# Modern limnology and varve-formation processes in Lake Żabińskie, northeastern Poland: comprehensive process studies as a key to understand the sediment record

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# ABSTRACT

Reconstruction of paleoclimatic and paleoenvironmental conditions from sediment records require a thorough knowledge of the physical, chemical and biological factors that influence sediment-formation processes and signal preservation in lake sediments. Lake Żabińskie, a eutrophic hardwater lake located in northeastern Poland (Masurian Lake District), provides a unique environment for the investigation of processes that lead to varve formation. During a two-vear observation period we investigated limnological and hydrochemical conditions within the water column, recent sediment fluxes and laminations preserved in the sediments of this lake to understand the relationship between the lake water properties and the sediment formation processes. We demonstrate that dimictic to meromictic mixing patterns may occur in Lake Zabińskie, depending on the meteorological conditions. Regardless of the water mixing pattern, the lake was stratified during much of the year which led to significant differences between surface and near-bottom water environments. The hypolimnion was characterized by higher conductivity and anoxic conditions with only short periods of available oxygen, which created conditions ideal for the formation and preservation of biogenic varves in Lake Zabińskie. The material collected from the sediment trap revealed notable changes in sediment fluxes with characteristic spring maxima and, optionally, a second late fall maxima. Considerable variability was also observed for the fluxes of total organic carbon, biogenic silica and calcite. Microscopic investigation of the topmost sediments revealed a complex structure of the varves showing a distinct spring calcite lamina followed by several fine calcite laminae interbedded with diatom-rich laminae and, finally, by an organic-rich lamina with minerogenic admixtures deposited during winter. This seasonal variability was also reflected in the chemical composition inferred from high-resolution XRF measurements which allowed for the recognition of individual seasons within one varve. A characteristic annual succession of elemental composition followed a distinct pattern: spring was marked with a silica peak followed by a major calcium peak; during summer and fall minor calcium peaks occurred as well as maxima in iron and sulphur; winter was characterized by a peak in potassium. This study shows the potential that the sediment record from Lake Żabińskie has as high-resolution paleoenvironmental archive.

Key words: Lake sediments, paleolimnology, mixing regime, sediment flux, biogenic varves.

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# **INTRODUCTION**

Lake sediments are among the most valuable environmental archives as they record physical, chemical and biological conditions and processes taking place in the lake water body as well as in the surrounding catchment and the atmosphere. The myriad of lake sediment proxies sensitive to a multitude of processes at a broad range of temporal scales, from seasonal changes to glacial-interglacial scales, documents many aspects of climate and environmental change (Brauer, 2004; Zolitschka, 2007). Howthe reconstruction of paleoclimatic ever. and paleoenvironmental data from sediment records requires a thorough knowledge of the conditions affecting sedimentation processes in lakes. It is crucial to understand which biological, chemical and physical factors influence sediment-formation processes and how this is recorded in the sediment deposits. Moreover, the process-level understanding of a particular sediment record is necessary because the atmosphere-catchment-lake system is unique for each individual site. This is especially important for annually laminated (varved) sediments, which offer the highest possible time-resolution of the archived sedimentary information (Tiljander *et al.*, 2002; Francus, 2004; Francus *et al.*, 2009). Only the combination of limnological measurements, sediment trapping and sediment analysis allows for the identification of the processes responsible for varve formation and for a better interpretation of seasonal signals preserved in the sediments (Ojala *et al.*, 2013). Such information provides an opportunity to calibrate varves and paleolimnological proxies against instrumental hydrological and meteorological data.

Although varved lake sediments have received worldwide growing scientific attention (Ojala *et al.*, 2012), very few studies have investigated specific processes (documented with observational data) that lead to varve forma-



tion and signal preservation in particular lakes. It has been established that the deposition of clastic and clastic-biogenic varves depends mainly on seasonal runoff and the associated discharge of suspended sediment from the catchment into the lake (Itkonen and Salonen, 1994: Lamoureux, 1999; Ojala et al., 2000). However, in lakes dominated by biogenic sedimentation the mechanism of varve formation is much more complex and includes interactions of physical, chemical and biological processes (Flower, 1990; Bluszcz et al., 2008; Tylmann et al., 2012). As these processes are highly variable and site-specific, even to extent that is more complex than processes related to seasonal catchment runoff and erosion for clastic and/or clastic-biogenic varves (Lamoureux, 1999; Ojala et al., 2013), it is essential to recognize the particle flux dynamics and seasonal changes in the sediment composition in order to understand the paleoenvironmental information recorded by biogenic varves.

Here we provide a detailed process study from the varved sediments of Lake Żabińskie (northeastern Poland), which consists of three pillars: i) in situ measurements of the water column; ii) particle flux measurements using sediment traps; and iii) analysis of sediments from the uppermost part of a sediment core. Our aim is to understand the relationship between lake water properties and sedimentformation processes in Lake Żabińskie. This lake has revealed excellent preservation of biogenic varves with high sedimentation rates, which offers a great potential for highresolution, quantitative paleoclimate reconstructions of the past millennium and beyond (Tylmann et al., 2013b; Amann et al., 2014; Hernández-Almeida et al., 2015; Larocque-Tobler et al., 2015). To exploit this potential, conditions for the deposition of these varved sediments must be recognized as a prerequisite for a reliable varve chronology and an appropriate interpretation of multi-proxy records. The observation period of two years with different climate conditions (very warm winter 2011/2012 and very cold winter 2012/2013) offers an opportunity to our process study: the limnological properties of the lake could be observed for conditions of both a mild and an extremely severe winter.

In this respect, we first report limnological and hydrochemical conditions that control the sedimentation processes in Lake Żabińskie. We then show how the different meteorological conditions influence the water mixing patterns in the lake, which leads to different sediment accumulation rates. Finally, we document seasonal variability of the sediment flux composition and the varve structure.

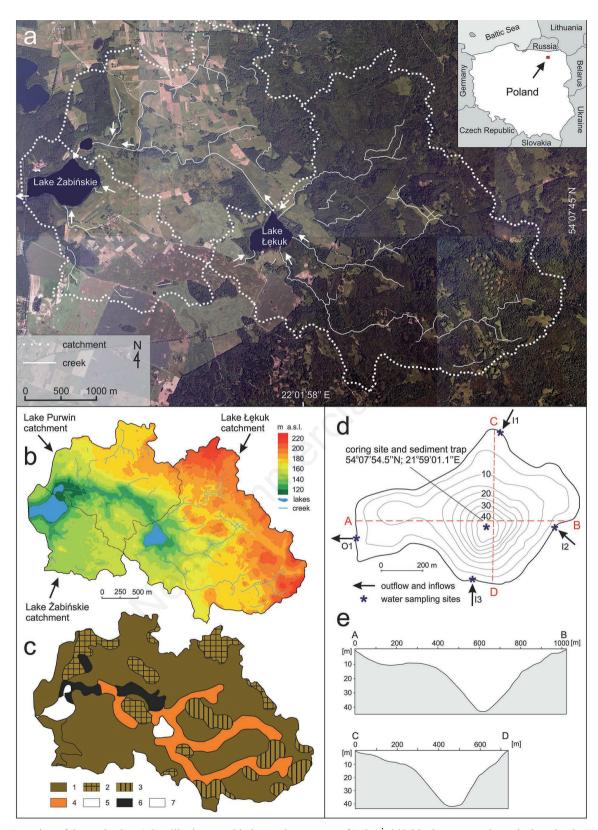
# **METHODS**

#### Study site

Lake Żabińskie is located in the Masurian Lake District in northeastern Poland (54°07'54"N; 21°59'01.1"E) at 117 m asl (Fig. 1 a,b). This region is characterized by well-preserved postglacial landforms and has the highest areal density of lakes in Poland, in some parts exceeding 20% (Choiński, 2007). The total catchment area (24 km<sup>2</sup>) expands eastward from the lake and comprises the catchment of three lakes: Lake Łękuk (13.2 km<sup>2</sup>), Lake Purwin (8.5 km<sup>2</sup>) and Lake Żabińskie (2.3 km<sup>2</sup>). It is dominated by glacial sediments deposited during the maximum stage of the Vistulian (Weichselian) glaciation ca. 15.2 ka BP (Szumański, 2000). The most common landform is a moraine plateau composed of glacial till (Fig. 1c). Moraine hills built of sand, gravel and boulders are widespread within the catchment, while kame hills and terraces occur in the central and south-eastern part. The plateau is cut by river valleys filled with fluvial sediments and by peat bogs in waterlogged areas. Outwash plains composed of fluvioglacial sands and gravels occupy the westernmost part of the catchment. The climate in this area is characterized by pronounced continentality compared to other regions of Poland. The mean annual air temperature is 6.5°C with the lowest temperatures in January (-5.6°C) and highest temperatures in July (17°C). Annual precipitation varies from 550 to 600 mm (Lorenc, 2005). Westerly and south-westerly winds predominate in the area (Hutorowicz et al., 1996).

Lake Żabińskie (Fig. 1 d,e) is a kettle-hole lake with typical characteristics, *i.e.*, a small surface area (41.6 ha) and a considerable maximum depth (44.4 m). The lake basin is aligned in a W-E direction and two basins may be distinguished: a deep basin in the central part and a relatively shallow one in the western part. The deepest basin of the lake is surrounded by 8°-14° steep slopes. The exposure index (ratio between the lake surface area and mean depth) is low (3.4) and suggests good protection of the deep waters from wind-induced mixing. Lake Żabińskie is an exorheic water body and has an outflow to the much larger Lake Goldopiwo on the western side. There is an inflow into Lake Żabińskie from small Lake Purwin which is situated immediately on northeastern side and two small creeks feed the lake from south with water from cultivated fields.

Presently, more than half of the catchment area is covered by a thick forest which dominates in the eastern and western parts of the catchment. Arable lands and meadows occupy a zone between Lake Żabińskie and Lake Łękuk (Fig. 1a). In AD 1713, the village of Żabinka was established ca. 0.5 km southeast of the lake. Today, the village has about 100 inhabitants living mostly from agriculture. Buildings can also be found on the northern shore of Lake Żabińskie where a recreation place was established in the years AD 1910-1920. In the 2<sup>nd</sup> part of the twentieth century increasing mass tourism in the region has caused considerable development and enlargement of the infrastructure in this place.



**Fig. 1.** Location of the study site. a) Satellite image with the catchment area of Lake Żabińskie, insert map shows its location in Poland. b) Catchment topography. c) Catchment geology (1, glacial till; 2, moraine sand, gravel and boulders; 3, glaciofluvial sand and gravel; 4, fluvial silt, sand and gravel; 5, lacustrine silt, sand and gravel; 6, peat; 7, lakes). d) Bathymetric map with indicated sites of coring, sediment trapping and water sampling. e) Lake basin morphology along two transects as marked in (d).

#### Modern limnology and varve-formation processes

# **Field work**

During 25 monthly field campaigns, physical and chemical parameters (temperature, conductivity, pH, oxygen saturation and concentration) of the water column were measured at 1-m depth intervals using a YSI 6820 meter (YSI, Yellow Spring, OH, USA). The concentration of chlorophyll-*a* (Chl-*a*) was measured along the same water profile using a Minitracka II C fluorometer (Chelsea Instruments, West Molesey, UK). Surface and near-bottom water samples were collected every month using a Van Dorn water sampler at water depths of 1 and 43 m. Additionally, we collected 32 water samples from inflows (I1, I2, I3) and the outflow (O1) in different seasons (Fig. 1d).

In May 2012, we installed a sediment trap built of two transparent PVC-liners (diameter 90 mm, height 800 mm, total active area 117 cm<sup>2</sup>) in the deepest part of the lake (Fig. 1d). The active area of the trap was exposed at 1 m above the sediment surface. The trap was recovered monthly except during the winter months when the lake was ice-covered. The collected sediment was transferred into a tight plastic container and stored in a cold room prior to analysis. A short sediment core (ZAB-12/01; 9 mm diameter, UWITEC gravity corer) was also collected from the deepest part of the lake in January 2012 (Fig. 1d). Immediately after collection, the core was tightly capped and transported to the laboratory at the University of Gdańsk where it was stored in a cold room until subsampling.

# Laboratory work

Chemical analyses of the water samples included: i) nutrient concentrations ( $N_{tot}$  and  $P_{tot}$ ) measured using colorimetric methods and a Spectroquant NOVA 400 spectrophotometer (Merck Millipore, Billerica, MA, USA); ii) concentrations of major cations ( $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ) and anions ( $SO_4^{2-}$ ,  $Cl^-$ ) determined by ion chromatography (ICS 1100, Dionex, Sunnyvale, CA, USA); and iii) HCO<sub>3</sub><sup>-</sup> measured by standard titration methods.

The samples collected from the sediment traps were used for smear slides preparation according to Limnological Research Centre methods (https://tmi.laccore.umn. edu/). Then samples were freeze-dried and sediment flux was calculated according to the formula:

# sediment flux $(g m^{-2}d^{-1}) = \frac{dry \text{ net weight } (g)}{active area (m^2) time (d)}$ (eq. 1)

Total carbon (TC), total nitrogen (TN) and total sulphur (TS) contents in the sediment samples were determined using a CNS analyzer Vario EL Cube (Elementar). Total inorganic carbon (TIC) contents were measured using the same analyzer after combustion of samples at 550°C to remove organic carbon. Subtracting TIC from TC allowed estimating total organic carbon (TOC). Calcite contents (CaCO<sub>3</sub>) were calculated stoichiometrically by multiplying the TIC by 8.33, assuming that all inorganic carbon is bound as calcium carbonate. Biogenic silica (BSi) concentrations were determined by the alkaline leaching method and ICP-OES measurements corrected for lithogenic Si (Ohlendorf and Sturm, 2008).

The core ZAB-12/01 was split lengthwise and subsampled for thin sections. Following Lotter and Lemcke (1999), a single sediment block (10 cm×2 cm×1 cm) was collected from the fresh core using an aluminum foil tray, frozen in liquid nitrogen, freeze-dried and impregnated with Araldite<sup>©</sup>2020 epoxy resin. The impregnated slab was sectioned and polished to the thickness of 25-30  $\mu$ m (MK Factory, Germany). The varve composition was investigated microscopically using a NIKON L100 petrographic microscope.

The impregnated slab was also scanned using an Itrax XRF Core Scanner (Cox Analytical Systems) at GeoPolar (University of Bremen) to characterize the variability of chemical elements (Boyle, 2000; Brauer *et al.*, 2009). We used a Cr tube (30 kV, 25 mA) to obtain better signals for the light elements and scanned with a spatial resolution of 200 µm and 60 s measurement time.

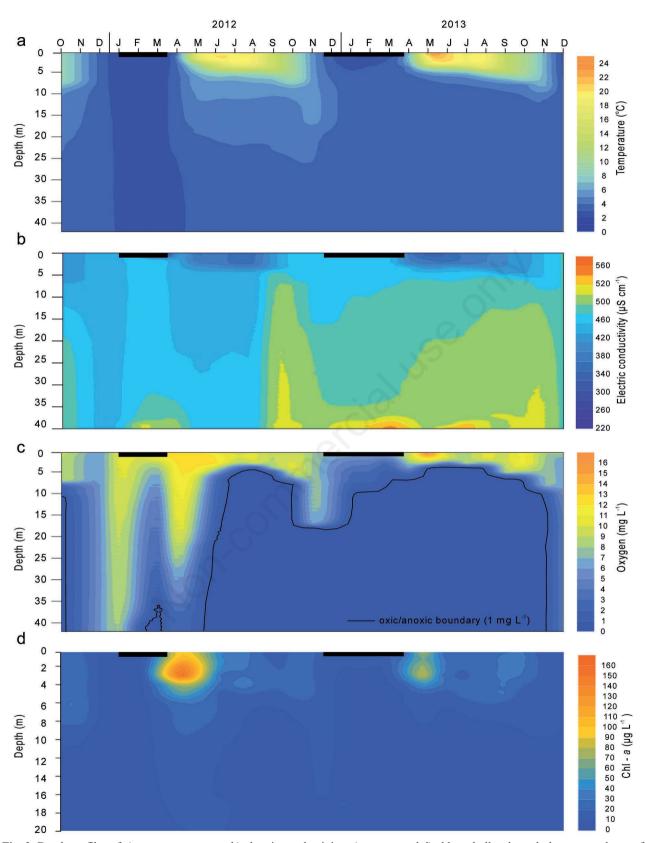
# RESULTS

#### Physical and chemical properties of the lake water

Water temperature, conductivity, oxygen, Chl-a, nutrients and other ions from monthly measurements (October 2011 to December 2013) are shown in Fig. 2 and Tab. 1. The water column measurements demonstrate that Lake Żabińskie presents different mixing regimes throughout the two years. After the establishment of the ice-cover in winter (black horizontal bar in Fig. 2), the water column was thermally homogenous in 2011/2012 and inversely stratified in 2012/2013 (Fig. 2a). Conductivity increased slowly with greater water depth towards the highest values recorded near the lake bottom (Fig. 2b). After the establishment of the ice cover, anoxic conditions  $(<1 \text{ mg } L^{-1})$  developed in the bottom waters and the oxicanoxic boundary started to move upward (Fig. 2c). This anoxic zone expanded upward to a water depth shallower than 11 m in 2013 due to unusually long freezing conditions during winter 2012/2013.

During the warm season (May-October) the lake was directly stratified in 2012 and 2013 with the epilimnion reaching a depth of 2-5 m. The thermocline was located between 2-10 m water depth and only slight temperature changes were observed down to 25 m water depth. The hypolimnion extended from about 10 m water depth to the bottom. Strong stratification of Lake Żabińskie was also confirmed by the electric conductivity profiles (Fig. 2b). The lowest values ( $220 \ \mu S \ cm^{-1}$ ) were found near the water surface during summer months while the highest values (>540 \ \mu S \ cm^{-1}) were recorded below 25 m water

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**Fig. 2.** Depth profiles of a) water temperature; b) electric conductivity; c) oxygen and d) chlorophyll-*a* through the water column of Lake Żabińskie from October 2011 to December 2013. The horizontal black bars mark the periods of ice cover. Panel (d) has different depth scale.

depth with a tendency to increase toward the end of the summer stratification-period. Only the surface waters were well-oxygenated and the oxic-anoxic boundary ranged between 3 and 6 m water depth (Fig. 2c). The deep waters of Lake Żabińskie remained anoxic throughout the entire stratification period. Maxima in oxygen concentration coincided with maxima in Chl-*a* measured in May at 0-4 m water depth (Fig. 2d). However, while Chl-*a* concentrations decreased with the beginning of the summer (after May) oxygen concentration still remained high. Chl-*a* concentrations decreased gradually until a minimum in August and early September.

Complete overturns occurred in December 2011, April 2012 and December 2013 when more than 1 mg L<sup>-1</sup> of oxygen in near-bottom waters was detected (Fig. 2c). However, incomplete fall overturn occurred in November 2012 when mixing reached only 17 m water depth. Rapid increases in air temperature in April/May 2013 coincided with immediate stratification after ice melting and, as a result, anoxic conditions in deep waters prevailed until December 2013 prior the full overturn in late-fall 2013. Along with fall mixing, increased Chl-*a* concentrations were also detected in both years, which suggests a second algal bloom. Subsequently, Chl-*a* concentrations decreased until the following ice cover development.

Tab. 1 reports the concentrations of nutrients and other elements from the three inflows (I1, I2, I3), the outflow (O1) and the lake water. Data show that concentration of dissolved substances in the inflows were significantly higher than in the lake water and in the outflow. The southern inflow (I3) seemed to be the most effective source of dissolved ions transported from the catchment into the lake. We observed strong seasonal changes for some of the elements in the lake water, *e.g.* P<sub>tot</sub> and Ca<sup>2+</sup> (Fig. 3). The maximum concentrations of P<sub>tot</sub> in the surface water occurred during late winter (Fig. 3b), i.e. in March, while the lowest concentrations were detected in early May (after the spring algal bloom) and late September (after the fall algal bloom). The highest  $Ca^{2+}$  concentrations in the surface water (Fig. 3d) were also detected during late winter, while the lowest  $Ca^{2+}$  concentrations were observed during the warm season (May-August). Both, nutrients and  $Ca^{2+}$  concentrations in near-bottom waters, were always significantly higher than in surface waters.

# **Recent sediment fluxes**

The material collected from the sediment trap (May 2012-Dec 2013) revealed important changes in all parameters during the observation period (Fig. 3). The lowest sediment mass fluxes were observed during winter time when the lake was ice-covered (Fig. 3a). Immediately after ice out, the accumulation rate increased rapidly, which coincided with maxima in Chl-a concentrations in the surface waters and high fluxes of BSi and TOC to the sediments. The spring maxima in sediment flux were recorded in May 2012 (2.09 g m<sup>-2</sup> d<sup>-1</sup>) and June 2013 (3.44 g m<sup>-2</sup> d<sup>-1</sup>). The highest values of diatom productivity, expressed by high BSi fluxes, occurred in early spring along with enhanced TOC and TN fluxes (Fig. 3 b,c). They were followed by high CaCO<sub>3</sub> deposition that occurred from May to July in both years (Fig. 3d). Periods with intense calcite deposition during spring and early summer were simultaneous with drops in Ca2+ concentrations in the surface water. Toward the end of summer stratification, the fluxes decreased gradually until a minimum in August/September. Depending on fall overturn intensity, two different scenarios developed during the observation period. In 2012, while mixing of the water column was incomplete, the sediment flux decreased consequently to lowest values during winter. In contrast,

**Tab. 1.** Chemical composition (mean and standard deviation SD) of surface and near-bottom waters of Lake Żabińskie, inflows and outflow (locations see Fig. 1).

	Surface (n=24)		Bottom (n=24)		Inflow 1 (n=8)						Outflow (n=8)	
$(mg L^{-1})$	Mean	SD		SD	Mean	SD	Mean	SD		SD	Mean	SD
pН	8.3	0.4	7.4	0.2	-	-	-	-	-	-	-	-
HCO <sub>3</sub> <sup>-</sup>	222.13	28.61	264.35	21.72	211.85	54.18	254.29	56.18	315.29	38.02	179.57	34.76
$Ca^{2+}$	66.1	8.2	75.6	4.2	73.0	25.3	95.6	13.8	110.5	21.9	59.3	10.7
$Mg^{2+}$	9.8	1.8	10.9	1.8	10.0	2.2	10.9	1.7	14.5	1.9	11.2	2.5
$Na^+$	4.2	0.6	4.9	0.5	3.4	0.9	3.7	0.5	5.3	1.5	4.3	0.6
$K^+$	2.0	0.3	2.2	0.4	2.3	1.3	1.5	0.4	5.2	1.5	2.4	0.2
$\mathrm{SO_4}^{2-}$	1.4	1.9	1.7	2.8	6.3	14.0	8.3	4.1	27.5	19.1	0.5	0.8
Cl-	5.6	1.0	6.5	1.1	7.4	6.3	6.4	1.5	18.8	6.6	7.5	1.7
$\mathbf{P}_{\text{tot}}$	0.06	0.03	0.32	0.13	0.16	0.10	0.09	0.05	0.17	0.12	0.08	0.05
N <sub>tot</sub>	1.54	1.14	2.08	1.44	1.28	0.71	2.02	0.75	6.63	3.34	1.57	0.67

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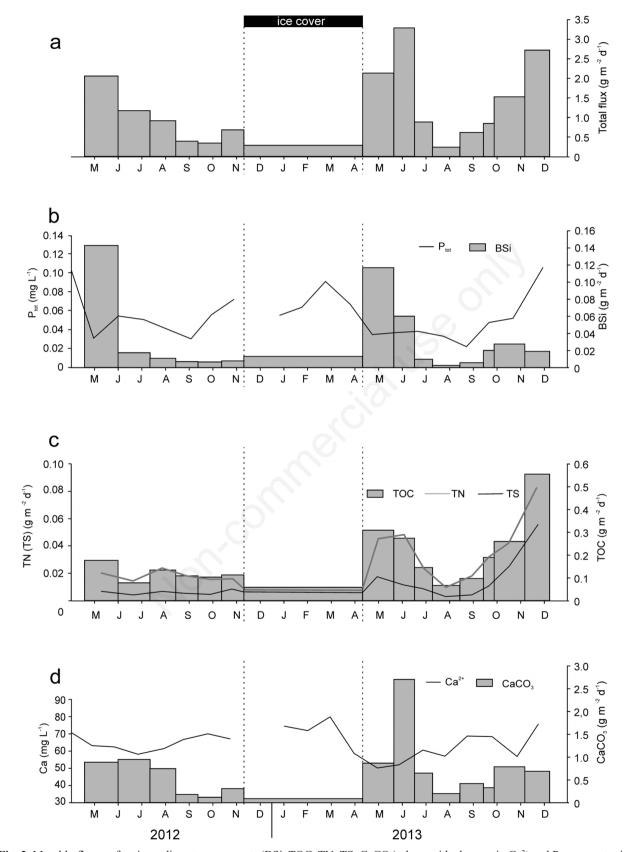


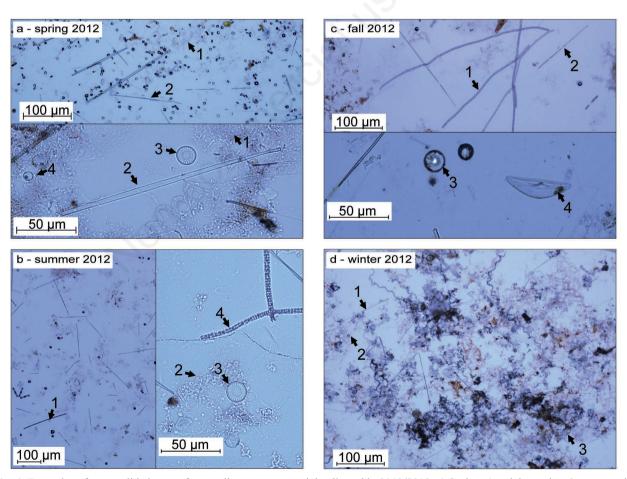
Fig. 3. Monthly fluxes of major sediment components (BSi, TOC, TN, TS,  $CaCO_3$ ) along with changes in  $Ca^{2+}$  and  $P_{tot}$  concentrations in surface waters.

during complete fall overturn in 2013, the second peak in the sediment flux occurred with total values almost as high as during spring and early summer, and with highest accumulation rates for some components (TOC, TN, TS) during the whole observation period (Fig. 3c).

The qualitative analysis of smear slides from sediment trap samples also showed distinct differences between the seasons (Fig. 4). The spring deposition consisted of calcite grains mainly, as well as pennate and centric diatoms. A similar composition was observed during summer; however, calcite grains were not as abundant. In late summer, a first appearance of blue-green algae (*Planktothrix rubescens* - Oscillatoriales) was detected. In both years, samples collected during fall were dominated by bluegreen algae accompanied by pennate diatoms, calcite grains and small amounts of amorphous organic matter. Chrysophyte cysts were common through the whole icefree period but no characteristic variability was observed. Deposition of amorphous organic matter, minerogenic detritus and scarce diatoms prevailed in winter time.

#### Varve structure and chemical composition

In order to diagnose common features and patterns of the varve structures, we performed microscopic analysis and  $\mu$ XRF scanning on the topmost 10 cm of sediment that covered varves from AD 1992-2011. A characteristic sequence of annual sediment deposition consisted of the following major components: one or more calcite laminae mixed with diatom-rich layers, chrysophytes, amorphous organic matter and minerogenic detritus (Fig. 5). Typically, the growing season in spring started with deposition of large amounts of calcite grains and diatoms. Intense calcite precipitation could form multiple calcite laminae deposited during spring, summer and also fall. During fall vivianite and pyrite were clearly recognizable in the thin section, while winter deposition consisted of amorphous



**Fig. 4.** Examples of smear slide images from sediment trap material collected in 2012/2013. a) Spring: 1, calcite grains; 2, pennate diatoms; 3, centric diatoms; 4, chryophyte cysts. b) Summer: 1, pennate diatoms; 2, calcite grains; 3, centric diatoms; 4, blue-green algae *Planktothrix rubescens*. c) Fall: 1, blue-green algae *Planktothrix rubescens*; 2, pennate diatoms; 3, chrysophyte cysts with air bubble; 4, pennate diatoms; 2, calcite grains; 3, organic detritus.

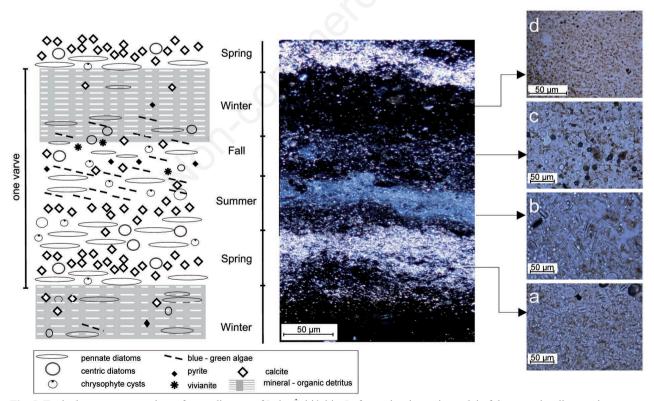
organic matter mainly with only minor contributions of other constituents such as diatoms or clay minerals. µXRF scanning provided detailed information regarding the seasonal variability of the elemental compositions. This helped identifying the sediment mineralogical composition and determining the boundaries between individual varves (Fig. 6). Varve thickness varied in the range 3.1-9.1 mm with a mean value of 5.1 mm. Changes in major elements (Si, S, K, Ca and Fe) showed specific annual patterns of deposition (Fig. 6a). Moreover, detailed analysis of each single varve indicated a characteristic annual pattern of chemical variability (Fig. 6b). Each varve year started with a Si peak in early spring followed by a local maximum of Ca counts. During late summer and fall, peaks in Fe and S occurred while winter layers were characterized by higher K counts.

# DISCUSSION

### Limnological and hydrochemical conditions

We observed different mixing regimes during the twoyear period of water-column investigation. Depending on meteorological conditions in late winter and early spring as well as late fall and early winter, the timing of ice break-up and subsequent development of summer stratification or the end of warm season stratification and subsequent ice cover development may change, which leads to complete or incomplete mixing of the water column in spring and fall. The winter 2011/2012 was relatively short and the ice cover melted already by the end of March, which provided sufficient time for spring mixing to be completed before the establishment of thermal stratification in May. However, freezing conditions and ice cover development in winter 2012/2013 started in December which led to incomplete fall overturn in 2012. Through the following year 2013, the lake was ice-covered until late April and summer stratification developed almost immediately after ice out, which prevented spring mixing. However, complete overturn was again possible in fall prior the late development of ice cover in January 2014. Therefore, the lake underwent only one complete mixing of the water column in each year, but in different seasons.

Although the observation period covered only two years, the limnological measurements helped us to under-



**Fig. 5.** Typical varve structure in surface sediments of Lake Żabińskie. Left panel: schematic model of the annual sedimentation pattern. Middle panel: microscopic image of one varve taken under cross-polarized light. Right panels: close-up showing the composition of individual laminae: a) calcite grains and diatoms; b) diatoms, less abundant calcite grains; c) diatoms, chrysophyte cysts, pyrite and single calcite grains; d) amorphous organic matter.

stand different scenarios of Lake Żabińskie hydrological cycle for different meteorological situations. Variability of winter/spring and fall/winter conditions in northeastern Poland indicates that Lake Żabińskie may undergo four different scenarios of annual mixing patterns depending mainly on the length of the period with ice cover:

- i) Complete overturn twice a year two consecutive mild winters (ice out in March and long spring may allow for complete spring overturn, while a long fall and a late development of ice cover not earlier than in late December allows for complete fall overturn);
- ii) Complete overturn in spring a mild winter followed by a long, early and severe winter (ice out in March and long spring may allow for complete spring overturn, while a short fall, rapid cooling and early development of ice cover in November/December prevents complete fall overturn);

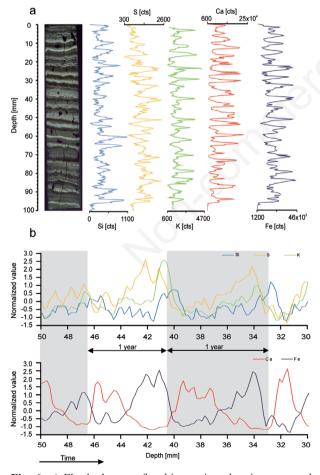


Fig. 6. a) Flat-bed scan of a thin section showing seasonal changes in varves AD 1992-2011 from Lake Żabińskie as characterized with  $\mu$ XRF scanning data. b) Detailed and typical seasonal changes in the elemental composition of individual varves.

- iii) Complete overturn in fall a long and severe winter followed by a mild winter (ice out in April and a short spring with rapid warming may prevent spring overturn, while a long fall and late development of ice cover not earlier than in late December allows for complete fall overturn);
- iv) Permanent stratification two consecutive long and severe winters (ice out in April and a short spring with rapid warming may prevent spring overturn, while a short fall, rapid cooling and early development of ice cover in November/December prevents complete fall overturn).

Although dimictic lakes are the most common ones in temperate climatic zones (Wetzel, 2001), deviations from typical dimictic to mono- or meromictic conditions between consecutive years are also well recognized (Melack and Jellison, 1998). This depends highly on the stability of the annual mixing pattern, which is a function of the lake morphometry and meteorological conditions. Air temperature variability is the most important factor, although changes in wind speed and wind direction might also play a significant role for the annual lake water mixing regime (Ragotzkie, 1987; Gaedke *et al.*, 1998). As a consequence, lakes do not necessarily show the same mixing pattern every year and, in some cases, this pattern can even change permanently (Boehrer and Schultze, 2008; Holzner *et al.*, 2009).

Regardless of the mixing pattern, Lake Żabińskie is stratified during much of the year which leads to significant differences between surface and near-bottom water environments (Tab. 1). The hypolimnion is generally characterized by higher conductivity and anoxic conditions with only short periods of oxygenation (up to several weeks). Periods with anoxia are not restricted to summer stratification and may cover much longer time intervals, *e.g.* up to 18 months as it occurred between spring 2012 and fall 2013 (Fig. 2). Concentrations of major ions as well as nutrients are higher in the hypolimnion and less variable compared to surface waters. Strong stratification and long periods of anoxic condition in the hypolimnion create ideal conditions for the preservation of varved sediments in the deepest basin of Lake Żabińskie.

#### Annual variability of sediment deposition

The mixing regime and productivity of the lake seem to be two major factors that control the variability of sedimentation processes in Lake Żabińskie. By comparing two different years we can demonstrate that different water column mixing patterns and seasonal variations in algal productivity have a direct influence on the flux and composition of the sediments (Fig. 3).

Immediately after ice-out, increasing Chl-*a* concentrations and nutrient depletion in surface waters suggest that green algae develop rapidly in spring. Subsequently (May/June), the sediment flux increased to ca 2-3.5 g m<sup>-2</sup> d<sup>-1</sup> as a result of calcite deposition (ca 1-2.7 g CaCO<sub>3</sub> m<sup>-2</sup> d<sup>-1</sup>), organic matter formation (ca 0.2-0.3 g TOC m<sup>-2</sup> d<sup>-1</sup>) and diatom sedimentation (ca 0.10-0.15 g BSi m<sup>-2</sup> d<sup>-1</sup>) (Fig. 3). During warm seasons we observed a strong decrease in Ca2+ concentrations in the epilimnion along with an increase of CaCO<sub>3</sub> flux to the sediment (r=-0.58, P=0.01). This suggests that the development of phytoplankton and photosynthetic activity together with rapidly increasing temperatures in the epilimnion affect carbonate oversaturation by decreasing CO<sub>2</sub> (aq), increasing pH, and favouring calcite precipitation (Kelts and Hsü, 1978; Groleau et al., 2000). Calcite has clearly the most important contribution to the total sediment mass flux. In summer and early fall the sediment flux reaches its minimum and the algal communities change (Figs. 3 and 4). Smear slide investigation reveals that centric and pennate diatoms are being replaced by blue-green algae which may be caused by increasing turbidity in the epilimnion and limited availability of light and nutrients as indicated by Amann et al. (2014). A similar process was also reported by Kufel (2001) for a series of Masurian lakes. Sedimentation in fall depends largely on the mixing regime. In 2012, when fall overturn was incomplete, only a slight increase in sediment flux was registered after the late summer minimum. However, when fall overturn is complete (e.g., in 2013), nutrients accumulated in the hypolimnion during summer might be redistributed in the water column and reach the photic zone. The fall algal bloom is much weaker than the spring one, but can stimulate calcite precipitation and leads to a second maximum of sediment flux in late fall (November/December). In the fall of 2013, complete water column mixing occurred and caused a prominent increase in sediment mass flux late in the year, which was comparable to the spring peak. However, the spring peak was mostly due to calcite precipitation ( $\approx 80\%$ of the total flux), while the late fall peak (December 2013) reflects a mixture of organic matter ( $\approx 40\%$ ), minerogenic particles ( $\approx 30\%$ ) and calcite deposition ( $\approx 25\%$ ). When ice cover develops, phytoplankton productivity ceases and the sediment flux is the lowest (December 2012-April 2013). During this cold time of the year only organic detritus and fine minerogenic particles are deposited at very low accumulation rates.

# Formation of varves and their potential for paleoclimate reconstruction

Microscopic investigation of the topmost sediments from Lake Żabińskie revealed that the seasonal laminae structure is consistent with the sedimentation pattern as obtained from the sediment trap study. A lamina rich in calcium carbonate forms in spring and summer, while a dark lamina composed mostly of organic and minerogenic detritus forms in fall and winter. This type of deposition is typically classified as biogenic varves according to Zolitschka (2007) and Ojala *et al.* (2012). Such varves are common under temperate climatic conditions and form in eutrophic hardwater lakes with seasonal anoxia in nearbottom waters (Anderson and Dean, 1988; Lüder *et al.*, 2006; Bluszcz *et al.*, 2008; Corella *et al.*, 2012). Biogenic varves have also been found in other lakes of northern Poland (Tylmann *et al.*, 2013b) and their potential for the construction of a precise chronology (Kinder *et al.*, 2013; Tylmann *et al.*, 2013a) and for reconstruction of paleoenvironmental changes has been shown by Ralska-Jasiewiczowa *et al.* (2003).

Biological processes in the water column (diatom productivity) and calcite precipitation are the most important factors controlling the formation and changes in the varve thickness of this type of varves (Brauer, 2004). Although Lake Żabińskie documents a similar deposition pattern, the sediment record exhibits more complicated structures. For the sediments of the last 20 years we observed the deposition of one to a maximum of four calcite laminae within a single year. Despite this complex structure, the annual pattern was clearly recognizable by a massive spring lamina that consists almost exclusively of small and tightly packed calcite grains. Summer/fall calcite laminae are much thinner and mixed with a lot of organic remains. This is consistent with the occurrence of the most prominent algal bloom in spring/early summer reflected by high Chl-a concentrations in the epilimnion, while weaker blooms can occur until late fall (Fig. 2d). Similarly, the mechanism of multiple calcite precipitation triggered by algal biomass development during the warm season was described for Lake Constance (Stabel, 1986) and for eutrophic hardwater lakes of northern Poland (Tylmann et al., 2012). The seasonal structure of sediment deposition is also recorded in the chemical composition inferred from µXRF measurements. A characteristic sequence of peaks for certain elements (Si, Ca, Fe, S and K) provides a unique diagnostic tool for the recognition of individual seasons within a varve. Early spring is marked by a Si peak being the result of BSi deposition after the first algal bloom. Then, a maximum in Ca counts shows intense calcite precipitation in spring. Minor calcium peaks may follow during the warm season. Fe and Mn maxima mark the late summer/fall deposition while the winter deposition is characterized by significantly higher K counts. Especially, K and Ca variability seem to have an excellent diagnostic potential for the determination of winter and spring conditions and, thus, provide essential information for varve counting.

Taking into account the well-documented mechanism of calcite deposition in Lake Żabińskie, different varve structures and their chemical composition may theoretically be used as a paleoproxy for reconstructing mixing regimes of the lake and, indirectly, reconstructing meteorological

conditions. Particularly, our process study demonstrates that the length of winter (ice cover) and temperature gradients in spring and fall determine the mixing regime of the lake. This, in turn, has implications for sediment accumulation rates. Annual variations in the sediment flux show how late fall mixing can increase sediment accumulation rates. It should then be expected that better conditions for water column mixing would result in relatively thick varves with higher mass accumulation rates. Understanding of seasonal deposition mechanisms and highly precise determination of boundaries for seasonal layers would also enable for using individual laminae thickness as a proxy for seasonal meteorological conditions. Although this conceptual model seems reasonable, further investigation of varve characteristics against long series of instrumental meteorological data are required which goes beyond the scope of this study.

# CONCLUSIONS

We investigated limnological conditions, modern sedimentation and varve structures in the lake water and sediments of Lake Żabińskie in northeastern Poland. With multiple lines of evidence we demonstrated that several different mixing patterns may occur in Lake Żabińskie, which depend largely on the variability of meteorological conditions during winter/spring and fall/winter. The sediment trap samples showed that these mixing patterns influence sediment accumulation rates and composition. Spring maxima of algal blooms (mainly diatoms) occur every year in April/May. Together with increasing temperatures in the epilimnion, the spring maximum in primary production leads to biogenic silica and calcite deposition in May/June. The spring peak in sediment mass flux is followed by a gradual decrease toward the end of summer stratification in August/September. Complete overturn of the water column during late fall leads to the second peak in sediment flux with highest contributions of organic matter. All of these processes are well reflected in the complex structure of varves showing distinct spring calcite-lamina followed by fine calcite laminae interbedded with diatom-rich laminae and, finally by organic-rich lamina with minerogenic contributions deposited during winter. This seasonal variability is also reflected in the chemical composition as inferred from high-resolution µXRF measurements. Typically, the annual succession of chemical elements concentrations is as follows: spring sediments are marked with a Si peak followed by a major Ca peak, during summer and fall minor Ca peaks may occur as well as maxima in Fe and S, and winter sediments are characterized by a peak in K.

Lake Żabińskie forms almost an ideal environment for the formation of biogenic varves with a strong climatic seasonality, considerable relative depth, a highly productive and calcium-rich epilimnion, long periods of stable stratification and a seasonally anoxic hypolimnion. The results of our study show that the sediment record from Lake Żabińskie has a remarkable potential for a reliable varve chronology and for multiproxy paleoenvironmental reconstructions. Relationships between meteorological conditions or even weather phenomena and characteristics of individual varves need to be tested against longer time series of meteorological and sediment data.

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