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Post-glacial acidification of two alpine lakes (Sudetes Mts., SW Poland), as inferred from diatom analyses

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ABSTRACT. Past environmental changes in mountain lakes can be reconstructed with the use of subfossil diatoms from post-glacial sediments. This study applied such an analysis to two mountain lakes in the Sudetes Mts. in Poland: Mały Staw (MS) and Wielki Staw (WS). Cores 882 cm long (MS) and 1100 cm long (WS) taken from the centre of each lake in 1982 were used to study the long-term acidification history of these lakes. Changes in vegetation indicate that the initial phase of MS started at the end of the Pleistocene. WS sediments began to accumulate shortly after that, at the beginning of the Holocene. The majority of the diatom assemblages are typical of oligotrophic acidic lakes located in alpine and arctic regions. A pH reconstruction based on diatoms (DI-pH) showed long-term acidification dating to almost the beginning of the lakes' existence. Natural acidification began after the deglaciation, and the most intensive acidification continued to the end of the mid-Holocene. Through the whole period studied, pH decreased by 1.4 in MS and 0.9 in WS. After a period of relatively stable lake water pH, it decreased rapidly during the last few decades of the 20th century, due to anthropogenic pollution: pH declined by 0.7 in MS and 0.3 in WS. Mały Staw, being shallower, smaller, and with a larger drainage basin than Wielki Staw, is more sensitive to acid deposition; this accounts for the difference in pH.

KEYWORDS: diatoms, long-term acidification, alpine lakes, Holocene, Sudetes Mountains

INTRODUCTION

Sediments of high mountain lakes are of great interest in paleolimnological research because such lakes are subject to extreme climatic and physicochemical conditions. Typically these high mountain oligotrophic ecosystems are sensitive to environmental changes. Even small fluctuations of climate can cause large changes in the biotic community (Rosén et al. 2001). Since the second half of the 20th century, surface-water acidification has become a significant ecological problem, and many lakes in Europe and North America have been classified as anthropogenically acidified waterbodies (e.g. Curtis et al. 2002, Marchetto et al. 2004, Battarbee et al. 2005). Intensive industrial development has been responsible for much of this increase in acidification. In several cases, geochemical and palaeobiological analyses of surface sediments have implicated air pollution as causing changes in lake ecosystems. However, recovery from acidification has been observed in some lakes in the last few decades (Larsen et al. 2006, Battarbee et al. 2008). A recent approach to lake acidity considers multiple factors, such as continued soil acidification during the post-glacial period, bedrock type, vegetation type, and changes in a lake's catchment, such as changes in base cation status (Battarbee et al. 2010). An analysis of long-term acidification can be aided by a more precise determination of some lake ecosystem processes. For example, it can be checked whether low water pH recorded recently is an effect of acid deposition and/or long-term natural processes (e.g. Renberg 1990, Battarbee et al. 2010); it can be shown whether long-term acidification has an influence on reduced catchment alkalinity, causing a lake to become more sensitive to acid deposition impacts (e.g. Battarbee 1990); and the extent and rate of earlier acidification can be compared with recent changes of pH (e.g. Ford 1990).

This study examined the Holocene evolution of Mały Staw and Wielki Staw lakes, and in particular their long-term acidification history, based on the record of subfossil diatoms. These algae are used as indicators of changes in environmental parameters such as pH, trophy, salinity, pollution, and water level (Shinneman et al. 2009). In these studies, diatoms have been employed mainly as markers of past acidity. The post-glacial acidification trends inferred from fossil diatoms have been studied in Europe since the second half of the 20th century (e.g. Nygaard 1956, Renberg & Hellberg 1982, Atkinson & Haworth 1990). Research aimed at estimating the extent of acidity from post-glacial sediments encompassing the entire Holocene has not been done so far in Poland.

Mały Staw (MS) and Wielki Staw (WS) are oligotrophic mountain lakes, classified as acidified waterbodies, located in the Karkonosze Massif (Sudetes Mountains, SW Poland). The lake waters are acidic due to both natural conditions and documented human impacts. The studied lakes are in one of Europe's most polluted regions, called the Black Triangle (Fig. 1), where the borders separating Poland, Germany and the Czech Republic converge.

Numerous analyses of both lakes have been performed. Many of them concern the chemistry of the lake water and precipitation (e.g. Kurzyca et al. 2005, Rzychoń & Worsztynowicz 2007) and the relative abundance of phyto- and zooplankton (e.g. Eloranta & Kwandrans 2002, Vrba et al. 2008). Samples of sediments from these lakes that accumulated during the last millennium were analysed by Sienkiewicz et al. (2006). Some researchers have analysed long cores from Mały Staw and Wielki Staw lakes spanning the entire Holocene. Palaeolimnological studies by Wicik (1984, 1986) and Boryczka et al. (1988) involved sedimentological analyses and reconstructions of Holocene climate cycles. The few palaeobiological analyses of Holocene sediments that have been done include studies of Cladocera remains

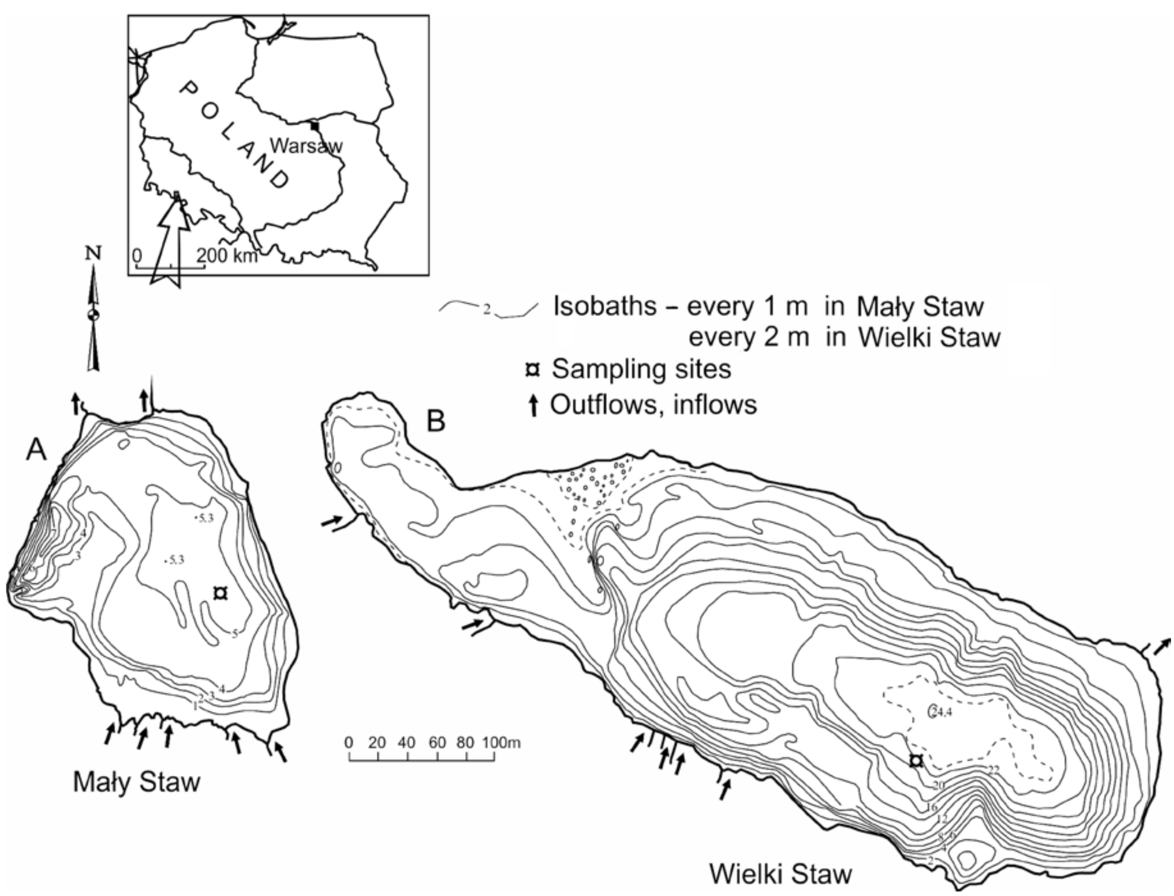

Fig. 1. Location and bathymetry of Mały Staw (**A**) and Wielki Staw (**B**) lakes

(Szeroczyńska 1993), diatoms (Sienkiewicz 2005), and pollen (Madeyska 2007 unpubl.).

Mały Staw and Wielki Staw lakes are located in glacial cirques in the north-eastern part of the Karkonosze Massif (Tab. 1). Their origin is related to local mountain glaciers present during the last glaciations. The Karkonosze Mts. are built of Variscan granite of various types, and Proterozoic metamorphic rock in minor parts of the massif (Kryza et al. 1997). This means that the bedrock is poorly buffered. The amount of alkali mobilised in the surface zone during chemical weathering is too low to neutralise natural and anthropogenic acidification. Acidic podzols, gley soils and initial mountain soils have developed from these rock types (Wicik 1986, Kalisz et al. 2007). Mały Staw's catchment area is forested with spruce, mountain ash and bird cherry. Dwarf-pine shrub surrounds Wielki Staw. The climate of the study area is typical for high mountain regions of Europe, with cold, short summers (mean July temperature +15°C) and long winters (mean January temperature –5°C). Snow cover lasts between 70 and 180 days annually.

Table 1. Location and selected environmental parameters of Mały Staw and Wielki Staw lakes

Parameter	Mały Staw	Wielki Staw
Latitude	50°44.57′N	50°45.30′N
Longitude	15°42.03′E	15°41.40′E
Elevation (m a.s.l.)	1183	1225
Area (ha)	2.88	8.32
Catchment area (km^2)	1.734	0.580
Max depth (m)	7.3	24.2
Secchi depth (m)	2.5	5.5
pH*	6.2	5.2
Conductivity (μS/cm)*	13	13
Dissolved oxygen (mg/dm^3)*	8.28	8.26
ANC (mmol/l)**	10	–8
TOC (mg/l)**	4.54	2.30
TP (μg/l)**	9.6	5.1
TON (mg/l)**	0.40	0.42

* measured in July 2002
** according to Vrba et al. (2008)

MATERIALS AND METHODS: CORING, LITHOLOGY, AND CHRONOLOGY

Sediment cores (882 cm from Mały Staw, 1100 cm from Wielki Staw) were collected in 1982 from the central part of each lake using a Więckowski piston corer. The cores were divided into 5 cm sections. The stratigraphy of the Holocene sediments is based on palynological analysis (Madeyska 2007 unpubl.). On the basis of pollen data, the periods distinguished in the sediments of Mały Staw lake are the Younger Dryas (YD), Preboreal (PB), Boreal (BO), Atlantic (AT), Subboreal (SB), and Subatlantic (SA); the sediments of Wielki Staw lake span the period from the Preboreal to the Subatlantic. Mały Staw's sedimentation began during the Younger Dryas, with a mean sedimentation rate of 0.75 mm year^{-1} for the whole core based on an age-depth model. Wielki Staw's sedimentation began later, at the end of the Preboreal, with a higher mean sedimentation rate for the sequence (1.12 mm year^{-1}). The biostratigraphic zones were correlated with radiocarbon dating from fragments of Norway spruce or dwarf pine (Tab. 2). Measurements of ^{14}C activity were made at the Institute of Physics, Silesian University of Technology (Gliwice, Poland). Radiocarbon dates were calibrated using Oxcal ver. 3.10 (Bronk Ramsey 2001). The core material consists mainly of gyttja, with interbedding of sand, silt, clay, and organic matter.

DIATOM ANALYSIS

Samples for diatom analysis were prepared according to Battarbee et al. (2001). Samples (1.5 g) were heated with 30% H_2O_2 until the organic matter was completely oxidised. Permanent slides were made with the use of Naphrax® (RI = 1.75). In each sample, ca 400 valves were counted using an Olympus BX40 light microscope with a 100× oil-immersion objective. Diatom taxonomy mainly follows Krammer and Lange-Bertalot (1986, 1988, 1991a,b) and Lange-Bertalot & Metzeltin (1996). Data from AlgaeBase (www.algaebase.org) were used for more recent diatom nomenclature. The results were plotted as percentage diagrams on a depth scale. The diatom local zones were defined based on classical clustering, and the significance of zones was validated by one-way analysis of similarity (ANOSIM) using

Table 2. Radiocarbon dating of sediments from the Mały and Wielki Staw lakes

Lake and sample symbol	Depth (cm)	Material dated	^{14}C yr BP	Age ranges
Mały Staw (MS 340)	340	Norway spruce	4983 ± 140	6000–5300 cal yr BP
Mały Staw (MS 800)	800	dwarf pine	9450 ± 210	11250–10150 cal yr BP
Wielki Staw (WS 670)	670–680	dwarf pine	5400 ± 90	6400–5940 cal yr BP
Wielki Staw (WS 980)	980–985	dwarf pine	7880 ± 150	9150–8350 cal yr BP

Euclidean distance and 9999 permutations (Clarke 1993). Both analyses were done with PAST ver. 3.10 (Hammer et al. 2001).

DIATOM-INFERRED PH (DI-PH)

The reconstruction of pH (DI-pH) from the sediments of both studied lakes was based on the AL:PE dataset for pH (Cameron et al. 1999). Of the total 183 diatom taxa recorded from the Mały Staw sediments, 101 taxa had >1% shares and more than 3 occurrences in the sample. Of the total 107 diatom taxa recorded from the Wielki Staw sediments, 82 had >1% shares and more than 3 occurrences in the sample. Only these regularly occurring taxa were used for pH reconstruction. The root mean square error of prediction (RMSE = 0.36 units pH) and the highest coefficient of correlation ($r^2 = 0.85$) were calculated using weighted-average (WA) regression and calibration with classical deshrinking (Birks et al. 1990). Both reconstructions were implemented using ERNIE ver. 1.0 (Juggins 2001).

RESULTS

DIATOM STRATIGRAPHY IN THE SEDIMENTS OF MAŁY STAW LAKE

In the Mały Staw core, six Diatom Assemblage Zones (DAZ: DMS 1–DMS 6) were distinguished based on changes in the diatom community (Fig. 2). The similarity indices showed that the diatom zones were statistically significant ($p = 0.0001$, $R = 0.72$). A total of 183 diatom taxa (30 genera) were recognised in the sediment sequence. The most abundant taxa included *Aulacoseira* spp., *Achnanthes* sensu lato, *Sellaphora seminulum* (Grun.) Mann, and *Naviculadicta schmassmanii* (Hust.). Ecologically indifferent taxa dominated in the sediment, comprising 24% to 78% of all taxa. The share of acidophilous diatoms varied between 0.5% and 70%. The share of alkaliphilous taxa ranged between 3% and 50%, while acidobiontic diatoms constituted up to 6.5% of the sample. Alkalibiontic taxa were not found.

DMS 1 (882–860 cm; Younger Dryas)

This zone contained only a few diatom taxa. The taxa occurring most frequently in the core were *Achnanthidium minutissimum* (Kütz.) Czarnecki, *Encyonema gaeumanii* (Meister) Krammer, *Naviculadicta digitulus* (Hust.) Lange-Bertalot & Metzeltin, and *N. schmassmanii*.

DMS 2 (860–740 cm; Preboreal–early Atlantic)

DMS 2 showed a rapid decrease in the dominant taxa of the previous zone. The lower part of the zone was dominated by *Fragilaria* sensu lato, *Psammothidium curtissimum* (Carter) Aboal, and *Sellaphora seminulum*, followed by an increase of *Aulacoseira alpigena* (Grun.) Krammer and *A. italica* (Ehrenb.) Simonsen.

DMS 3 (740–420 cm; middle-late Atlantic–middle Subboreal)

The main diatoms in DMS 3 were *Aulacoseira alpigena* and *A. italica*. Some benthic species declined (e.g. *Navicula* sensu lato, *Fragilaria* sensu lato). The upper part of the zone was marked by a decrease of *Aulacoseira italica*, accompanied by a considerable increase of *A. alpigena*.

DMS 4 (420–240 cm; middle Subboreal–early Subatlantic)

This zone showed an increase of *Aulacoseira lirata* (Ehrenb.) Ross., and a decline of *A. alpigena* and *A. italica*. Peaks in the abundance of some acidophilous taxa (e.g. *Eunotia incisa* Gregory, *Tabellaria flocculosa* (Roth) Kützing, *Pinnularia polyonca* (Bréb.) W. Smith) were also noted.

DMS 5 (240–60 cm; middle Subatlantic)

This zone was dominated by *Aulacoseira alpigena* and *A. lirata*. This sediment sequence contained the first appearance of indifferent *Cavinula cocconeiformis* (Greg.) Mann & Stickle and *C. intractata* (Hust.) Lange-Bertalot. A small increase of benthic *Psammothidium* spp. (e.g. *P. acidoclinatum* Lange-Bertalot, *P. curtissimum*, and *P. helveticum* (Hust.) Bukht. & Round) was noted.

DMS 6 (60–0 cm; late Subatlantic)

DMS 6 showed the maximum abundance of *Aulacoseira lirata* (up to 40% at 50 cm) and an increase in the frequency of *Tabellaria flocculosa*. In the uppermost sediments of this zone, *Eunotia* spp. and *A. lirata* decreased.

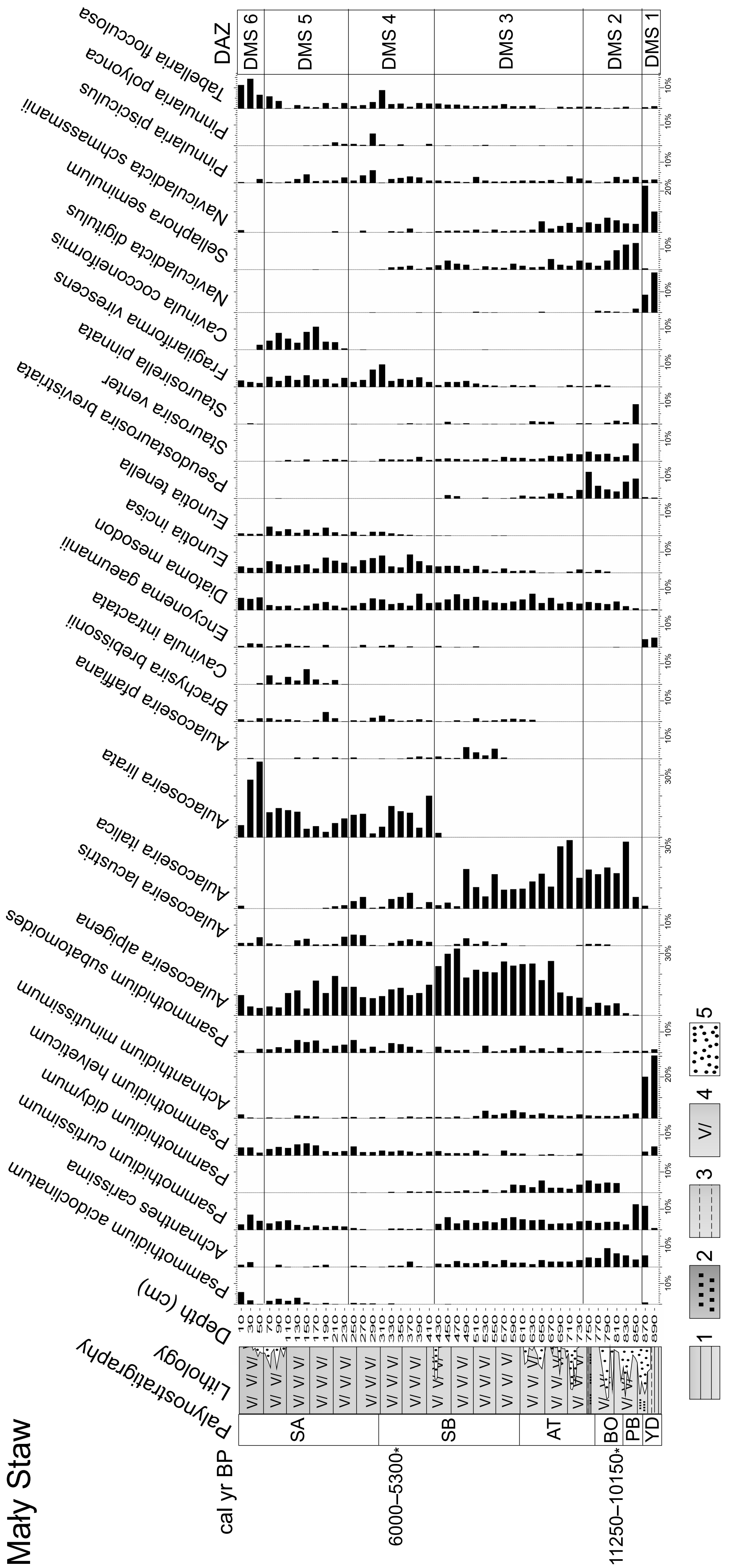

Fig. 2. Relative frequency of the most dominant diatom taxa (>5% in any one sample) recorded in sediment of Mały Staw. Lithology: **1** – clay, **2** – sand, **3** – silt, **4** – gyttja, **5** – sandy inter-bedding. Palynostratigraphy: **YD** – Younger Dryas, **PB** – Preboreal, **BO** – Boreal, **AT** – Atlantic, **SB** – Subboreal, **SA** – Subatlantic

DIATOM STRATIGRAPHY IN THE WIELKI STAW SEDIMENTS

In the Wielki Staw core, four Diatom Assemblage Zones (DAZ: DWS 1–DWS 4) were distinguished on the basis of changes in the diatom community (Fig. 3). As with the sediments of Mały Staw, the zonation was statistically significant ($p = 0.0001$, $R = 0.65$). Altogether, 107 diatom taxa belonging to 20 genera were identified. The most abundant taxa were *Aulacoseira* spp., *Psammothidium curtissimum*, *Brachysira brebissonii* Ross, and *Tabellaria flocculosa*. Most of the diatoms in these lake sediments were acidophilous (18.5–87.5%). The shares of indifferent taxa varied between 7% and 71.5% in the core, and up to 13% of the diatoms were acidobiontic. Alkaliphilous diatoms did not exceed a 9.5% share, and alkalibiontic forms were not found.

DWS 1 (1100–1045 cm; Preboreal)

The most frequent diatom taxa in DWS 1 were *Aulacoseira italica*, *Pseudostaurosira brevistriata* (Grunow in Van Heurck) D.M. Williams & Round, *Achnanthidium minutissimum*, *A. carissima* Lange-Bertalot, and *Tabellaria fenestrata* (Lyngb.) Kützing. An abundance of *Tabellaria flocculosa* and *Psammothidium curtissimum* was also found.

DWS 2 (1045–820 cm; Boreal–middle Atlantic)

Aulacoseira distans and *Psammothidium curtissimum* dominated this zone. *Encyonema gaeumannii* reached its maximum frequency in this zone. *Aulacoseira italica* rapidly declined. *Aulacoseira alpigena*, *Eunotia rhomboidea* Hustedt, and *E. tenella* (Grun.) Hustedt appeared in the lower part of the zone. In the middle part, tychoplanktonic *Aulacoseira pfaffiana* (Reinsch) Krammer was observed for the first time. An increase of the frequency of *Eunotia* taxa [e.g. acidobiontic *E. paludosa* var. *paludosa* Grunow, acidophilous *E. pectinalis* (Kütz.) Rabenhorst, *E. nymanniana* Grunow, *E. incisa*] was noted.

DWS 3 (820–110 cm; middle Atlantic–early-middle Subatlantic)

The frequency of *Aulacoseira pfaffiana* was higher in DWS 3 than in the previous zone. *A. alpigena* and *Frustulia saxonica* Rabenhorst increased in the middle of the zone and then gradually decreased. *Brachysira brebissonii*, *Encyonema gaeumannii*, *Eunotia incisa*, and *Tabellaria flocculosa* showed relatively constant occurrence.

DWS 4 (110–0 cm; late Subatlantic)

The zone was characterised by an increase of *Psammothidium acidoclinatum*. *Tabellaria flocculosa* and *Brachysira brebissonii* also had large frequencies. *Aulacoseira alpigena*, *A. distans*, and *A. pfaffiana* decreased.

RECONSTRUCTION OF pH (DI-pH) FROM THE MAŁY STAW AND WIELKI STAW SEDIMENTS

The reconstructed pH of the Mały Staw sediments (Fig. 4A) ranged between 7.1 at 850 cm depth and 5.7 at 310 cm depth. Diatom-inferred pH declined by 1.4 pH units along the core. The bottom of the core (882–850 cm) showed an increase of pH by 0.5 units (pH 6.6→7.1). The biggest decrease of pH, by 1.0 units, occurred between 850 cm and 570 cm (pH 7.1→6.1). The next period of pH variation was from 570 cm to 0 cm. The pH curve was more or less stable, falling by 0.4 units from 6.1 to 5.7. There was 82–97% agreement between the fossil taxa from the MS sediments used for pH reconstruction and the modern training set.

The pH of the Wielki Staw sediments (Fig. 4B) varied between 6.4 (1085 cm depth) and 5.5 (710, 290, 230, 65, 25 cm depths). Over the whole studied core, DI-pH declined by 0.9 units. From 1100 cm to 1085 cm it increased slightly from 6.3 to 6.4. From 1085 cm to 710 cm, DI-pH declined from 6.4 to 5.5. In the remaining sediments the pH value was relatively stable, fluctuating by 0.3 within the range 5.8–5.5. Between 72% and 96% of the diatoms from the WS sediments used for pH reconstruction are in the modern calibration dataset.

DISCUSSION

The majority of subfossil diatom assemblages occurring in Mały Staw and Wielki Staw lakes are typical of the clear, oligotrophic acidic lakes of alpine and arctic regions (Laing et al. 2002, Marchetto et al. 2004). These two waterbodies differ mainly in their hydrochemistry, morphometry, and drainage basins. Mały

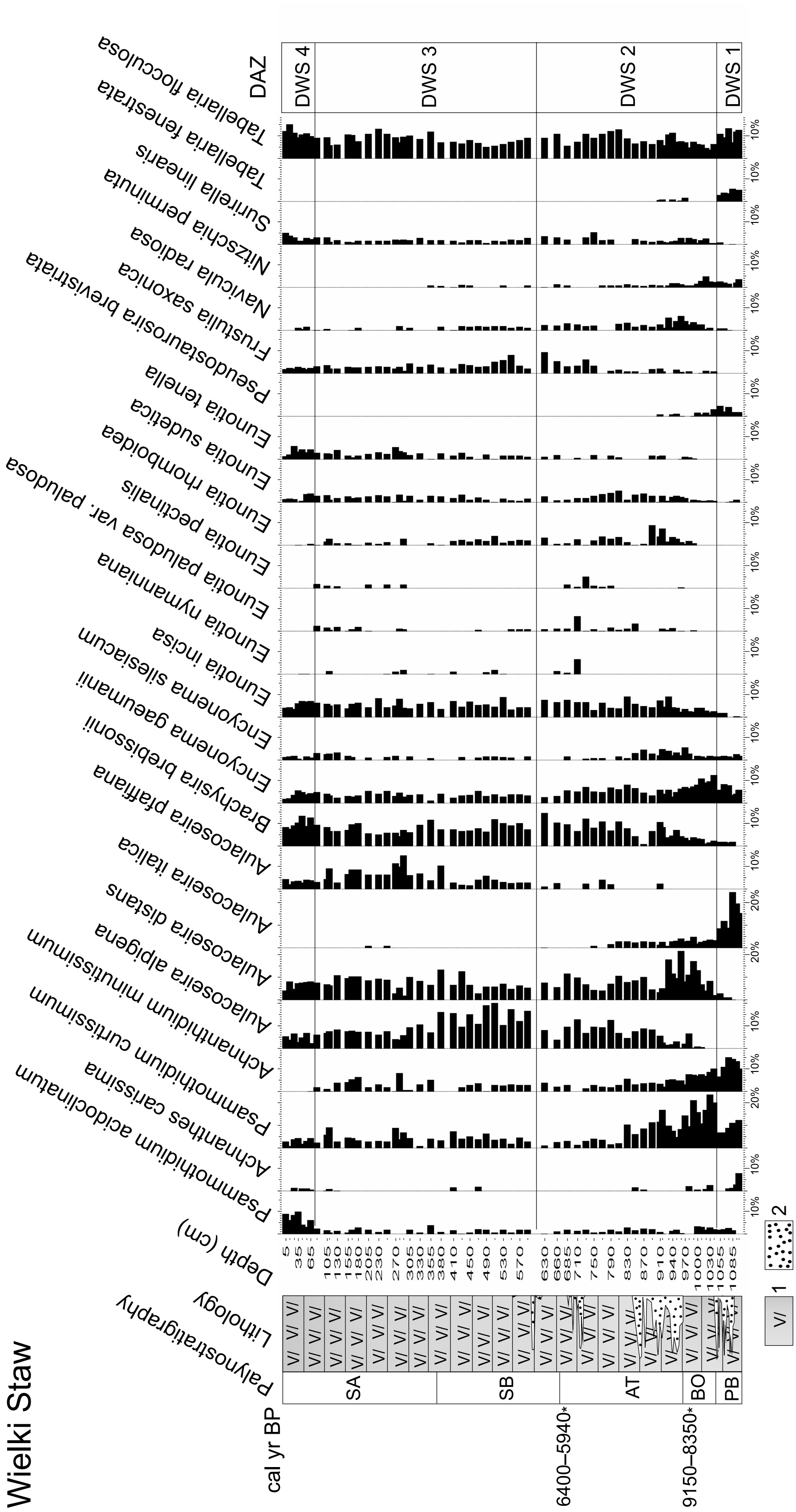

Fig. 3. Relative frequency of the most dominant diatom taxa (>5% in any one sample) recorded in sediments of Wielki Staw. Lithology: **1** – gyttja, **2** – sandy interbedding. Palynostratigraphy: **PB** – Preboreal, **BO** – Boreal, **AT** – Atlantic, **SB** – Subboreal, **SA** – Subatlantic

Staw is smaller and shallower but its catchment area is almost three times greater than Wielki Staw's catchment. Benthic diatom flora dominated at the beginning of these lakes' existence. Probably the waterbodies were not deep enough for other taxa to develop. With time the frequency of tychoplanktonic diatoms increased. Only a few planktonic species were found in the Mały Staw sediments. The lack of typical diatom plankton in the Wielki Staw sediments probably was due to lower water pH (Koinig et al. 1998). Most of the diatoms in Mały Staw were indifferent taxa, with less than a 3% share of eutrophic species such as *Aulacoseira granulata* and *Asterionella formosa* (not shown in Fig. 2). Analyses of hydrochemistry (Vrba et al. 2008) and diatom communities suggest higher trophy in Mały Staw than in Wielki Staw, trending towards oligo-mesotrophy.

Except for a very short episode of increased water pH in the Preboreal, the diatom-inferred pH curves of both lakes indicate a trend of acidification up to around the end of the Subboreal in Mały Staw and the end of the Atlantic in Wielki Staw (Fig. 4A, B). From that time to the end of the studied period (1980s), DI-pH indicates small fluctuations in both lakes. Generally, an increase of natural acidification began in the early post-glacial period. Probably this change is related to the development of acidic organic soils, a result of the vegetation transitioning from arctic tundra to forest (Battarbee 1990).

The development of vegetation suggests that the initial phase of lake formation took place at the end of the Pleistocene for Mały Staw and at the beginning of the Holocene for Wielki Staw (Madeyska 2007 unpubl.).

At the Younger Dryas-Holocene transition, only a few benthic diatom taxa (e.g. *Achnanthidium minutissimum*, *Naviculadicta digitulus*, *N. schmassmanii*) dominate in the Mały Staw sediments. The occurrence of these taxa

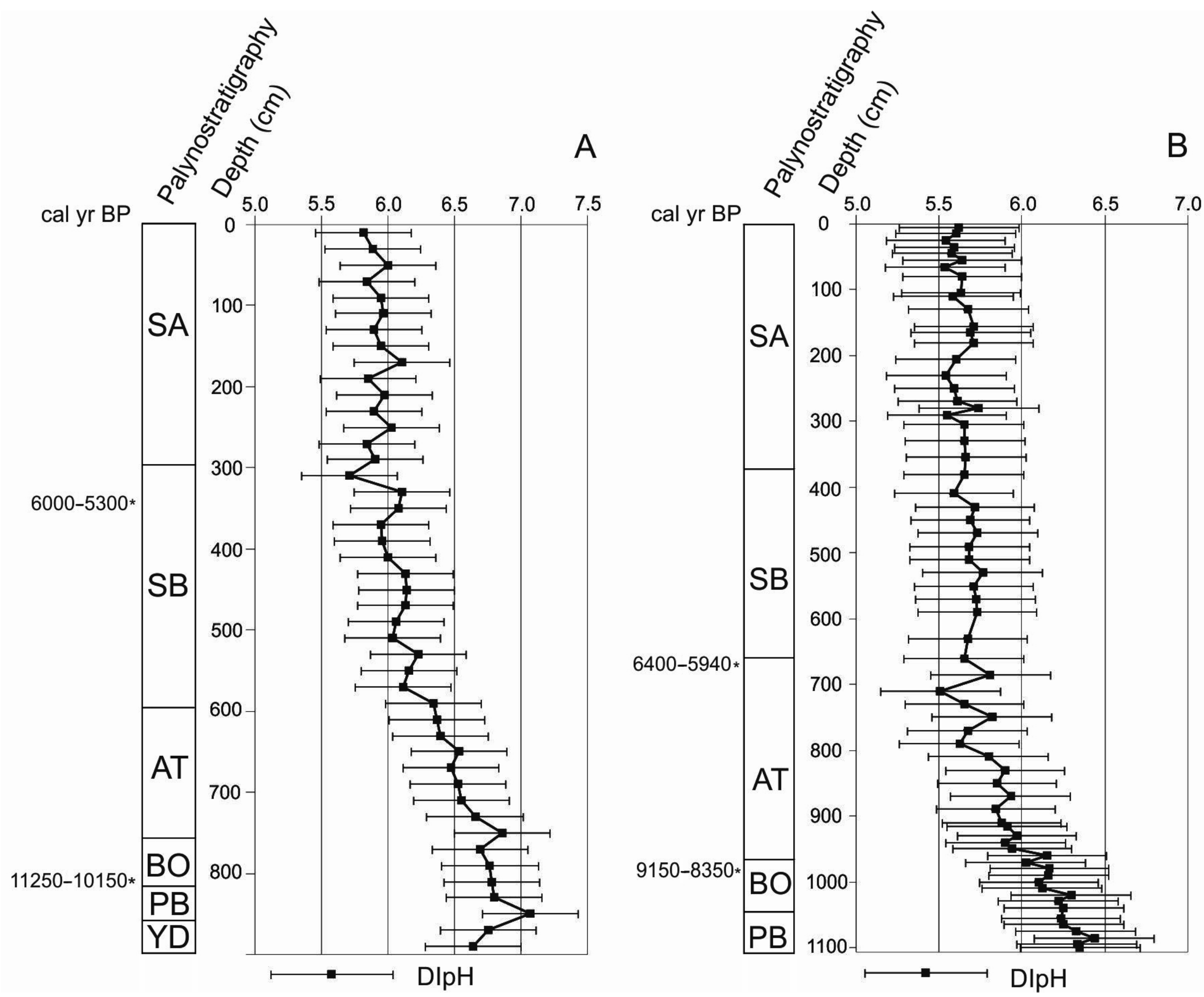

Fig. 4. Diatom-inferred pH (DI-pH) for Holocene sediments of Mały Staw (**A**) and Wielki Staw (**B**) lakes. Palynostratigraphy: **YD** – Younger Dryas, **PB** – Preboreal, **BO** – Boreal, **AT** – Atlantic, **SB** – Subboreal, **SA** – Subatlantic

suggests that the lake was shallow and nutrient-poor in this period. Pollen analyses indicate the initial spread of forest-tundra communities dominated by pine and birch (Madeyska 2007 unpubl.). In the sediment from the beginning of the Holocene (DMS 2; DWS 1), small *Fragilaria* sensu lato taxa appeared; they are species typically occurring in sediments after deglaciation (Weckström et al. 2006), indicating unstable physical and/or chemical conditions. These taxa are often found in cold environments such as arctic tundra lakes and shallow nutrient-poor waterbodies, where they can thrive under a short growing season with prolonged lake-ice cover (Rühland et al. 2003). The development of tychoplanktonic *Aulacoseira* spp. requires water turbulence and/or high water levels for suspension in the water column (Köster & Pienitz 2006). The frequency of these algae can be spurred to increase by intense water mixing and/or a rise in the lake's level (DMS 2–DMS 3, Preboreal-middle Subboreal; DWS 1–DWS 2, Preboreal-middle Atlantic). The maximum occurrence of alkaliphilous taxa (>50% at 850 cm) in the Mały Staw core and the increase of planktonic Cladocera (Szeroczyńska 1993) suggest an increase in nutrient supply. More alkaline conditions during this time are indicated by a pH increase of 0.43 inferred from the Mały Staw sediments and 0.09 units inferred from the Wielki Staw sediments. This increase of water pH took place in the Preboreal in both lakes (Fig. 4A, B). The change of pH was very slight in Wielki Staw but DI-pH reached its maximum value for the entire core (Fig. 4B).

During the deglaciation, unfavourable conditions for the development of phytoplankton may have been created by a combination of low nutrient levels and high input of mineral matter to the lake (Bradshaw et al. 2000). The final melting of the cirque glacier may have occurred in this period. As a consequence of deglaciation, intensive soil and catchment erosion contributed base cations and nutrients to the lakes. More alkaline and circumneutral conditions in the Late Glacial and the earliest Holocene have been shown for lakes in other regions (Whitehead et al. 1986, Renberg 1990, Atkinson & Haworth 1990, Seppä & Weckström 1999, Bradshaw et al. 2000). In lake Vuoskkujárvi (northern Sweden), pH increased immediately by ca 0.5 after the deglaciation (Bigler et al. 2002), similar to the process in Mały Staw lake. Similar increases of pH have been observed in lakes in Norway (e.g. Velle et al. 2005) and other parts of Europe (e.g. Birks et al. 1990).

Generally, following deglaciation and/or a short episode of DI-pH increase in lakes on crystalline bedrock, water pH started to decrease due to poor buffering from rock in the catchment (Atkinson & Haworth 1990, Velle et al. 2005). In the studied lakes, typical oligotrophic diatoms which often occur in acidic waters replaced diatoms that prefer higher trophy. In the Mały Staw sediments the frequency of alkaliphilous taxa (e.g. *Pseudostaurosira brevistriata* and *Staurosirella pinnata*) gradually decreased, but the abundance of acidophilous diatoms preferring oligotrophic lakes with low conductivity (e.g. *Aulacoseira alpigena*) increased (DMS 3, approximately since the second half of the Atlantic). The diatom assemblages in the Wielki Staw sediments also showed an increase of acidophilous diatoms (e.g. *Aulacoseira distans*, *A. alpigena*, and *Brachysira brebissonii*), with an average share of ca 60% in this part of the core (DWS 2, since the Boreal). Higher occurrence of acidobiontic diatoms was noted, and some alkaliphilous taxa declined and/or disappeared (e.g. *Pseudostaurosira brevistriata*) in this lake. The pollen spectrum, which showed a gradual decrease from the maximum of *Ulmus*, accompanied by the expansion of spruce, indicates that acidification, as inferred from the diatom record of the Wielki Staw sediments, was most intense at the Atlantic-Subboreal transition. The lowest DI-pH value appeared earlier in this lake, in the upper part of the Atlantic. Algal populations react more rapidly than pollen spectra do; due to the short life cycle of diatoms, they respond quickly to changes in their environment.

In the core from Mały Staw, the lowest pH value reconstructed from diatom analyses occurred at the Subboreal-Subatlantic transition.

A similar gradual and long-term natural acidification process has been demonstrated in lakes in many regions (Davis 1987, Larocque & Bigler 2004). Progressive acidification began in the early Holocene, when erosion was reduced and stabilised. After that, the volume of material transported to the lakes from eroded areas of the watershed decreased. The gradual development of acidic soils and changes in the catchment vegetation contributed to the increase of acidification in that period (Seppä & Weckström 1999, Bradshaw et al. 2000). Moreover, declining nutrient input led to a reconfiguration of the diatom community. The frequency of acidobiontic and acidophilous diatoms increased, as compared with the earliest phase of lake formation (Renberg 1990).

From the late Holocene to recent times [upper DMS 4 to DMS 6; DWS 3 (except lower part of zone) to DWS 4], pH declined but the rate of change of pH slowed. In this period the diatom-inferred pH was more or less stable. Changes in catchment vegetation caused by climatic and human factors (e.g. extensive logging by the iron industry) may have increased the leaching of organic and inorganic acids from soil into the lakes. To the present day the lakes have also been supplied with acidic water from peat bogs in the lakes' drainage basins (Knapik R. 2010 pers. com.). Still, the diatom-inferred pH remained below 6.5 in Mały Staw and 6.0 in Wielki Staw. The diatom assemblages developed similarly in the two lakes. Despite the lower rate of acidification as compared with the earliest periods, and the relatively stable pH, the abundance of acidobiontic and acidophilous diatoms increased (e.g. *Aulacoseira lirata*, *A. pfaffiana*, *Psammothidium acidoclinatum*). At the same time, the frequency of indifferent and alkaliphilous taxa (e.g. *Sellaphora seminulum*, *Staurosira cosnstruens* f. *venter*) decreased in the sediments of Mały Staw (DMS 4–DMS 6). Wielki Staw had more acidic water than in Mały Staw (Fig. 4A, B), and in consequence the share of alkaliphilous *Pseudostaurosira brevistriata* was low (a few percent) only in the initial stage of lake development, when water pH was highest (DWS 1–DWS 2; Preboreal-Boreal), and the taxon disappeared in the Atlantic period. The diatom-inferred pH values indicate that both lakes have remained acidic to the present day. The acidification trend was more conspicuous in the Mały Staw sediments, especially the upper part of the core.

In the middle to late Holocene, but before the Industrial Revolution, pH in naturally acidified waterbodies around the world remained more or less constant (Larocque & Bigler 2004, Seppä & Weckström 1999). Minor oscillations of lake-water pH may have occurred as a result of changes in vegetation dynamics affecting soil chemistry, weathering rates, hydrology, and organic acid production (Whitehead et al. 1986). Short-term variation of pH probably was associated with inwashing of material from the catchment (Birks et al. 1990). Reconstructions of the pH of Sudetic lakes during this period show similar trends to diatom-inferred pH in other mountain lakes of Europe (Atkinson & Haworth 1990, Bigler et al. 2002).

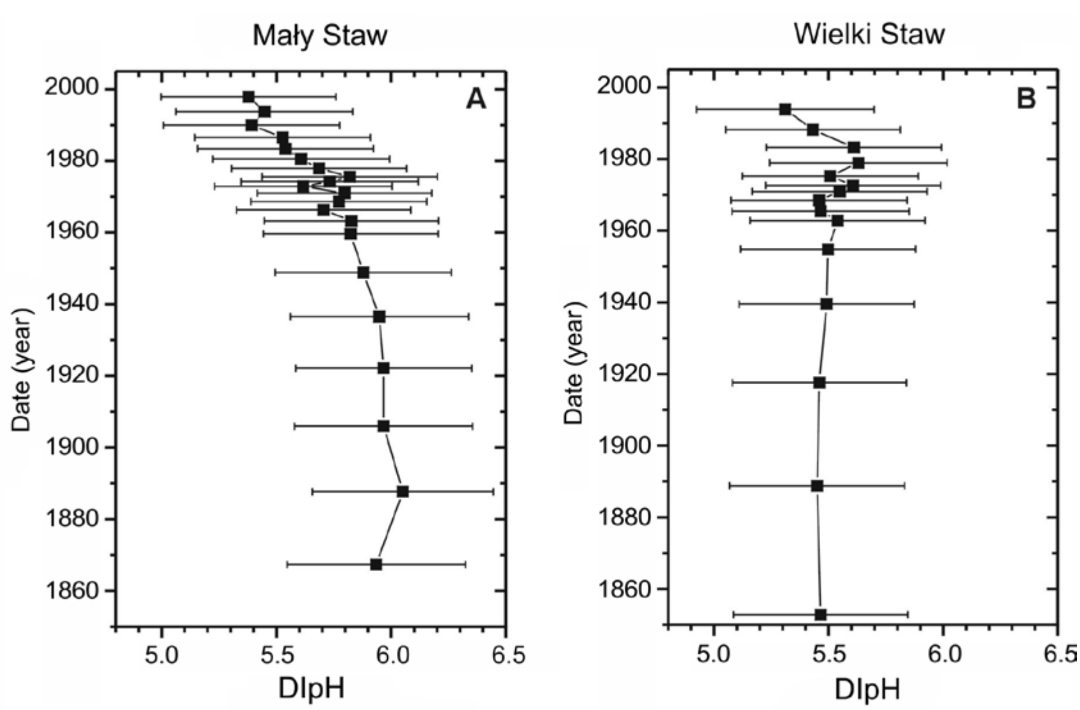

Fig. 5. Diatom-inferred pH (DI-pH) for Mały Staw (**A**) and Wielki Staw (**B**) lake sediments accumulated during the last 150 years, according Sienkiewicz et al. (2006)

Surface sediments were collected from both studied lakes in 2002. The cores were analysed for acidification over the last 150 years (Sienkiewicz et al. 2006). Based on ^{210}Pb dating, the diatom-inferred pH values confirm that an increase of acidity began in the 1970s in the studied lakes. The inferred pH decreased by 0.7 in Mały Staw and 0.3 in Wielki Staw (Fig. 5). The reduction of sulphur and nitrogen oxide emissions in the Black Triangle since the 1990s was not reflected in the composition of the diatom communities up to 2002, probably due to hysteresis of biological recovery, that is, a delay in the reaction of the biocenoses to the reduction of air pollution. In the most recent sediments of Mały Staw, the frequency of acidophilous diatoms increased to ca 70%. In the Wielki Staw sediments, however, acidobiontic diatoms comprised almost 15% of the total diatom population. The most recent studies confirm decreased acidification and better edaphic conditions in both lakes (Rzychoń & Worsztynowicz 2007, Vrba et al. 2008).

Changes in lake ecosystems connected with progressive acidification after the Industrial Revolution are noted in many alpine, arctic, and subarctic waterbodies (Cameron et al. 1999, Tolotti 2001, Ginn et al. 2007). Since ca 1900, acid deposition has played an important role in the decrease of pH (Renberg 1990). In areas of high acid deposition (e.g. south-western Scotland, south-western Sweden) the decrease of water pH was significant, while in regions where levels of airborne pollutants were much lower (e.g. north-western Scotland, central Norway) the decrease water pH was not significant. There is evidence of a strong relationship between increasing acid deposition and decreasing water pH (Smol 2008). A rapid increase of anthropogenic acidification usually is not correlated with watershed events (Davis 1987). Changes in catchment vegetation can also impact the lake water pH. Natural spread and/or afforestation of Norway spruce (*Picea abies*) can lead to lower pH (Korsman et al. 1994).

CONCLUSIONS

The Mały Staw and Wielki Staw lakes have been impacted by natural long-term acidification. Following the deglaciation and a short period of DI-pH increase, pH decreased. Acidity was highest at the Subboreal-Subatlatic transition in Mały Staw and at the Atlantic-Subboreal transition in Wielki Staw (natural acidification). Both lakes were also strongly impacted by acid rain, especially since the 1960s (anthropogenic acidification); a few years later this was followed by changes in the phytoplankton communities toward an increase of diatom taxa preferring acidic conditions. As a result of differences in morphometry and catchment area between the two lakes, probably the same load of acidity affected Mały Staw more than it affected Wielki Staw. Waterbodies that are small and shallow but have a large drainage basin may be more affected by acidity than larger, deeper lakes. The small size and shallowness of Mały Staw, combined with its large catchment, makes this lake more sensitive to natural long-term acidification (e.g. soil acidification following changes in catchment vegetation) and anthropogenic pollution. Over the entire history of the studied lakes, DI-pH inferred from the diatoms in sediment cores decreased by 1.4 in Mały Staw and 0.9 in Wielki Staw. Recent chemical and biological analyses of the two lakes show recovery from acidification (Rzychoń & Worsztynowicz 2007, Vrba et al. 2008). Thus, a new period of important changes in pH accompanied by biological changes is beginning in these Sudetic lakes.

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