions of functioning of spring-fed bogs in the southern part of the* Łódź *Hills*. Czas. Geogr., 3-4: 175-196. https://www.researchgate.net/publication/289237338_Conditions_of_functioning_of_spring-fed_bogs_in_the_southern_part_of_the_Lodz_Hills

Żurek S., Michczyńska D., Pazdur A. 2002. *Time record of palaeohydrologic changes in the development of mires during the late glacial and holocene, north Podlasie Lowland and Holy Cross Mts*. Geochronometria, 21: 109-118. http://www.geochronometria.pl/pdf/geo_21/geo21_13.pdf