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Natural evolution of artificial lakes formed in lignite excavations based on diatom, geochemical and isotopic data

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Abstract TR-31 and TR-33 are post-mining lakes located within the Łuk Mużakowa Geopark (western Poland). They were created after the end of lignite exploitation in the second half of the nineteenth century. Although they are located in neighbouring excavations and currently have neutral pH levels, they developed differently. Based on the diatom communities, elemental analyses and isotopic data, TR-33 experienced a natural neutralization process from an acidic state to nearly neutral due to the presence of lignite residuum at the bottom of the excavation. Pyrite is common in lignite deposits and gangue, and its oxidation causes acidity in aquatic ecosystems. The primordial state of the acidic water in TR-33 was confirmed by the development of diatoms belonging to the *Eunotia* genus, which can tolerate acidic environments. The excavation in TR-31 was filled by rain and groundwater, and the pH of the water was neutral or nearly neutral from the beginning of lake's existence. This is indicated by the diatom assemblages during the initial phase of lake formation and the reconstruction of the water pH. The relatively low values of the C/N ratio in the deep layers of the core indicate the lack of lignite deposits at the bottom of TR-31.

Keywords Mining lakes · Diatoms · Elemental analyses · Isotopic data

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Introduction

In many post-mining areas around the world, the inactive excavations that remained after the mines closed became lakes (Harrison et al. 2003; Moser and Weisse 2011; Sienkiewicz and Gąsiorowski 2016). Over time, the excavations have become filled by rain and groundwater. Although most pit lakes are acidic or extremely acidic ($\text{pH} < 3$), some have neutral or even alkaline water (Sienkiewicz and Gąsiorowski 2018). Such acidic characteristics are mostly caused by the oxidation of pyrite and its high acid-producing potential (Moser and Weisse 2011). Other sulphide minerals are not major sources of acids, but are the main sources of dissolved metals in acidic pit lakes (Castro and Moore 2000). Currently neutral or alkaline mine water bodies are usually in contact with a source of carbonate, such as clay deposits, limestone or dolomite in the host rocks. The effects of pyrite oxidation can be neutralized by the high adsorption capacity of clay minerals; the dissolution of one mole of limestone consumes one to two moles of acidity and can release alkalinity into solution (Nkonyane et al. 2012). However, if the carbonate is depleted, the water can become acidic again due to further pyrite oxidation. On the other hand, the delivery of alkaline water into an acidic lake will help to neutralize the water's pH. In both cases, the water body can temporarily become neutral or acidic. Many pit lakes contain a high concentration of one or more heavy metals that are toxic for the phytoplankton and zooplankton living in these lakes. The chemical composition of pit lakes depends on the alkalinity of the local groundwater, the presence of carbonate in the surrounding areas, the amount of ore remaining in the excavation, the composition of the host rocks and the quality and quantity of runoff from the catchment (Castro and Moore 2000). The neutralization of acidity is also accelerated by anaerobic microbial processes, but their effectiveness depends on the concentration and availability of organic carbon. This factor can be limited by the intrinsic stability of the organic matter (i.e., its origin and degree of diagenesis; Laskov et al. 2002). The activity of sulphate-reducing bacteria (SRB) naturally improves the water quality in pit lakes. The energy required for the growth of SRB is provided by the oxidation of organic compounds or hydrogen with the reduction of sulphate to sulphide (i.e., the decrease of sulphate concentration in the lake water). In addition to the decrease of sulphates, SRB also remove metals from solution by the precipitation of sulphide (Castro and Moore 2000). Another important feature influencing the water chemistry in pit lakes is the length of time since the end of mining. As a rule, in the case of natural neutralization, younger lakes that form after the end of ore exploitation are more acidic and have higher concentrations of trace metals than older lakes (Sienkiewicz and Gąsiorowski 2017). However, the period of natural neutralization depends primarily on the factors above-mentioned. Thus, both abiotic and biotic factors have significant influences on the length of time needed for the natural neutralization of pit lakes.

The goal of this study was to determine and compare the development of two mining lakes (TR-31 and TR-33) that were formed after the end of lignite exploitation. For the lake management in the case of post-mining lakes, one of the most important issue to improve water quality is the choice between natural neutralization from acidification and the restoration of pit lakes controlled by human. The first option can be connected with a long-lasting process, and the second can be too expensive. Acidic pit lakes can be neutralized for example by the continued addition of soda ash as has been done for Lake Bockwitz in the Central Germany (Schultze et al. 2010). The changes in the water quality and diatom assemblages in TR-31 and TR-33 were caused only by natural factors that is, the lakes have never been filled by well-buffered water to neutralize their acidic character and there was no addition of alkali substances. The water bodies formed 'an anthropogenic lake district' have also never been monitored. The results of analyses show historical rate in the water pH changes and algal community composition.

The studied lakes are located in the area of the Łuk Mużakowa Geopark along the Polish-German border. The lignite mines, which activity caused formation of these lakes, operated from the second half of the nineteenth century until the 1970s. Presently, the pH of the water in the lake district varies from extremely acidic (about 2.5) to alkaline (about 8.8). The studied lakes are located in neighbouring inactive lignite excavations and formed at the same time. We expected that their evolutions would be similar to each other, at least in terms of changes in diatom flora, which was the main criterion used to identify individual stages of the lakes' development. The results of elemental analyses: total organic carbon (TOC), total organic nitrogen (TON), sulphur and C/N ratio and isotopic data ($\delta^{13}C$, $\delta^{15}N$) were also used to compare the changes during the lakes' developments.

Study sites

TR-31 and TR-33 are located within the Łuk Mużakowa Geopark (western Poland). They are anthropogenic lakes that formed after the end of lignite exploitation. The Łuk Mużakowa is a moraine 40 km long and 3–5 km wide, and it originated as a result of intensive glacial activity during the Riss glaciation. The Miocene sediments and extensive lignite deposits were folded and created an arch-shape form. Approximately 100 anthropogenic lakes are located in the Polish region of the Geopark, which formed following lignite, gravel, sand and clay exploitation. After the Second World War as a result of the agrarian reform in 1945, the area where the pit lakes are located was additionally afforested. In the second half of the twentieth century, the lakes with neutral or almost neutral water (mostly clay pits) were stocked with fish. Beside creation of the touristic geopath in small area of the geopark, the lakes are located in pristine region without special management. Many of them are situated in remote area, among dense cover of trees and shrubs what is a limit in using of them to recreation, irrigation or agriculture.

Both lakes are located in neighbouring inactive excavations approximately 1 km apart (Fig. 1). They are some of the oldest lakes in the geopark; they are approximately 150 years old. Currently, the water in TR-33 is slightly acidic, whereas TR-31 has neutral water. Table 1 presents selected morphometric and chemical parameters measured in September 2013 and historical data by Solski et al. (1988).

Materials and methods

The results of analyses of a core from TR-33, including dating, the diatom and Cladocera stratigraphy, the reconstruction of the diatom-inferred pH, and geochemical and isotopic analyses, were presented in Sienkiewicz and Gąsiorowski (2016, 2017).

A core from TR-31 was collected in September 2013 from the deepest part of the lake using a Kajak-type gravity corer. The core was 60 cm long and two lithological different segments can be distinguished (Fig. 2a). The first (depths of 60–50 cm) was composed of dark silt with a significant amount of black debris. This sediment was characterized by high dry densities (0.4–0.6 g cm^{-3}), low water contents and relatively low TOCs (up to 6%). The second (depth 50–0 cm) was dark olive silty gyttja with a lower dry density (0.05–0.2 g cm^{-3}) and higher organic matter content. The sediments core was subsampled every 1 cm in the field and packed in plastic bags.

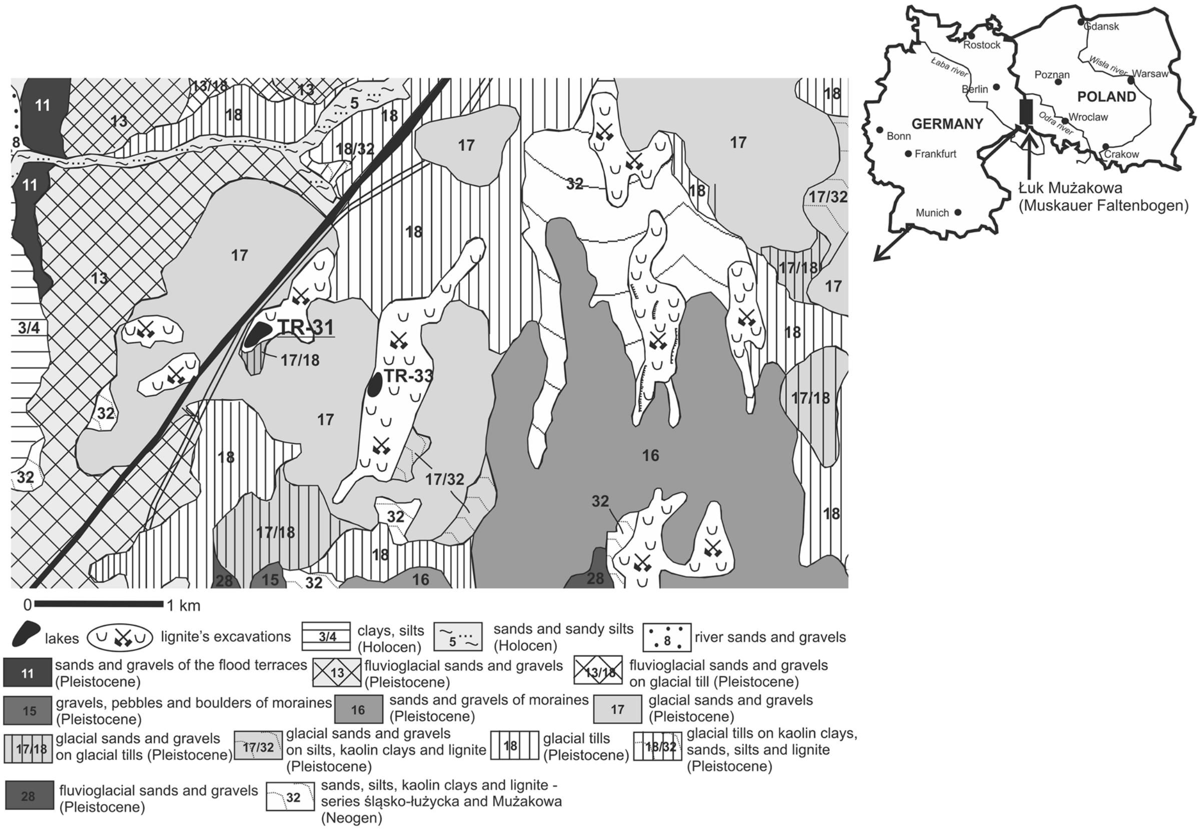

Fig. 1 Location and geological setting of lakes TR-31 and TR-33. The geological data are based on the Detailed Geological Map of Poland, Trzebiel sheet (Bartczak and Gancarz 2001)

Table 1 Morphometric and chemical characterization of lakes TR-31 and TR-33

	TR-31		TR-33	
Latitude	N 51°37′00.1″		N 51°36′23.3″	
Longitude	E 14°47′28.7″		E 14°48′11.2″	
Length (m)	235		215	
Width (m)	100		70	
Area (ha)	1.7		1.0	
Max. depth (m)	7.0		10.0	
	1986	2013	1986	2013
pH	7.0	7.05	5.4	6.47
EC (µS cm^{-1})	N.A.	200	N.A.	136
O_2 (mg L^{-1})	7.9	3.64	8.5	5.44
Temperature (°C)	27.5	15.9	24.5	17.1
DOC (mg L^{-1})	N.A.	12.0	N.A.	8.94
N (mg L^{-1})	N.A.	0.97	N.A.	2.02
Ca (mg L^{-1})	26.0	29.6	13.0	14.6
Mg (mg L^{-1})	29.0	4.27	38.0	3.02
Na (mg L^{-1})	3.3	4.51	2.6	3.43
K (mg L^{-1})	2.8	2.24	1.9	2.79
Fe (mg L^{-1})	0.29	3.14	0.06	0.44
Mn (µg L^{-1})	N.A.	0.172	N.A.	0.057
Al (µg L^{-1})	N.A	0.023	N.A.	0.033
P (µg L^{-1})	N.A.	0.016	N.A.	0.009
Si (mg $L^{-1}L^{-1}$)	N.A.	9.24	N.A.	0.93
S (mg L^{-1})	N.A.	2.72	N.A.	13.4

N.A. not available

Parameters measured in 1986 by Solski et al. (1988)

Samples for the diatom analysis were prepared according to the standard procedure (Battarbee 1986), and permanent slides (sample volumes of 1 cm^3) were mounted in Naphrax® with a refractive index of 1.74. An Olympus BX51 light microscope with a 100 × oil immersion objective was used to identify the diatoms, which were identified according to Krammer and Lange-Bertalot (1986, 1988, 1991a, b) and Lange-Bertalot and Metzeltin (1996). The more recent nomenclature of diatoms AlgaBase (www.algabase.org) was also used. Phases of diatoms development were distinguished based on a CONSLINK (constrained single link cluster analysis) using ZONE software, version 1.2 (Juggins 1992). It is a method of single link agglomerative clustering in which clusters are constrained to consist of adjacent samples or sample groups.

For the elemental (TOC, TON, sulphur, C/N ratio) and isotopic analyses, the samples were dried at 65 °C for 48 h and ground in an agate mortar. The samples were then treated with 10% HCl to remove carbonate, washed in distilled water and dried again. Elemental analyses (TOC, TON and S contents) were carried out using a Vario MicroCUBE elemental analyser. The measurements were calibrated to the sulfanilic acid standard. The isotopic analyses were performed using a Thermo Flash EA 1112 HT elemental analyser connected to a Thermo Delta V Advantage isotope ratio mass spectrometer in a continuous flow system. The measurements were calibrated to the USGS 40, USGS 4 and IAEA 600 standards, and the results were reported as per mill (‰) deviations versus atmospheric N_2 ($\delta^{15}N$) and the Vienna Pee Bee Belemnite ($\delta^{13}C$). Typical standard deviations were 0.43‰ and 0.33‰ for $\delta^{15}N$ and $\delta^{13}C$, respectively. The elemental analysis was performed in the U-Series Laboratory, and the isotopic analysis was performed at the Stable Isotope Laboratory of the Institute of Geological Sciences, Polish Academy of Sciences in Warsaw.

The chronology of the sediment cores was based on ^{210}Pb activity measurements. For the ^{210}Pb analysis, five cubic centimetre samples of homogenized sediment were collected from each level. The sediment samples were weighed, dried, and weighed again to determine the bulk density and water content. The ^{210}Pb activity of the sediments was indirectly determined by alpha-spectrometry measurements of ^{210}Po (E_α = 5.31 MeV, $T_{1/2}$ = 138 days) activity (Flynn 1968) in the U-Series Laboratory at the Institute of Geological Sciences, Polish Academy of Sciences in Warsaw. A known amount of $^{208}Po + {}^{209}Po$ was added to the weighed samples as an internal yield tracer. Polonium was separated from the samples using strong hydrochloric and nitric acids and then deposited onto silver discs (Flynn 1968). The activities of ^{210}Po, ^{208}Po and ^{209}Po were measured using a DUO alpha spectrometer produced by EG&G ORTEC. A constant rate of unsupported ^{210}Pb supply (CRS) model was used to calculate the sediment age (Appleby 2001). The activity of unsupported (allochthonous) ^{210}Pb was calculated from the total activity of ^{210}Pb by subtracting the supported (authigenic) ^{210}Pb activity. The activities of unsupported ^{210}Pb were plotted on a cumulative dry mass scale

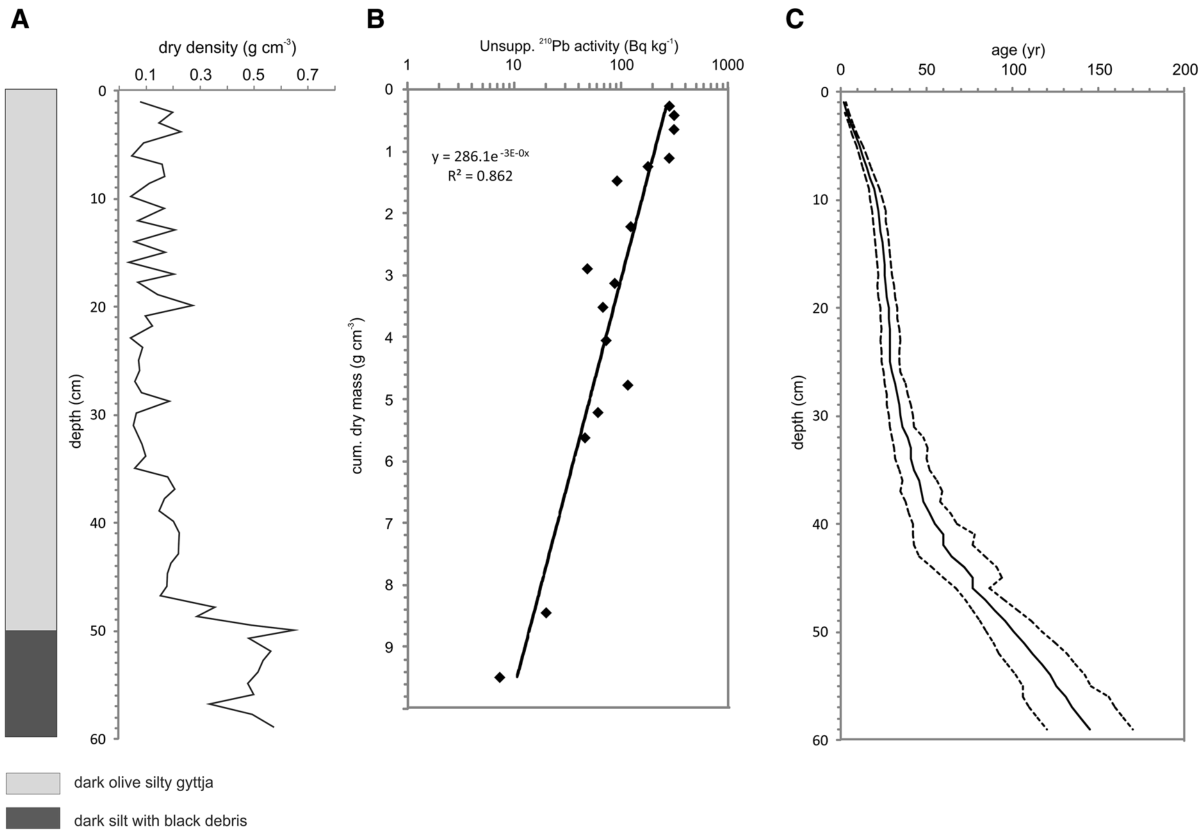

Fig. 2 Dry density (**a**), specific activity of unsupported ^{210}Pb (**b**) and age-depth model (**c**) for the sediment sequence from lake TR-31. Lithologies: 1—dark silt with terrestrial plant debris, 2—fine gyttja detritus

(Fig. 2b). An age-depth function was calculated using the randomization method with the MOD-AGE algorithm (Hercman and Pawlak 2012; Hercman et al. 2014).

Results

Dating

The specific activity of ^{210}Pb was measured every 2–3 cm along the core. Sediments without unsupported ^{210}Pb were noted below the depth of 54 cm, and the supported ^{210}Pb was 10 Bq kg^{-1}. Generally, the activity of unsupported ^{210}Pb decreased with depth in the sediment column. Small deviations from the model (too low activities) occur in the uppermost part of the sequence and at 12 and 23 cm. The calculated age-depth model (Fig. 2c) indicates that the deepest sediments are 150 ± 25 years old. The sedimentation rate varied during sediment deposition. The highest sedimentation rate occurred between 40 and 10 cm, which corresponds to the age between 55 and 21 years, whereas the slowest deposition occurred at the beginning of the lake's existence.

Diatom analysis of TR-31

A total of 106 diatom species belonging to 28 genera were identified (Fig. 3). The most common genera were *Fragilaria* sensu lato (13 taxa), *Eunotia* (12), *Navicula s.l.* (11), *Achnanthes s.l.* (10), and *Cyclotella s.l.* (7). The sediments were divided into five local diatom zones (DAZ 1-DAZ 5) based on a CONSLINK analysis (Gordon and Birks 1972), and the diatom assemblage zones were defined using the ZONE software, version 1.2 (Juggins 1992). Most of the diatoms preferred neutral and alkaline waters. Only single diatom valves were observed in DAZ 1 (1868–1906; 59–51 cm), such as *Eunotia* spp.,

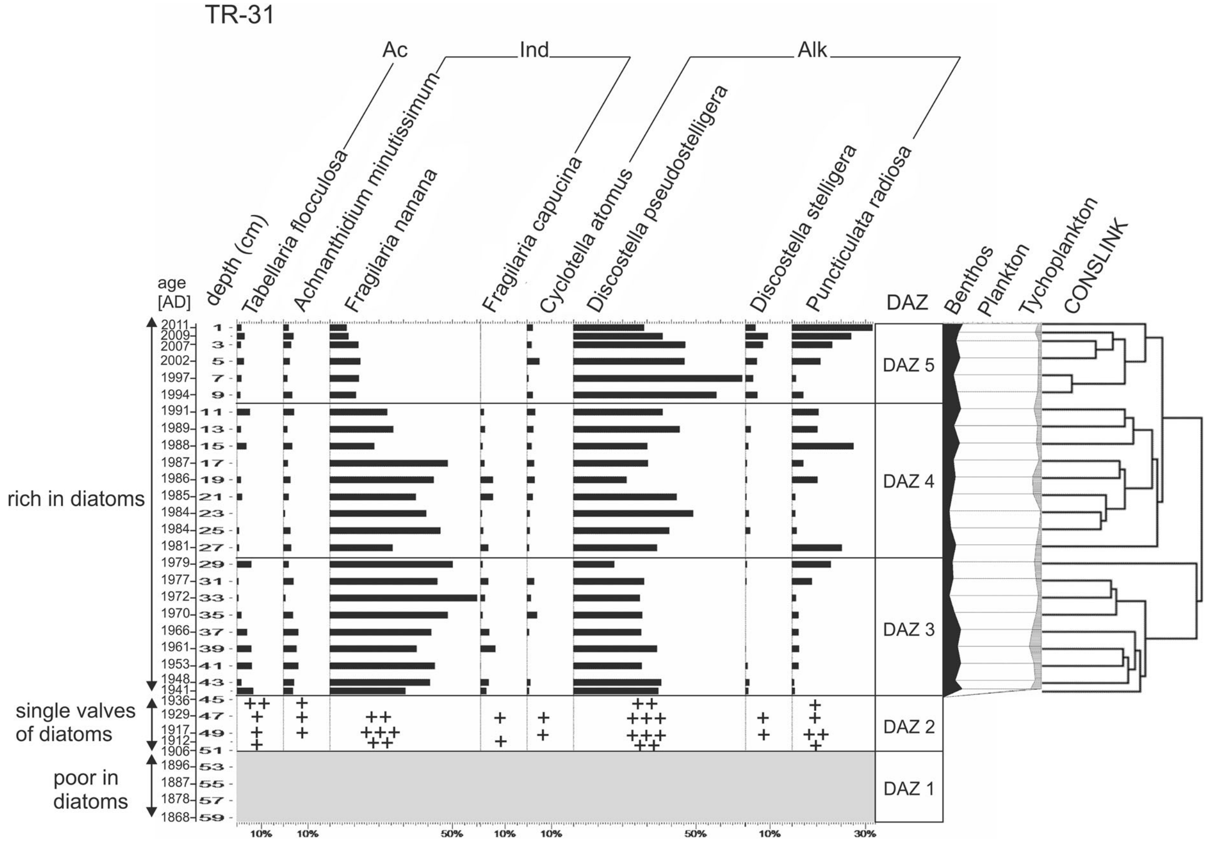

Fig. 3 Diatom stratigraphy of lake TR-31. The cross symbols in the lower part of the diagram indicate quantity classes of diatom remains

Fragilaria spp., *Aulacoseira* spp., *Navicula* spp., and *Nitzschia* spp. In DAZ 2 (1906–1941; 51–44 cm), the frequency of diatoms was higher, but the number of valves was still < 150 (not significant statistically); the individual species are marked by crosses in the diagram (e.g., *Discostella pseudostelligera* (Hust.) Houk & Klee, *Fragilaria nanana* Lange-Bertalot, *Achnathidium minutissimum* (Kütz.) Czarnecki, *Tabellaria flocculosa* (Roth) Kützing, and *Cyclotella atomus* Hustedt). In the remaining part of the core, the diatom valve counts were in the range of 300–400. DAZ 3 (1941–1980; 44–28 cm) was dominated by planktonic diatoms such as *Fragilaria nanana* and *Discostella pseudostelligera*. Planktonic taxa were the dominant diatoms until the present. DAZ 4 (1980–1993; 27–10 cm) contained the same dominant species as in DAZ 3, and the planktonic *Puncticulata radiosa* increased in frequency. A decrease of *F. nanana* was observed in the youngest sediments in DAZ 5 (1993–2011; 10–0 cm), whereas *P. radiosa* reached its maximum frequency, similar to *D. pseudostelligera*. A small increase of planktonic *Discostella stelligera* was also noted.

Reconstruction of diatom-inferred pH (DI-pH) from the sediments of TR-31 and TR-33

To compare the differences and similarities between the changes in acidity in TR-31 and TR-33, a reconstruction of the pH of the water (DI-pH) was performed (Fig. 4). The reconstructions of DI-pH for both lakes were performed using the Mining pH training set created for pit lakes (Sienkiewicz and Gąsiorowski 2017). The values of the reconstructions were determined using the weighted averaging (WA) method with classical and inverse deshrinking. The apparent root mean square errors for the training set were $\mathrm{RMSE}_{\mathrm{WA\_Cla}} = 0.74$ (classical deshrinking) and $\mathrm{RMSE}_{\mathrm{WA\_Inv}} = 0.69$ (inverse deshrinking), and the corresponding square correlation between the inferred

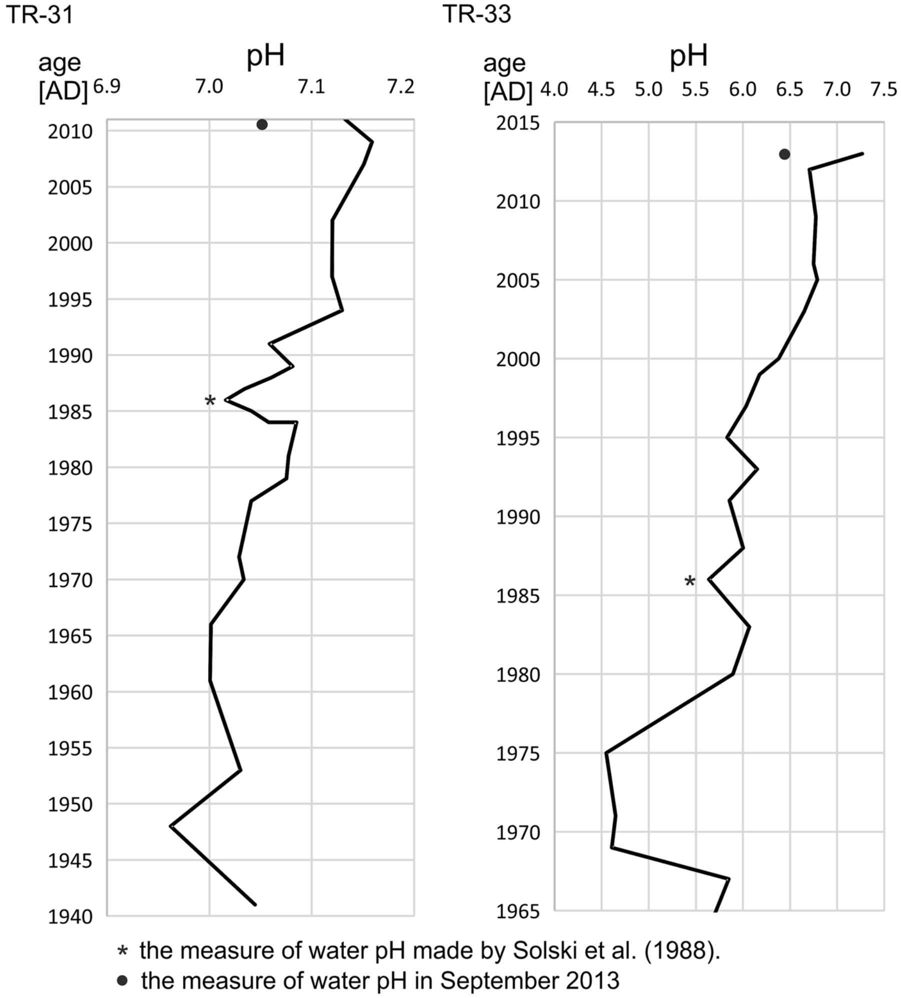

Fig. 4 Diatom-inferred pH reconstructions for lakes TR-31 and TR-33

and observed values (R^2) was equal to 0.87. The WA method with inverse deshrinking was chosen to show the changes in DI-pH due to the lower RMSE compared to classical deshrinking. In the modern dataset, the representation of fossil diatoms from the sediments of TR-33 varied between 89 and 99%, and that for TR-31 ranged between 99.3 and 100%. The reconstructions of DI-pH for both lakes were performed until the numbers of diatom taxa were statistically significant. The values of DI-pH for the sediments of TR-31 were nearly constant and ranged between 6.96 and 7.16; i.e., the changes were within the error of the method. The fluctuations of the water pH in TR-33 were larger, and the values of DI-pH varied between 4.55 and 7.27 (Sienkiewicz and Gąsiorowski 2016). The lowest DI-pH values were observed in the 1970s, whereas the current value is the highest.

Isotopic and elemental analyses of the sediments of TR-31

The values of $\delta^{13}C$ for TR-31 varied between −26.12 and −35.7‰, whereas $\delta^{15}N$ ranged between −0.41 and + 2.69‰ (Fig. 5). The carbon stable isotope curve has a slightly decreasing trend and the nitrogen stable isotopes have an increasing trend. An increase in total organic carbon (TOC) was noted, especially since the 1970s, but the amounts throughout the core ranged from 3.7 to 14.95%. The total organic nitrogen (TON) was relatively low (0.15–1.67%). For more than 50 years after the lake's formation, the source of organic matter was a mixture of aquatic phytoplankton

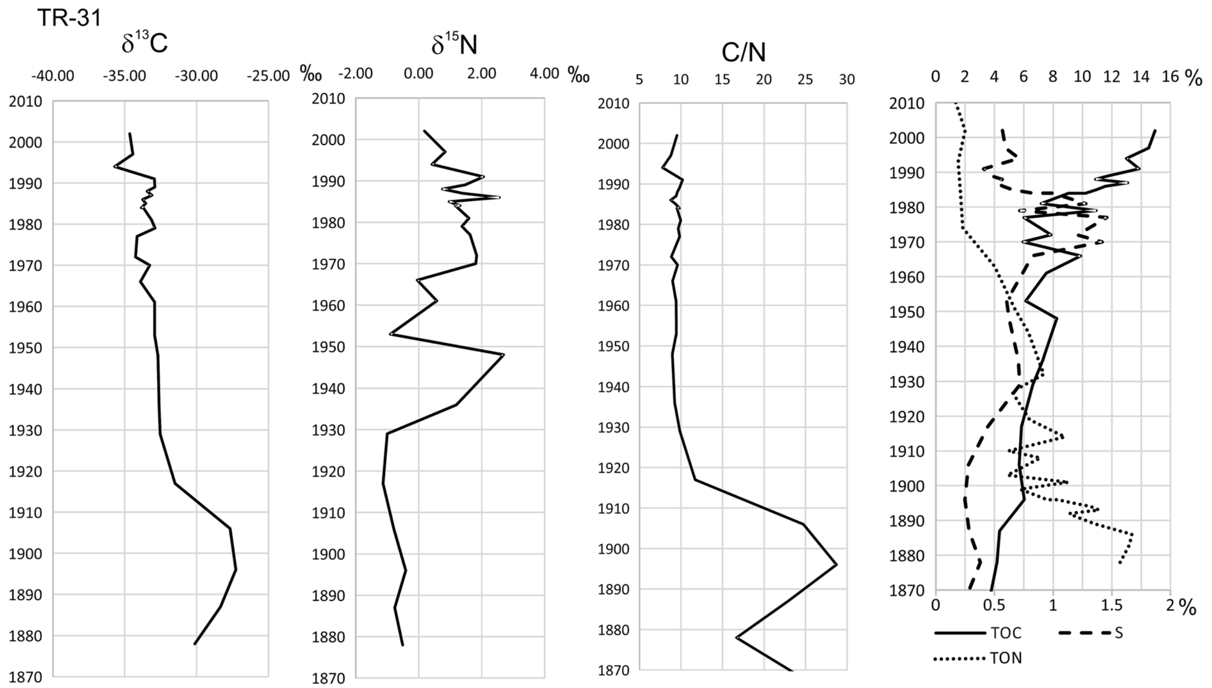

Fig. 5 Isotopic (δ^{13}C, δ^{15}N) and elemental (C/N, TOC, TON, S) analyses of organic matter from the TR-31 sediment profile

and terrestrial plants (C/N = 11.7–28.7). From the beginning of the 1930s, the C/N ratios indicate that the organic matter mainly consisted of aquatic plants (C/N = 7.7–10.1). The amount of sulphur in the core varied between 2.0 and 11.6% with the highest concentration of S occurring in 1970–1980.

Discussion

The studied lakes (TR-31 and TR-33) were created after the end of lignite exploitation at almost the same time (i.e., the second half of the nineteenth century). Presently, both lakes have neutral (TR-31) or nearly neutral (TR-33) water pH and the main diatom taxon living in them is planktonic *Discostella pseudostelligera*. However, changes in the diatom assemblages during the lakes' existence indicate different stages of lake development. In the initial phase of the lakes' formation, small amounts of diatoms inhabited the water bodies. TR-31 (DAZ 1) mainly contained benthic diatoms, such as *Eunotia* spp., *Fragilaria* spp., *Nitzschia* spp. and *Navicula* spp. A few tychoplanktonic and/or planktonic *Aulacoseira* spp. were also identified in these sediments. However, the relative frequencies of the diatoms were too low to calculate the percentage occurrence of individual species. The clearly higher density of sediments and the admixture of terrestrial plant debris may indicate that these parts of the sediment sequence originated from the pre-lake stage of basin development. Only shallow, temporary water bodies probably existed at this time. Similarly, in the sediments of TR-33 only a few valves of diatoms were found in this time period and the only taxa belong to *Eunotia*. The presence of this genus suggests a low water level in the lake, a lack of nutrients and acidic water. *Eunotia* spp. are diatoms that tolerate low pH water and often occur in acidic and even extremely acidic water bodies (Koschorreck and Tittel 2002; Sienkiewicz and Gąsiorowski 2017). The first period of the lake's development, during which *Eunotia* dominated, lasted for 77 years (i.e., two times longer than the first phase in TR-31 (Fig. 6). The close proximity of the lakes to each other suggests that both water bodies were supplied by the groundwater with similar mineralization. Both lakes are situated on similar bedrock (Fig. 1), so the differences in the durations of the initial phases of the lakes' evolution and the large difference in the diatom autecology between the lakes in this time period may

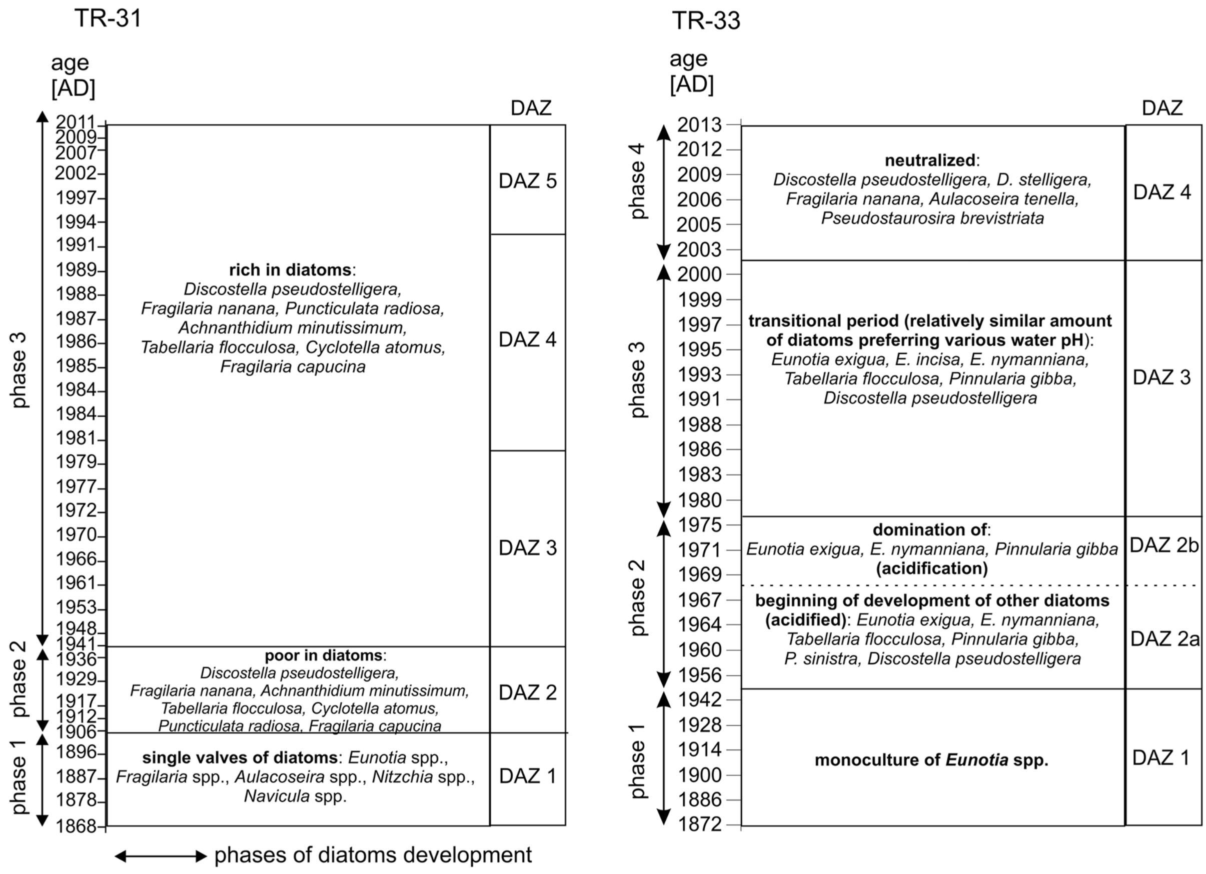

Fig. 6 Main stages of diatom assemblage development in lakes TR-31 and TR-33

have been caused by the different amounts of lignite residuum remaining in the excavations. It is the most likely reason because both lakes have similar shape and physical parameters (Table 1) and catchment limited almost exclusively to the lake area. The water pH in TR-33 remained low for a relatively long time due to the significant amount of pyrite from lignite debris, whereas almost all of the lignite in TR-31 was extracted.

A slight increase in diatom valves was observed in TR-31 over the next 35 years (approximately to the 1940s; DAZ 2). The composition of the algal community indicates better conditions for diatom flora development compared to the previous phase. The rise of planktonic *Fragilaria nanana* and *Discostella pseudostelligera* indicates greater water depth and better nutrient availability. However, the conditions for diatom development in this aquatic ecosystem were still were not highly favourable, which was confirmed by the insignificant number of diatom taxa in this period. In TR-33, at the beginning of the 1950s (DAZ 2a), the quantity of more diverse diatoms increased, but most were taxa that tolerate acidic water. Since the 1960s, their frequency has been statistically significant, and the lake has been dominated by *Eunotia exigua, E. nymanniana* and *Pinularia gibba*. At this time, the presence of teratological forms of diatoms was observed. Very acidic water with high concentrations of trace metals can caused deformation of the valve's morphology and structure (Cooper et al. 2003). For more than 100 years (i.e., from the beginning of lake's existence to the 1980s), the water in TR-33 retained toxic properties that limited the development of phytoplankton and zooplankton (Sienkiewicz and Gąsiorowski 2016). During this period, excluding DAZ 1 and the lower part of DAZ 2a, the DI-pH had the lowest values of approximately 4.5 (DAZ 2b).

In the sediments of TR-31, zones DAZ 3-DAZ 5, which were distinguished based on the diatom community and a CONSLINK analysis (Fig. 3), can be included in the last phase of the lake's development (Fig. 6). Over the past 70 years, the DI-pH (about 7) and the ratio of benthic, planktonic and tychoplanktonic diatoms were nearly constant (Fig. 3). The differences in the frequencies of the individual diatoms appear to have been mainly caused by the nutrient concentrations in the lake rather than changes in the water pH because the DI-pH values varied over a very small range. A higher frequency of planktonic *Cyclotella s.l.* was observed in DAZ 5 compared to the previous zones. Most of the taxa in TR-31 were alkaliphilus and indifferent. In conclusion, this lake was never acidified despite the extraction of lignite ore approximately 150 years earlier. This is unexpected because this type of reservoir is usually characterized by the presence of pyrite and other sulphide compounds that acidify the aquatic environment, at least in the initial phase of the lake's development.

In TR-33, substantial changes in the algal community were observed at the beginning of the 1980s. The amount of acid-tolerant taxa, which dominated the previous zone, decreased, and the frequency of planktonic diatoms increased, especially at the end of the twentieth century. However, the frequencies of acidophilous and indifferent taxa were comparable during this period, so it was a transitional period between typical acidic and neutral conditions in the lake. The DI-pH values varied between 5.5 and 6.5; diatoms with pH optima typical for acidic and neutral waters can live in this range of water pH. This period lasted for 25 years, and the lake has subsequently become neutral. Acidophilus diatoms decreased in frequency or disappeared, and the domination of alkaliphilus taxa such as *Discostella* spp. was observed (Sienkiewicz and Gąsiorowski 2016). At this time, the DI-pH varied between 6.5 and 7.3.

Several stages of lake evolution can be distinguished in both lakes (Fig. 6). The similarity between the development of TR-31 and TR-33 is indicated by the quantity of diatoms inhabiting aquatic environments during the initial phases of the lakes' formation. Initially, the low frequency of diatoms was a result of adverse conditions, which caused low primary production in the reservoirs due to very shallow water and the lack of nutrients available for algae. With increasing water levels and the delivery of nutrients from the catchment, the lakes gradually became richer in diatoms. Additionally, in TR-33, the acidic water limited the growth of many diatom taxa. Because of the low productivity in the initial phases of the lakes' development, the organic matter consisted primarily of plant material rich in cellulose and lignin. Generally, the organic matter in pit lakes may be of aquatic, terrestrial and lignite origin. The organic matter in the studied lakes had different sources. However, we can assume that the lignite deposit was in the bedrock of TR-33 due to the high C/N ratios (approximately 90) in the deep layers of the core (Sienkiewicz and Gąsiorowski 2016). The presence of lignite significantly increases the C/N ratio of soil (Zikeli et al. 2002). However, TR-31 likely contained little or no lignite residuum because the relatively low C/N ratios (below 30) in lower part of the core indicate that the source of organic matter was a mixture of phytoplankton and terrestrial plants without lignite in the gangue. The C/N ratios > 10 confirm that the organic matter consisted of aquatic plants with some input from terrestrial plants (Zong et al. 2006), but the value of C/N ratio for lignite is much higher (about 100) (Zikeli et al. 2002).

The $\delta^{13}C$ curves in both lakes have decreasing trends, and the highest values occur in the lower parts of the cores (Fig. 5; Sienkiewicz and Gąsiorowski 2016). Values of $\delta^{13}C$ between -31 and approximately -35‰ are often observed in acidic mine lakes with higher primary production (Laskov et al. 2002), and the C/N ratio is usually approximately 10, which indicates that aquatic plants were the source of the organic matter. Similar results were observed in the sediments of the studied lakes, which confirms the gradual increase of productivity in both lakes over the last few decades. Higher primary production in the lakes was also indicated by an increase of TOC. In the lower parts of the studied cores, the high C/N ratios and $\delta^{13}C$ indicate that the aquatic organic matter was low, probably because of low autochthonic productivity in the lakes and fast mineralization. Furthermore, the $\delta^{13}C$ values (approximately -25‰) show that the samples may contain lignite (Laskov et al. 2002). The $\delta^{15}N$ records of the lakes vary. The positive trend in $\delta^{15}N$ in TR-31 is associated with an increasing trophic level of the lake. This increasing trend was stopped between the 1950s and 1970s (also visible in slight drop in TOC values; Fig. 5). The slight reverse from eutrophication may be related to intensive afforestation of the area in the second half of the twentieth century, but there are any other data suggesting the reason for this change. Usually, values of $\delta^{15}N$ increase in water bodies that are changing from oligotrophic to eutrophic (Brenner et al. 1999). The trophic level was higher in TR-31 than in TR-33, where the $\delta^{15}N$ had a negative trend. Decreases of total organic nitrogen were observed in both lakes. The amount of sulphur measured from the sediments was relatively low with small peaks in the 1960s in TR-33 (Sienkiewicz and Gąsiorowski 2016) and in the 1970s in TR-31, whereas the total organic nitrogen had decreasing trends in both lakes.

The diatom-inferred pH was reconstructed if the number of counted diatom valves was > 300 per sample, which was related to sufficient water levels in the lakes and the availability of nutrients. In the case of TR-31, the reconstruction of DI-pH could be performed since the 1940s, whereas the reconstruction of DI-pH for TR-33 was carried out in the sediments that accumulated 25 years later (i.e., since 1965). The presence of the lignite deposit at the bottom of TR-33 caused longer-term adverse environmental conditions (i.e., low water pH) for the development of diatom flora compared with TR-31. The DI-pH in TR-31 was constant during the entire period for which the reconstruction was done. The values of DI-pH and the pH measurements performed in the water column indicate neutral water in this lake, and the fluctuations in DI-pH were within the error of the reconstruction method (Fig. 4). Three phases of the DI-pH changes can be distinguished in TR-33. The water can be assumed to have been acidic at the beginning of the lake's existence because only the monoculture of *Eunotia* spp. was present during this period. *Eunotia* taxa are often found in acidic waters. Among the diatoms in TR-33 (DAZ 1), many of *Eunotia exigua* and *E. nymanniana* were observed, which have optimum pHs of 3.76 and 3.95, respectively (Sienkiewicz and Gąsiorowski 2017). Until the 1980s, TR-33 had relatively acidic water (< 6.0). From then until 2003, the DI-pH oscillated between 5.5 and 6.5. After 2003, the diatom-inferred pH exceeded 6.5, which indicates neutralization of the lake. The measurements performed in 1986 (Solski et al. 1988) were consistent with the DI-pH values in both lakes, whereas the water pH measured in 2013 slightly exceeds the value of the error method used to reconstruct the diatom-inferred pH in TR-31.

Studies of many acidic pit lakes indicate that natural neutralization of this type of water bodies may require period ranging from a few years to some decades and depends on surrounding geology, catchment interaction, type and size ore deposit remaining in the excavation etc. (Schultze et al. 2010; Blanchette and Lund 2016; Sienkiewicz and Gąsiorowski 2016). The neutralization process can be artificially accelerated, such as by the addition of ash soda or filling a lake with well-buffered river water. However, re-acidification of these lakes may occur in the case of high loads of products of pyrite oxidation in groundwater. From the economic point of view, current in situ "active treatment" is expensive and unsustainable as well as risky due to possibility of re-acidification (Schultze et al. 2010; Blanchette and Lund 2016). In the case of pit lakes located within the Polish part of the Łuk Mużakowa Geopark, the natural neutralization was, up to now, the only way to restoration of these water bodies, mainly because of an economic conditions.

Conclusions

1. Lakes TR-31 and TR-33 formed approximately 150 years ago after the end of lignite exploitation. Despite of similar shape, size and closely localization between each other, the development of diatom flora was differential, especially in the initial phase of lakes' evolution.
2. The reason of these differences was the presence of lignite residuum in TR-33, and likely various degrees of activity of anaerobic microbial processes.
3. In contrast to TR-33, TR-31 has never been strongly acidified. In both lakes, only very few valves of diatoms were noted at the beginning of the lakes' formation, which was a result of the small volumes of water and the paucity of nutrients. In TR-33, the remaining lignite deposit in the gangue contributed to the acidification of the lake.
4. The reconstruction of DI-pH showed that TR-33 was completely neutralized in 2003, whereas TR-31 has been neutral since the 1940s. The changes in the natural neutralization process of TR-33 was mirrored in the oscillation of DI-pH. Over the last 50 years, the values of DI-pH changed from 4.6 to 7.3 (i.e., 2.7 units of pH). The DI-pH in TR-31 was

neutral almost from the beginning of lake's existence.

5. Due to the lack of the economic opportunities, currently acidic lakes located in the Łuk Mużakowa Geopark will undergo of natural neutralization. The main advantage of these lakes is use of them as the fishponds.

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