Limited acid deposition inferred from diatoms during the 20th century — A case study from lakes in the Tatra Mountains

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ABSTRACT

Mountain lakes are usually sensitive to the effects of global and regional environmental changes. 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 anthropogenically acidified. Additionally, following reduction in emissions of sulfur (S) and nitrogen (N) compounds, recovery from acidification has been observed in many lakes. In this study, we used changes in diatom communities to reconstruct the pH histories based on changes recorded in nine Tatra lakes (Western Carpathians, Poland) since approximately 1850 AD. Overall, results indicate that acidic precipitation had little influence on lake-water pH in the Tatra Mountain lakes. Changes in diatom-inferred pH (DI-pH) generally were small and showed little evidence of acidification during the time of the highest air pollution (since the 1960s), and have shown little change since the reduction of acidic deposition since the 1990s. Lakes that showed some evidence of acidification included dystrophic lakes with low acid neutralizing capacity. However, as illustrated by the PCA trajectories of the diatom assemblages, the majority of the lakes currently contain diatom assemblages that are unlike the diatom floras that existed ca. 1850.

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Introduction

High mountain lake ecosystems are typically sensitive to environmental changes and are therefore of great interest for paleolimnological research. Many high-altitude lakes have been studied for the effects of acid rain and the recovery from human acidification (e.g., Stoddard et al., 1999; Mosello et al., 2002; Kopáček et al., 2006a, 2006b; Sienkiewicz et al., 2006). Since the second half of the 20th century, many lakes in regions of Europe and North America receiving acidic deposition have become anthropogenically acidified (e.g., Curtis et al., 2002; Battarbee et al., 2005). This acidification, which began particularly during the Industrial Revolution, intensified with time (Kopáček et al., 2001). According to historical data, in central-eastern Europe, the earliest industrial development occurred in Bohemia (after 1848) and in the Kingdom of Poland (ca. 1850–1890), which became the most economically developed areas of the Habsburg’s Monarchy and the Russian Empire (Leslie et al., 1980). With increases in economic growth, environmental quality deteriorated as industry developed and emissions of pollution originating from the combustion of fossil fuels increased.

The most significant increase in air pollution occurred in the 20th century, particularly at the beginning of the 1960s, which was corroborated by geochemical and palaeobiological analyses of lake sediments and monitoring data (e.g., Kopáček et al., 2001, 2003; Vrba et al., 2003). Emissions of gaseous forms of sulfur and nitrogen oxides are transformed into sulfuric and nitric acids, $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$, respectively, when contacted by water. These acids are transported in the atmosphere and

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Mountains: nonsensitive (NS) lakes with pH > 6 and ANC > 25 μeq/L; and extremely sensitive (ES) lakes with pH < 5 and ANC < 0 μeq/L. Generally, based on acid-base status, three primary groups of lakes are categorized in the Tatra Mountains: nonsensitive (NS) lakes with pH > 6 and ANC > 25 μeq/L; acid-sensitive (AS) lakes with 5 < pH < 6 and ANC 0–25 μeq/L; and extremely sensitive (ES) lakes with pH < 5 and ANC < 0 μeq/L (Kopáček et al., 2004).

However, in some of these lakes, acidic deposition lowered the diversity of zooplankton and caused the extinction of oligotrophic and two dystrophic, with acidic to slightly acidic water (Keputz et al., 2009). The process of eutrophication has also begun within recent decades (e.g., Bombónowa and Wojtan, 1996; Gliwicz, 1985; Kurzycza et al., 2009; Sienkiewicz and Gąsiorowski, 2014, 2016a, 2016b). Diverse analyses and observations are used to determine changes in lake ecosystems, including chemical and palaeoecological investigations and monitoring data. Although many scientists have studied the diatom flora of the Tatra Mountains (e.g., Fott et al., 1999; Eloranta and Kwandrans, 2002; Kownacki et al., 2006; Kwandrans, 2007), investigations have primarily focused on epilithic diatoms, which are collected in different periods of vegetation. For this study, lake sediment cores were examined that were collected between April 2003 and March 2013. The diatom stratigraphy of these lakes, except for lake Czarny Staw Polski (CSP) (Appendix A Fig. S1), was presented in Gąsiorowski and Sienkiewicz (2010a, 2010b) and Sienkiewicz and Gąsiorowski (2014, 2016a, 2016b). Papers have focused on the trophic status of the lakes, the 20th century climate warming and changes of isotopic composition in lake sediments. Sedimentary diatom assemblages with taxa ordered by pH optima are shown in Appendix A Figs. S1–S4.

The aim of this paper was to examine the paleolimnological record to determine the intensity of acidity changes in lake ecosystems from the beginning of the Industrial Revolution (ca. 1880 AD) to ca. 2000 AD. This represents the synthesis of the acidification process recorded in most of the biggest lakes located in the Polish part of the Tatra Mountains. Diatom analysis is a primary tool among paleolimnological methods used to trace the pH and acidification history of lakes because diatoms are highly sensitive organisms that respond quickly to alterations in their environment.

The novelty of this study was the determination of changes in the distribution of algae grouped ecologically by pH preference to reconstruct diatom-inferred pH (DI-pH) from dated mountain lake sediments. Estimation of historical acidification can help determine catchment, surface water and diatom communities’ response to acidic deposition. Additionally, these changes were correlated with the deposition of sulfur and nitrogen compounds. Changes in the diatom community and DI-pH every few years can be estimated because of the relatively low sedimentation rate, and for current lake management, this is helpful information because effective management requires long-term environmental data collected at the shortest possible time intervals (Smol, 1992). We selected nine lakes in the Polish section of the Tatra Mountains (central Europe) of which seven were oligotrophic and two dystrophic, with acidic to slightly alkaline waters. Most of the lakes are currently classified as nonsensitive water bodies (ANC > 25 μeq/L and pH > 6); however, the acid-neutralizing capacity and water pH can change, even within a relatively short time. From the beginning of the reduction in air pollution to approximately the present day, the values of both factors generally increase with time (Table 1). Although ANC data collected before the 1980s and pH measurements before the 1960s are available to some extent, the reliability is highly uncertain (Kopáček et al., 2004). Thus, with the exception of the last few decades, we do not have reliable information on changes in pH in recent lake history. Although diatom analysis does not provide an actual ANC value, the diatom-inferred pH can approximate estimated shifts in ANC and determine whether a specific lake was sensitive to acidification in the past.

1. Methods

1.1. Study sites

All studied lakes have a glacial origin and are in different valleys of the Tatra Mountain range (Poland, central Europe). The catchment bedrock consists primarily of crystalline rocks (granites) with quaternary glacial sediments and rock debris cones. We investigated the following lakes (Fig. 1): Zielony Staw Gąsienicowy (ZSG) and Czarny Staw Gąsienicowy (CSG) from the Gąsienicowa Valley; Morskie Oko (MOK) and Czarny
<table>
<thead>
<tr>
<th>Lake name</th>
<th>Location Code</th>
<th>Altitude (m a.s.l.)</th>
<th>Catchment area (ha)</th>
<th>Lake area (ha)</th>
<th>Max. depth (m)</th>
<th>pH (^a) (1993–1994)</th>
<th>pH (^b) (1996–1997)</th>
<th>pH (^c) (2004)</th>
<th>ANC (^a) (μmol/L) (1993–1994)</th>
<th>ANC (^b) (μmol/L) (1996–1997)</th>
<th>ANC (^c) (μmol/L) (2004)</th>
<th>TP (^d) (μg/L)</th>
<th>TON (^e) (μmol/L)</th>
<th>Ch-(a) (^c) (μg/L)</th>
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<td>Zielony Staw Gąsienicowy</td>
<td>ZSG</td>
<td>49°13′44″N 19°59′59″E</td>
<td>1672</td>
<td>33</td>
<td>3.84</td>
<td>15.1</td>
<td>6.3</td>
<td>6.33</td>
<td>6.85</td>
<td>78</td>
<td>74</td>
<td>108</td>
<td>10.07</td>
<td>7.0</td>
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<tr>
<td>Czarny Staw Gąsienicowy</td>
<td>CSG</td>
<td>49°13′52″N 20°01′05″E</td>
<td>1620</td>
<td>205</td>
<td>17.94</td>
<td>51</td>
<td>6.2</td>
<td>6.09</td>
<td>6.49</td>
<td>27</td>
<td>25</td>
<td>51</td>
<td>7.32</td>
<td>5.6</td>
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<td>Morskie Oko</td>
<td>MOK</td>
<td>49°11′49″N 20°04′12″E</td>
<td>1395</td>
<td>630</td>
<td>34.93</td>
<td>50.8</td>
<td>6.3</td>
<td>6.56</td>
<td>7.13</td>
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<td>116</td>
<td>145</td>
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<td>49°11′20″N 20°04′37″E</td>
<td>1580</td>
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<td>20.64</td>
<td>76.4</td>
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<td>6.72</td>
<td>7.14</td>
<td>126</td>
<td>123</td>
<td>159</td>
<td>6.18</td>
<td>5.8</td>
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<td>49°12′45″N 20°02′58″E</td>
<td>1668</td>
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<td>34.6</td>
<td>6.4</td>
<td>n.d.</td>
<td>7.23</td>
<td>186</td>
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<td>245</td>
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<td>12.7</td>
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<td>79.3</td>
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<td>6.58</td>
<td>7.03</td>
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<td>84</td>
<td>10.07</td>
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<td>Smreczyński Staw</td>
<td>SME</td>
<td>49°13′21″N 19°51′52″E</td>
<td>1226</td>
<td>n.d.</td>
<td>0.75</td>
<td>5.3</td>
<td>4.5</td>
<td>n.d.</td>
<td>4.95</td>
<td>–37</td>
<td>n.d.</td>
<td>–8</td>
<td>63.46</td>
<td>44.5</td>
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<tr>
<td>Toporowy Staw Niżni</td>
<td>TSN</td>
<td>49°17′00″N 20°01′52″E</td>
<td>1089</td>
<td>–45</td>
<td>0.62</td>
<td>5.7</td>
<td>5.2</td>
<td>5.33</td>
<td>5.57</td>
<td>4</td>
<td>16</td>
<td>24</td>
<td>68.31</td>
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</tr>
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</table>

\(^a\) After Stuchlík et al., 2006.
\(^b\) After Kopáček et al., 2006a.
\(^c\) After Kopáček et al., 2006b.
\(^d\) Data (Kopáček et al., 2006a, 2006b) calculating according to the molybdate method, n.d.: no data. Acid Neutralizing Capacity (ANC) and pH: nonsensitive (NS) lakes; acid sensitive (AS) lake is type with italic; extremely sensitive (ES) lake is type with bold. Abbreviations of parameter names: TP — total phosphorus; TON — total organic nitrogen; Ch-\(a\) — chlorophyll \(a\).
Staw pod Rysami (CSR) from the Rybi Potok Valley; Przedni Staw Polski (PSP), Czarny Staw Polski (CSP) and Wielki Staw Polski (WSP) from the Pięć Stawów Polskich Valley; Smreczyński Staw (SME) from the Pyszniański Valley; and Toporowy Staw Nizni (TSN) from the Sucha Woda Valley. Among these lakes, only three (MOK, SME, TSN) are below the modern tree line. SME and TSN lakes are dystrophic forest tarns; the others are oligotrophic mountain lakes. Primary morphological and chemical characteristics are given in Table 1. SME and TSN lakes are situated on a moraine shaft, and the shores of these lakes are overgrown by marsh plants and sediments contain a high content of organic matter. The other lakes are located in glacial cirques. Generally, the lakes are surrounded by dwarf mountain pines. MOK is the only lake with a natural fish population; however, it was additionally stocked in 1881, and some of the lakes, including ZSG, CSG and PSP, were also successfully stocked, primarily with trout (Gliwicz and Rowan, 1984). The ice-free period is typically from May/July to November.

1.2. Core retrieval, dating and diatom analysis

Short cores of the sediments were collected from the deepest part of the lakes using a Kajak-type gravity corer (Gąsiorowski and Sienkiewicz, 2010a, 2010b). Cores were dated by $^{210}$Pb methodology up to 150 years ago, and older sediments were dated by radiocarbon methodology (Gąsiorowski and Sienkiewicz, 2010a, 2010b, 2013). Age-depth models were calculated using the MOD-AGE algorithm applying the randomization method and LOESS procedure for function fitting (Hercman and Pawlak, 2012; Hercman et al., 2014). The results of dating are presented in Supplementary material (Appendix A Figs. S5–S8). Samples for diatom analysis were prepared according to standard procedure (Battarbee, 1986). From each sample, more than 300 diatom valves were counted using an Olympus BX 51 biological microscope and 100× oil immersion objective. In this paper, a percentage frequency of diatoms was classified according to pH as follows: alkali (Alk), indifferent (Ind), acidophilous (Ac) and acidobiontic (AcB). Diatoms were divided into ecological groups based on pH preferences, and results are presented in histograms.

1.3. DI-pH modeling

For the reconstruction of lake water pH (DI-pH) we used the European Diatom Database (EDDI) and the ERNIE software, version 1.0 (Juggins, 2003). The Alpine database (AL:PE) was chosen as the modern calibration dataset. The AL:PE training set consists of surface-sediment diatom assemblages from 118 high-altitude or high-latitude lakes located in the Alps, Norway, Svalbard, Kola Peninsula, UK, Slovenia, Slovakia, Poland, Portugal, and Spain. Diatom-inferred pH was calculated by using a weighted averaging (WA) method with inverse deshrinking, because the reconstructed values were close to the mean in the training set (Birks et al., 1990). The lowest root mean square error of prediction (RMSEP) was 0.37 pH units and the highest coefficient of correlation ($r^2$) was 0.78.

1.4. Deposition and correlation with changes in diatom communities

The results of the diatom-inferred pH were correlated with data on sulfur and nitrogen deposition in the Tatra Mountains. Model calculations by Kopáček et al. (2001) were used to generate these data. The values obtained for SO$_2$ emissions were based on the consumption of fossil fuels; for NO$_x$ based on the consumption of fossil fuels and mobile sources; and for NH$_3$ based on livestock production and nitrogenous fertilizer production and consumption. Long-term deposition
trends were estimated from the relation between measured values of bulk deposition at the Chopok meteorological station (northern Slovakia) for 1978–1999 and pollution emission for the identical period. The uncertainty of the estimation of deposition (coefficient of variation of the mean) was estimated at <30%.

The stages of pollution deposition were correlated with changes in diatom communities. The variations in diatom assemblages were expressed as changes in principal component analysis (PCA) results. Then, the PCA results for each lake were grouped according to time into 3 groups related to pollution deposition-recovery stages. The significance of changes in diatom assemblages during transitional periods was determined with one-way analysis of similarities (ANOSIM) used with the Euclidean distance (Chapman and Underwood, 1999). Only between-groups-differences in diatom assemblages with values of \( p \leq 0.05 \) were treated as statistically significant.

2. Results

2.1. Pollution deposition

The modeled and measured deposition of N and S compounds demonstrated a significant increase in environmental pollution of Tatra after 1960 (Kopáček et al., 2001). The bulk deposition showed three primary stages of deposition magnitude in the region (Fig. 2). The first stage (I; until 1960), which included the Industrial Revolution, was a period of semi-natural level of deposition. A strong increase in the deposition of S and N compounds was recorded in the 1960s, and this trend continued during the 1970s with a peak in the deposition in the 1980s (stage II; 1960–1990). However, at the end of this stage, in 1990, the deposition of pollution decreased to the level at the beginning of the 1960s. After 1990, the deposition of SO4-S and NH4 declined substantially; whereas the decrease in NO3 deposition was less prominent (stage III; 1990 to the present). This decline in deposition was related to increased consumption of fossil fuels in transportation, based on the nitrogen isotopic composition (Gąsiorowski and Sienkiewicz, 2013).

2.2. Communities of diatom species and diatom-inferred pH (DI-pH)

2.2.1. Pięć Stawów Polskich Valley (Wielki Staw Polski, Czarny Staw Polski and Przedni Staw Polski lakes)

In the sediments of these three lakes (Fig. 3), diatoms classified as acidophilous, indifferent and alkaliphilous were identified. In each lake, a low percentage frequency of diatoms with unknown autecology was also observed. A few diatom taxa that preferred a low pH (acidobiontic) were found in WSP or among the single valves in CSP. In both lakes, the highest frequencies were indifferent diatoms. The species composition in PSP was significantly different from diatom flora in nearby WSP and CSP. In the sediments of PSP, alkaliphilous species were the dominant group of diatoms, with a frequency exceeding 50% in the core. Acidobiontic taxa were not observed, and acidophilous species occurred only in low percentages.

Fig. 2 – Bulk deposition of S and N compounds in Tatra Mountains during the last 200 years (data from Kopáček et al., 2001). Shaded area is the period of highest pollution deposition.

Reconstruction of water pH (DI-pH) to the 1960s showed a small decrease in PSP and CSP (Fig. 4), whereas the pH increased in WSP. The pH of water declined in PSP between 1960 and 1990 (at the end of the 1980s), with small fluctuations in WSP and CSP. In the third period (after 1990 AD), pH values were relatively stable in PSP and CSP but tended to increase in WSP. DI-pH remained below 7 for this period in the three lakes.

2.2.2. Rybi Potok Valley (Morskie Oko and Czarny Staw pod Rysami lakes)

In both lakes, identical ecological diatom groups classified by pH preference were found but at different frequencies (Fig. 5). Indifferent taxa were the most numerous among the diatom communities in both MOK and CSR. The frequency of alkaliphilous taxa was different between these lakes, with these taxa representing greater than 40% of the diatom assemblage in CSR but not exceeding 20% in that of MOK. In MOK, the diatom community was 20% acidophilous diatoms and rare valves of acidobiontic species were also observed. A few diatoms with unknown autecology were also identified.
Fig. 3 – Changes in diatom communities grouped according to tolerance of pH in the lakes of Pięć Stawów Polskich Valley. AcB: acidobiontic taxa, Ac: acidophilous taxa, Ind: indifferent taxa, Alk: alkaliphilous taxa, AlkB: alkalibiontic taxa. Histograms for the diatom community in entire cores are also reported. Codes of the lakes as in Fig. 1.

Fig. 4 – Diatom-inferred pH reconstruction of studied lakes. Codes of the lakes as in Fig. 1. Shaded area is the period of highest pollution deposition.
Based on the diatom-inferred pH before the 1960s, small fluctuations occurred in both lakes. In MOK, the pH first decreased and then increased, whereas in CSR, DI-pH was relatively constant (Fig. 4). In both MOK and CSR, the curve of pH values was almost unchanged after 1960, and in 1985 only, a decrease of 0.1 units was observed. The reconstruction of pH for the youngest sediments indicated that the water in both lakes was circumneutral.

2.2.3. Gąsienicowa Valley (Zielony Staw Gąsienicowy and Czarny Staw Gąsienicowy lakes)

In CSG and ZSG, indifferent diatoms dominated (>60%), while acidophilous taxa occurred approximately in 20% frequency (Fig. 6). Diatoms preferring more alkaline waters were present in both lakes in comparable quantity. Acidobiontic taxa were observed only in CSG.

In ZSG, before 1960 AD, the curve of pH was approximately constant, with the exception of a decrease in DI-pH in one sample, approximately in 1870, whereas the diatom-inferred pH in CSG decreased 0.3 units in the identical period (Fig. 4). During the maximum emissions of S and N compounds, i.e., after 1960, the DI-pH in the sediments of ZSG was constant, but a small decrease in the pH of water was observed in CSG at the end of the 1980s. In the youngest sediments, fluctuations of DI-pH within ca. 0.1 units were maintained in both lakes.

2.2.4. Pyszniańska Valley (Smreczyński Lake) and Sucha Woda Valley (Toporowy Staw Niżni Lake)

More than 80% of diatom species in SME represented taxa that preferred acidic and very acidic waters (acidophilous and acidobiontic species). Indifferent diatoms and a very low abundance of alkalophilous taxa were the other taxa in this
lake. In the sediments of SME, an unequivocal trend in DI-pH was not observed. The diatom-inferred pH changed within approximately 0.3 units, and the values of reconstructed water pH were less than 5.4 in the entire core (Fig. 7).

In contrast to SME, in the sediments of TSN, acidobiontic taxa were found only occasionally. Approximately half the algal community was represented by acidophilous diatoms, with indifferent and alkaliphilous species also at a relatively high frequency (approximately 20%). In TSN, the abundance of diatoms with unknown autecology was a low percentage.

In TSN, diatom-inferred pH changed in the sediment sequence within a range of approximately 0.8 pH units. A particularly acidic tendency occurred after 1960 (a decrease of diatom-inferred pH by 0.5 pH units since the second half of the 1980s in the 20th century). In the period of reduced air pollution, i.e., after 1990, the DI-pH continued to indicate acidic values (Fig. 4).

2.3. Correlations between stages of deposition and diatom communities

The stages of pollution deposition were correlated with changes in diatom communities (Fig. 8). Notably, WSP and TSN were the only two lakes in which the changes in diatom communities in response to changes in acidification were significant ($p \leq 0.05$). The diatoms of WSP and TSN reacted clearly to the increase in pollution in the 1960s, although the responses were different in magnitude and mode. The change in WSP was expressed on a PCA diagram, with a strong shift to positive values of the first and to negative values of the second component. However, after this shift, the sample scores showed relatively wide variation, and any response to changes in pH could not be clearly defined. TSN also showed significant changes in PC values after 1960, with some changes in the 1980s. Moreover, this change towards PC1
values with positive scores also continued after 1990, and no signs of recovery from acidification were observed (insignificant changes, $p = 0.230$). In diatom community history, 1990 was a significant date only in CSG ($p = 0.032$); however, in that lake, DI-pH decreased at this time.

3. Discussion

To track the process of acidification in the Tatra Mountains, we studied lake sediments accumulated during the last 150 years. By analyzing the distribution of diatoms grouped by pH preference, the amount of change in algal community composition for three defined periods of time could be estimated, i.e., after the beginning of the Industrial Revolution (ca. 1850 AD), the period of highest increases in emissions of air pollution beginning in the 1960s and the period of recovery after 1990. The estimates of periods of industrial development were determined according to historical data and measurements of sulfur and nitrogen deposition in the Tatra Mountains (Poland and Slovakia). According to Henriksen et al. (1992), analyses of water chemistry in most of the lakes indicate that the highest acidic deposition in the Polish section of the Tatra Mountains was between 1984 and 1991. The early period of lake water recovery from acidification in the region occurred between 1993 and 1994 (Kopáček et al., 2004). Lakes at different altitudes, with different morphology and catchment area, but generally situated on sensitive bedrock (primarily granites), were selected for these studies. Areas rich in granites with some conglomerates and sandstones may have low alkalinity and therefore, poor buffering capacity. As a result of rocks with poor buffering capacity in a catchment, even small amounts of pollutant input to an oligotrophic lake may disturb the environmental balance.

Fig. 7 – Changes in diatom communities grouped according to tolerance of pH in the dystrophic lakes of Pysznińska and Suchej Wody Valleys. AcB: acidobiontic taxa, Ac: acidophilous taxa, Ind: indifferent taxa, Alk: alkaliphilous taxa, AlkB: alkalibiontic taxa. Histograms for the diatom community in entire cores are also reported. Codes of the lakes as in Fig. 1.
Fig. 8 – PCA results of changes in diatom communities grouped into main diatom class according to their acid tolerance. The samples were coded according to their age into 3 periods: pre 1960 (pale gray circles), 1960–1990 (dark gray circles) and post-1990 (open circles). The significance of changes in diatom communities during the major shifts in air pollution magnitude (marked with bold, dashed lines) were checked with analysis of variance (ANOSIM) and p-values are reported. Codes of the lakes as in Fig. 1.
However, alkaline compounds have an important influence on the buffering system. One of the factors responsible for calcium concentration in lakes is easily weathered alkaline minerals, which occurred in all watersheds and are delivered by erosion to the lakes (Kameník et al., 2001; Kopáček et al., 2006a; Cartier et al., 2015). High concentrations of chemical compounds caused by physical weathering of rocks are found in lakes in large and steep catchments (Kameník et al., 2001). Thus, increases in weathering processes increase the content of base cations and therefore the alkalinity in acid-sensitive water bodies.

Dystrophic lakes are less sensitive to acidity than oligotrophic ecosystems and were also investigated in the Polish section of the Tatra Mountains (TSN and SME). Typically, these water bodies are characterized by a high concentration of dissolved organic carbon (DOC), particularly of allochthonous origin, and rich in organic carboxylic and phenolic acids that constitute a natural buffer (Gorham et al., 1986; Kulberg et al., 1993; Korosi and Smol, 2012). Although TSN and SME are both dystrophic forest lakes, the diatom communities were very different. Diatoms that tolerated acidic water dominated both lakes; however, the number of diatom species in SME was only 37 (primarily acidobiontic and acidophilous taxa), compared with 122 species in TSN (primarily acidophilous taxa). Most likely, this lowest number of diatom taxa among study lakes was due to the relatively low pH (4.20–4.95) and presence of humic substances (HS). High concentrations of HS (e.g., humic acids, fulvic acids and humin) cause the formation of stable complexes with nutrients, and as a consequence, phosphorus and nitrogen are bound. Low nutrient concentrations in combination with a low pH in water can effectively limit the development of phytoplankton.

Based on loss on ignition, the sediments in SME and TSN had average values of 70.5% and 63.5% organic matter, respectively (Gąsiorowski and Sienkiewicz, 2010a, 2010b). Most likely, the amounts of humic substances and decomposing peat and plant remains in SME were sufficient to effectively minimize effects from the inputs of air pollution. Throughout the entire record of SME sediments, the values of diatom-inferred pH were low and fluctuated without any clear trends. Moreover, no correlations were detected between the values of DI-pH and the three time periods (i.e., until 1960, 1960–1990, 1990–today) marked on the graph (Fig. 8). Likely, the values of reconstructed pH could be underestimated to some extent because three dominant taxa in the fossil record occurred in small amounts in the modern calibration dataset. In the training set, the maximal frequency of *Navicula hoefleri*, *Navicula subtilissima* and *Eunotia rhomboidea* amounted to 8.7%, 1.6% and 2.8%, respectively, while20-50% above 50%. For that reason the values of the DI-pH should probably be treated with caution. In TSN, a decrease in the DI-pH was distinct (0.5 pH units), particularly at the beginning of the 1980s, which was an anthropogenic effect from the combustion of fossil fuels that was also clearly visible in the stable isotopic signal (Gąsiorowski and Sienkiewicz, 2013). With less organic matter and humic substances in TSN, this lake was likely more sensitive to the same load of atmospheric contamination that was received in SME, and the increase in air pollution was reflected in the sediments of TSN by the decrease in DI-pH since the 1960s (Fig. 6). The decrease in sulfur and nitrogen oxide emission noted at the beginning of the 1990s was not reflected in the diatom flora of the two lakes (Fig. 6). Because these lakes had marshy shores that were continually overgrown and evolving from peat bogs, diatoms were most likely in continuous contact with acidic water. Thus, despite the decrease in air pollution, the algae community remained composed of acidophilous and acidobiontic taxa. Moreover, even after the decline in S emissions, SO₂ resorption from soil could be, as was found previously, an important source of acidification for these lake ecosystems (Kopáček et al., 2001).

By contrast, the current pH values in lakes in the Rybi Potok Valley (MOK and CSR) are very close to neutral (Fig. 4), and no significant changes in diatom-inferred pH occurred in the sediments of these water bodies during the last century. Recently, both lakes had relatively high ANC (Table 1), which supported the buffering of acidic deposition. In MOK after 1880, an increase of alkaliphilous diatoms that preferred more fertile water than oligotrophic waters, and a decrease of acidophilous and indifferent taxa, were observed. This change might be connected with artificial fish stocking in MOK in 1881 (1850 specimens of *Salmo trutta m. lacustris* and non-native brook trout *Salvelinus fontinalis* (Mitchell) that originated from North America), which increased the number of trophic levels within the lake (Sienkiewicz and Gąsiorowski, 2014, 2016a, 2016b). Between 1960 and 1990 in MOK and CSR, the abundances of alkaliphilous taxa decreased compared with increases of indifferent and, to a lesser extent, acidophilous taxa. Therefore, the changes in algal community composition were likely caused by atmospheric inputs of pollution, particularly in the second half of the 1980s, although changes in the DI-pH were low and equaled 0.1 pH units (Fig. 4). Thus, a minor shift in water pH could be connected with the input of weathering rocks and soils from the catchments of the lakes, including alkaline minerals, which might prevent lake acidification. This delivery was mirrored in the C/N ratio, particularly in CSR in which the C/N ratios were above 18 in the entire core. In the 1960s in MOK, the C/N ratio increased to approximately 14 (Sienkiewicz and Gąsiorowski, 2016a, 2016b), and a C/N ratio > 10 indicates that the source of organic matter consisted of a mixture of aquatic and terrestrial plants, i.e., supply of allochthonous materials to the lake (Meyers and Teranes, 2004). At the beginning of the 1990s, the frequency of alkaliphilous taxa increased as a consequence of the higher DI-pH values observed in MOK, whereas in CSR, indifferent taxa dominated during this period.

A decrease in the pH of PSP in the Pięć Stawów Polskich Valley was observed in the second half of the 1980s (Fig. 4). These fluctuations were a little more pronounced than in MOK (ca. 0.2 units pH), and they showed a slight tendency towards more acidic pH values. In the youngest sediments, diatom-inferred pH was relatively constant at ca. 6.7. Changes in the frequencies of individual diatom groups based on pH preference were small, but during the most polluted period (1960–1990), alkaliphilous diatoms decreased and indifferent diatoms increased. For the recovery period (after 1990 AD), the relation began to reverse, i.e., the number of alkaliphilous taxa started to increase and that of indifferent diatoms decreased. These groups of diatoms were dominant throughout the entire record, although the frequencies fluctuated in response to changes in the deposition of sulfur and nitrogen compounds. Currently, PSP has the highest acid neutralizing capacity among
the lakes (Table 1), and the very low occurrence or absence of acidophilous taxa in earlier years suggested that this lake was also characterized by high alkalinity in the past. Positive values of ANC indicate less acidic and more favorable conditions for the development of acid-sensitive taxa (Neal et al., 1999). Development of alkaliphilous diatoms is also observed in Austrian alpine lakes on crystalline bedrock covered by acidic soils. This growth in alkaliphilous diatoms was most likely caused by an external source of an alkalinity derived from eroded soils (Cartier et al., 2015). In PSP, C/N ratios were above 12 in the 1960s, which indicated that the input of organic matter from the catchment supported the buffering capacity during the period of highest atmospheric contamination (Sienkiewicz and Gąsiorowski, 2016a, 2016b).

The buffering capacity in WSP and CSP was much smaller than that in PSP. Therefore, based on pH preferences, indifferent diatoms were dominant in these lakes, with a relatively high number of acidophilous and alkaliphilous diatoms that exceeded 10% in most samples (Fig. 3). In WSP and CSP, a slight decrease in diatom-inferred pH was marked at the end of the 1980s that was coincident with the chemical signals from acidic deposition. However, the changes in DI-pH were low and did not exceed 0.2 pH units in both lakes. Thus, anthropogenic activity, including pollution from fuel combustion and other sources, did not substantially affect these algal communities. Notably, in WSP, the values of diatom-inferred pH were lower after 1990 than those in the 1960s. Presumably, the decrease in pH was correlated with the decrease in delivery of allochthonous material since the 1970s; this was corroborated by C/N ratios <10, indicating that phytoplankton were the primary source of organic matter in the lake during this period (Sienkiewicz and Gąsiorowski, 2016a, 2016b).

Investigations of the epilithic diatoms and water chemistry in 2000 by Kawecka and Galas (2003) also showed that WSP and CSP are non-acidified water bodies. Among the lakes in the Pięc Stawów Polskich Valley, the largest increase in DI-pH in the final period occurred in WSP.

In the Gąsienicowa Valley, CSG and ZSG lakes were investigated. Indifferent diatoms were characteristic of ZSG and CSG and were found in comparable frequencies. In the sediments of CSG, the first decrease in diatom-inferred pH was noted after 1880, and the decrease was relatively substantial at approximately 0.3 units. This decrease, particularly since the 1960s, might be an effect of increased NO deposition originating from vehicle exhausts, and the trend towards more negative values in δ¹⁵N in the youngest sediments likely corroborated this relation (Heaton, 1990; Gąsiorowski and Sienkiewicz, 2013). In the second half of the 1980s, the decline in diatom-inferred pH was minimal. After 1990, another small decrease in pH occurred. Based on the analyses performed by Kopáček et al. (2001), sulfur and nitrogen budgets in the Tatra Mountains during the last period decreased significantly. The absence of a positive reaction by acidophilous diatoms to this decrease was a result of acidic soils within the catchment (folic podzols; 3.5 < pH < 5.0). With low pH soils, the pH and acid neutralizing capacity of CSG were lower than those in ZSG over the years of the study (Table 1). Changes in the DI-pH in ZSG between the beginning of the Industrial Revolution and the present were low and ranged between 0.2 pH units. Possibly, weathering alkaline minerals were delivered to the lake in sufficient amounts to buffer acidic inputs reflected in the DI-pH. An increase in weathering processes was also corroborated by C/N ratios greater than 10 (Gąsiorowski and Sienkiewicz, 2013).

Based on water chemistry and atmospheric deposition, particularly of S and N compounds in the study area, recovery from acidification began in the 1990s (Kopáček et al., 2001; Schöpp et al., 2003, Stuchlík et al., 2006). Nevertheless, these changes varied temporally and spatially not only among regions but also within a specific region, depending on global and regional climatic changes, the magnitude of pollution deposition, and catchment characteristics, among other factors (Dillon et al., 2003; Skjelkvåle et al., 2005).

Presently, among the oligotrophic lakes, the lowest pH is in CSG. From the west, the lake is surrounded by the steep crystalline walls of Mt. Kościelec (up to 533 m high), poor in soil and vegetation cover, which meant that inputs of base cations to the lake were limited. In consequence, excluding dystrophic water bodies, CSG has the lowest buffering system in the studied lakes. Values of ANC varied between 25 and 51 μmol/L during 1993–2004 (Table 1). The decrease of DI-pH in CSG as well as in other lakes (Fig. 4) occurred much earlier than the highest emissions of air pollution, i.e., before the 1960s. Most likely this was an effect of gradual deterioration of environmental conditions due to Industrial Revolution-related development and/or a sufficient amount of naturally occurring organic acids in the lakes lowering water pH without acidic deposition. Although the curves of DI-pH did not show a spectacular recovery after the 1990s, the predominant amounts of indifferent and alkaliphilous diatoms over acidophilous species in oligotrophic lakes and the values of DI-pH close to 7 point to the decline of acidification. However, currently in the Polish and Slovak Tatra Mountains there are lakes with acidic water pH. The most acidified lakes are water bodies located in the alpine zone (> 1800 m a.s.l.) (Stuchlík et al., 2006). Most likely, the acidity was associated with the relatively high altitude, shorter ice-free period and lower density of vegetation cover, among other factors, which resulted in a low acid neutralizing capacity. At high elevations, spring melt typically starts later than in lake catchments at lower altitudes, and at lower altitudes, conditions are favorable for surface water recovery because warmer temperatures cause an increase in the rate of weathering of base cations. The catchments of high-elevation lakes typically have small drainage areas, thin glacial till deposits, low rates of bedrock weathering and low soil base saturation (Stuchlík et al., 2006; Strang et al., 2010). Because of these factors, these water bodies are more sensitive to acidification than the Tatra lakes at lower elevations due to the depleted carbonate buffering system (low ANC) and lower inputs of base cations from the catchments. In studies performed by Kownacki et al. (2006) on small Mnichowe ponds in the alpine zone (1883–1869 m a.s.l.), the diatom flora were found to prefer acidic conditions, probably because of trickling into the lake from surrounding peat bogs that causes a progressive decrease in water pH. Although a decrease in the pH of these ponds has been observed for more than 40 years, (Wojtan and Galas, 1994), the diatom flora remain nearly identical and consist of acidophilous and acidobiontic species typical for small lakes poor in nutrients.

Processes located in the catchments and atmospheric deposition impacted the lakes' ecosystems, which was
Oligotrophic mountain lakes are very good indicators of changes in acidification because they typically respond rapidly to pollution loads. The Tatra lakes have been affected by air pollution since the 1960s, primarily by sulfur and nitrogen oxides, which is reflected in chemical measurements. However, in lake sediments, increases in pollution were not always associated with changes in the biotic communities of the lakes. Changes in diatom assemblages before the 1960s were caused by environmental factors unique to individual lakes, with changes that were generally small or non-existent, with the exception of TSN, and that were not connected with the consequences of industrial development. Since the beginning of the 1960s, in almost all the oligotrophic lakes, a slight decrease in the DI-pH occurred, particularly at the end of the 1980s, when the highest acidic deposition was recorded in the Polish and Slovak areas of the Tatra Mountains. Reconstruction of the diatom-inferred pH showed that the decrease in pH ranged from 0.1 to 0.5 units after 1960, which was synchronous with the increasing emissions of air pollution. Except for dystrophic TSN and SME, which were acid-sensitive to extremely sensitive water bodies (4.5 > pH > 6; ANC < 20 μeq/L), the other lakes were classified as nonsensitive during past centuries. However, the absence of an unequivocal trend in the DI-pH in sediments of SME might be masked by the buffering properties of carboxylic and phenolic acids that occurred with the high DOC content, and the poor fit of the dominant fossil taxa to the modern calibration set.

To conclude, the rate and level of acidification in the oligotrophic Tatra lakes primarily depended on local geology (i.e., either easy or hard to weather rocks in the catchment), inflow of acidic water from surrounding peat bogs or acidic lakes, elevation, changes in catchment vegetation as a result of climate changes, e.g., warming, and/or human influences such as acidic deposition originating from combustion of fossil fuels, deforestation, and forest fires, among others. Although deposition of S and N compounds in the High Tatra Mountains was significant, major alterations of diatom assemblages in most lakes did not occur because of the relatively high ANC during the previous century.

4. Conclusions

Oligotrophic mountain lakes are very good indicators of changes in acidification because they typically respond rapidly to pollution loads. The Tatra lakes have been affected by air pollution since the 1960s, primarily by sulfur and nitrogen oxides, which is reflected in chemical measurements. However, in lake sediments, increases in pollution were not always associated with changes in the biotic communities of the lakes. Changes in diatom assemblages before the 1960s were caused by environmental factors unique to individual lakes, with changes that were generally small or non-existent, with the exception of TSN, and that were not connected with the consequences of industrial development. Since the beginning of the 1960s, in almost all the oligotrophic lakes, a slight decrease in the DI-pH occurred, particularly at the end of the 1980s, when the highest acidic deposition was recorded in the Polish and Slovak areas of the Tatra Mountains. Reconstruction of the diatom-inferred pH showed that the decrease in pH ranged from 0.1 to 0.5 units after 1960, which was synchronous with the increasing emissions of air pollution. Except for dystrophic TSN and SME, which were acid-sensitive to extremely sensitive water bodies (4.5 > pH > 6; ANC < 20 μeq/L), the other lakes were classified as nonsensitive during past centuries. However, the absence of an unequivocal trend in the DI-pH in sediments of SME might be masked by the buffering properties of carboxylic and phenolic acids that occurred with the high DOC content, and the poor fit of the dominant fossil taxa to the modern calibration set.

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Appendix A. Supplementary data

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