Manuscript ID bg-2020-362 titled "Holocene phototrophic community and anoxia dynamics in meromictic Lake Jaczno (NE Poland) using high-resolution hyperspectral imaging and HPLC data".

Comments to the Author:

Dear Dr. Makri,

It is with great pleasure that I read your revision and I am happy to recommend it for publication in BG provided that you fix a few small issues that I noticed. Overall, may I encourage you to double-check the text for typos. Please see for instance line 293 (In zone III (6700–500 cal BP), most pigments concentration increase gradually.). Furthermore, there are some problems with the references (lines 524 and 557 etc) likely due to the conversion from the citation manager.

Thank you very much for fixing these. Looking very much forward to seeing your work published in BG.

My very best regards,

Tom Battin

Response:

We would like to thank the Editor for these last remarks and helpful comments to improve the quality of our manuscript. We have corrected the grammatical errors in line 293, the references content in lines 524 and 557, and we have doubled checked the entire manuscript for typos and further editing errors. Below we attach the manuscript with track changes where all last corrections are visible.

# Holocene phototrophic community and anoxia dynamics in meromictic Lake Jaczno (NE Poland) using high-resolution

## 3 hyperspectral imaging and HPLC data-

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15 Abstract. Global spread of hypoxia and altered mixing regimesless frequent mixing in freshwater systemslakes is 16 a growing major environmental concern. Climate change and human impact are expected to increasingly 17 deteriorate aquatic ecosystems. The study of processes and drivers of such changes in the past provides a great 18 asset for prevention and remediation in the future. We used a multi-proxy approach combining high-resolution 19 bulk pigment data measured by Hyperspectral Imaging (HSI) pigment data, with lower resolution specific HPLC 20 chlorophylls and carotenoids measured by HPLC to examine Holocene trophic state changes and anoxia evolution 21 in meromictic Lake Jaczno, NE Poland. A redundancy analysis (RDA) including pollen-inferred vegetation cover, 22 temperature and human impacts provides insight into specific conditions and drivers of changing trophic and redox 23 states in the lake. Anoxic and sulfidic conditions established in Lake Jaczno after initial basin infilling 9500 years 24 ago. Until 6700 cal BP, lake trophy was relatively low, water turbidity was high, and green sulfur bacteria (GSB) 25 were abundant within the phototrophic community, suggesting a deep oxic-anoxic boundary and weak 26 stratification. The period between 6700-500 cal BP is characterized by constantly increasing lake production and 27 a gradual shift from GSB to purple sulfur bacteria (PSB), suggesting a shallower oxic-anoxic boundary and 28 pronounced stratification. Yet, the presence of spheroidene and speroidenone in the sediments indicates 29 intermittent anoxia. After 500 cal BP, increasing human impact, deforestation and intensive agriculture promoted 30 lake eutrophication, with a shift to PSB dominance and establishment of permanent anoxia and meromixis. Our 31 study unambiguously documents the legacy of human impact on processes determining eutrophication and anoxia. 32

Keywords: Paleolimnology, Anoxia, Meromixis, Varved sediments, North–East Europe, Holocene, Sedimentary
 pigments, Human impact

#### 35 1. Introduction

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Eutrophication and subsequent oxygen depletion have become primary water quality issues for most freshwater
 and coastal marine ecosystems globally (Schindler, 2006; Jenny et al., 2016a). Rising mean global temperature
 can potentially worsen lake anoxia by enhancing water stratification and algal blooms (Adrian et al., 2009;

Woolway and Merchant, 2019). Higher lake trophy and reducing conditions in anoxic bottom waters can have diverse and profound negative effects on lake ecosystems, such as toxic algal blooms, fish kills, biodiversity loss (Smol, 2010; Battarbee and Bennion, 2012; Makri et al., 2019), and nutrient recycling into the water column from the sediment through redox processes (Gächter, 1987; Tu et al., 2019). Hence, the global spread of hypoxia grows into a major environmental concern\_(Diaz and Rosenberg, 2008).

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45 Temporal and spatial extents of hypoxia/anoxia are influenced by both biological (aquatic production, organic 46 matter decomposition) and physical (water stratification and lake mixing) factors (Smith and Schindler, 2009; 47 Friedrich et al., 2014; Jenny et al., 2016b). Environmental and climatic effects such as temperature, seasonality 48 and extreme events, catchment vegetation, land use, human impact and nutrient input affect lake production and 49 oxygen supply in the bottom waters.

51 Observational data of anoxia and aquatic production cover usually only very short periods, which restricts the 52 understanding of relevant processes and the knowledge of pre-disturbance conditions. This is most relevant for 53 lake management or restoration. Although recent anoxia and eutrophication have been very well studied and 54 understood (Naeher et al., 2013; Friedrich et al., 2014; Jenny et al., 2016a), less is known about the onset, cessation 55 and specific conditions of these changes in the past due to the lack of effective and easily measurable proxies 56 (Friedrich et al., 2014; Makri et al., 2020). More specifically, to assess lake trophy and/or bottom water 57 oxygenation, proxies such as sedimentary pigments (Lami et al., 2000; Leavitt and Hodgson, 2001; Guilizzoni and 58 Lami, 2002), lipid biomarkers (Naeher et al., 2012), diatom (Bennion and Simpson, 2011) and chironomid records 59 (Little et al., 2000), stable isotopes (Pearson and Coplen, 1978), and redox sensitive elements such as Fe, Mn, Mo, 60 V, and U (Naeher et al., 2013; Wirth et al., 2013; Costa et al., 2015), have been extensively used so far. 61 Nonetheless, on long-term Holocene time-scales, most of these proxy records are typically established at a 62 centennial resolution at best.

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64 Laminated lake sediments are valuable archives of natural and anthropogenic impacts, providing long-term records 65 via various biogeochemical proxies. Sedimentary photosynthetic pigment records can be effectively used to infer 66 both changes in algal composition and lake oxygen conditions (Guilizzoni et al., 1983; Leavitt, 1993; Lami et al., 67 2000). Chlorophylls, together with their derivatives, and various carotenoids specific to particular groups of algae 68 can be used to reconstruct overall primary production and the composition of past photosynthetic communities 69 (Leavitt and Hodgson, 2001). Pigments such as okenone and isorenieratene, which are specific to phototrophic 70 sulfur bacteria that live in the anoxic sulfidic zones, are regarded as very good indicators of anoxia (Züllig, 1989; 71 Guilizzoni and Lami, 2002). HPLC-inferred pigments have a coarser temporal resolution due to laborious sample 72 preparation and time-consuming HPLC measurements. Scanning Hyperspectral Imaging (HSI), a novel non-73 destructive method to quantitatively infer the abundance of algal (TChl: chlorophyll and b, and their derivatives) 74 and bacterial pigments (Bphe: bacteriopheophytins a and b), offers insight into past trophic and oxygen conditions 75 at unprecedented µm-scale (sub-seasonal) resolution (Butz et al., 2015; Makri et al., 2020), but with lower 76 speciation sensitivity.

In this study, we use the varved sediment record of Lake Jaczno (NE Poland) to explore the specific conditions and mechanisms of trophic and oxygen state changes in the Holocene, under changing climatic and environmental Formatted: Font: Italic Formatted: Font: Italic

79 conditions. Our research has been guided by the following questions: i) Which conditions drove algae dynamics 80 and oxygen state changes in the Holocene before any significant human intervention? ii) How did climate, 81 catchment vegetation and erosional input affected the phototrophic community in the lake and iii) How does the 82 current trophic state and mixing regime of the lake compare with the past? For this, we combined a high-resolution 83 HSI-inferred record of TChl and Bphe, X-ray fluorescence (XRF) elemental data, and an HPLC pigment record at 84 eoarser resolution a low-resolution pigment record using HPLC analysis with high compound specificity, which 85 cannot be achieved by the HSI record.but specific in the analysis. Our dataset was compared with vegetation and 86 temperature reconstruction data to investigate the environmental conditions at times of aquatic primary production 87 and bottom water oxygenation changes. Lake Jaczno provides ideal conditions to answer these questions. It 88 contains an entirely varved Holocene sediment record, which has so far only been analyzed for the last 1700 years 89 for productivity, anoxia (Butz et al., 2016, 2017) and historical land use (Poraj-Górska et al., 2017). Pollen records 90 have revealed that human pressure was low until the 17th century, when landscapes opened and agriculture 91 intensified (Marcisz et al., 2020). This is rare in Europe. Therefore, this site provides a unique opportunity for a 92 long-term Holocene assessment of the natural causes and dynamics of meromixis and hypoxia with limited 93 anthropogenic impact until historic times.

## 94 2. Study site

95 Lake Jaczno (54°16'25.5" N 22°52'15.9" E, 163 m a.s.l, Fig. 1a) is a small, 26 m deep, exorheic, kettle-hole lake 96 formed sometime after the Weichselian deglaciation ca. 15 ka BP in the Suwałki Lakeland in NE Poland 97 (Krzywicki, 2002). Lake Jaczno has a total surface area of 0.41 km<sup>2</sup> separated in five distinct basins with narrow 98 sills. It is fed by three permanent inflows (N and W) and one outflow in the south (Fig. 1b). Jaczno is classified as 99 dimictic and mesotrophic (Tylmann et al., 2013), with incomplete mixing or possibly even meromixis during some 100 years (Butz et al., 2016). Butz at al. (2017) found that anoxic, and even meromictic conditions, established naturally 101 for most of the past 1700 years. Meromixis was interrupted repeatedly following sediment slumping or flood 102 events.

103 Microscopic and geochemical analyses in of the sediments of Lake Jaczno have revealed seasonal layers 104 (calcareous biogenic varves) with a complex succession of diatoms and calcite, detrital siliciclastic material 105 (quartz, clays), organic fragments, and finally amorphous organic matter (Tylmann et al., 2013; Butz et al., 2016; 106 Poraj-Górska et al., 2017). The lake is surrounded by steep slopes and gullies with ephemeral or perennial water 107 flow, transporting detrital material to the lake (Fig. 1c).

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109The catchment area (ca. 9 km²) is covered by glacial tills, sands and fluvioglacial deposits. Modern soils are110classified as cambisols and podsols in the northern part and ferralic cambisols in the southern part of the catchment.111Agricultural lands dominate in the central and northern parts and forests in the southern parts (Fig. 1c). The lake112is surrounded by peatlands and forests dominated by birch, alder and spruce (Weisbrodt et al., 2017). The climate113of the region is continental with a mean annual temperature of 6.8°C and a mean annual precipitation of 600 mm114(IMGW-PIB, 2017). The lakes in the area typically remain ice\_-covered from December to March (Amann et al.,1152014).

<sup>116</sup> Archeological investigations in the Suwałki region indicate sparse or only seasonal human occupation during the

118 increases in the region with stronghold settlements, animal husbandry and fishing (Kinder et al., 2019). Yet, the

119 area around Lake Jaczno remained isolated from human influences (Marcisz et al., 2020). Pollen and charcoal

120 data, and increased soil erosion indicate extensive forest clearance, forest fires and intensified agriculture,

121 suggesting permanent settlements and higher human impact since 500 cal BP, especially after 150 cal BP (1800

122 CE) (Kinder et al., 2019; Marcisz et al., 2020). The 1970s are marked by a regeneration of forest cover and a 123 significant increase of fertilizer use in agriculture (Poraj-Górska et al., 2017; Kinder et al., 2019), which markedly

124 increased lake primary production (Butz et al., 2016; Poraj-Górska et al., 2017).

#### 125 3. Materials and methods

126 Two parallel cores ca. 12.5 m long were retrieved in September 2017, using a UWITEC piston corer. The coring 127 site was located at the deepest part (24 m water depth) of the lake in the southern basin that . which is protected 128 from direct external inputs (Fig. 1b). The cores were split lengthwise and then described following 129 Schnurrenberger et al. (2003) and the Munsell color chart (Munsell Color (Firm), 2010). Flood deposits and slumps 130 were identified based on grain size, mineral content, and sediment structure. First, the core halves were analysed 131 using non-destructive methods and further analytical measurements were performed after subsampling. The 132 sampling interval for LOI, CNS and dry-bulk density analysis was 10 cm (ca. 80-year resolution, discrete 133 sampling). For the HPLC and spectrophotometer analysis, 46 discrete samples (1-2 cm<sup>3</sup>) were taken every ca. 30-134 35 cm (ca. 230 years resolution) taking into account the HSI scanning data and optimization for the proxy-to-proxy 135 calibration of the HSI indices with spectrophotometer data (Butz et al., 2015). The top 10 cm (last ca. 50 years) 136 were subsampled continuously every 1 cm.

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138 The chronology is based on 18 radiocarbon Accelerator Mass Spectrometry (AMS) AMS-dates on taxonomically 139 identified terrestrial plant macrofossils (Table 1) measured at the Laboratory for Radiocarbon Analysis at the 140 University of Bern. Samples with < 300 µg C were measured using the gas-source input of the MIni CArbon 141 DAting System (Szidat et al., 2014; Zander et al., 2020). The age-depth model was calculated using Bacon (rbacon 142 v. 2.4.2; (Blaauw and Christen, 2011; Blaauw et al., 2020)\_Blaauw et al., 2020; Blaauw and Christeny, 2011) and 143 the IntCal13 calibration curve (Reimer et al., 2013). Event layers (>3 cm) and slumps were excluded from the age 144 calculation (Fig. 2). According to changes in lithology, we used model parameters that allowed for a higher 145 sedimentation rate in the lowermost 137 cm (Fig. 2).

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147 XRF scanning was performed at continuous 2 mm steps using an ITRAX μXRF core scanner (exposure time 20 s,
148 30 kV and 50 mA) equipped with a Cr-tube at the University of Bern. The results are given as counts (peak area).
149 From the detected elements, Ti was used as proxy for erosional input from the catchment, Ca as a proxy for
150 endogenic calcium carbonates, Si/Ti as a proxy for biogenic silica, S, Fe, Mn, and Mn/Fe as proxies of changing

- 151 redox conditions (Koinig et al., 2003; Croudace and Rothwell, 2015).
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153 Hyperspectral imaging scanning (HSI) was performed on the freshly oxidized core halves using a Specim PFD-

154 CL-65-V10E camera (400 to 1000 nm spectral range; 2.8 nm spectral resolution). We used a spatial resolution of

- 155 ~68 μm per pixel with a spectral sampling of 1.57 nm. Data were processed using the ENVI software version 5.4
- 156 (Exelis Visual Information Solutions, Boulder, Colorado) following Butz et al. (2015). The relative absorption
- 157 band depths (RABDs) were calculated based on spectral endmembers analysis in ENVI. The RABD<sub>673</sub> (spectral

region 590–730 nm) was used to detect chlorophyll  $\underline{a}$  and  $\underline{b}$ s and their diagenetic products (TChl) and served as a proxy for aquatic primary production (Leavitt and Hodgson, 2001). The RABD<sub>845</sub> (spectral region 790–895 nm) was used to detect total bacteriopheophytin a and b (Bphe) (Butz et al., 2015, 2016), which is a proxy for anoxia and meromixis as described in Makri et al. (2020). Bphe a and b is produced by anoxygenic phototrophic purple sulfur and non-sulfur bacteria that proliferate in illuminated anoxic habitats (Yurkov and Beatty, 1998; Madigan and Jung, 2009). Green sulfur bacteria produce bacteriochlorophyll c, d and e, which do not absorb in the RABD<sub>845</sub> range. Therefore, HSI-inferred Bphe reflects purple bacteria abundance.

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166 The spectral indices were calibrated with absolute pigment concentrations of 46 selected sediment samples (1 cm<sup>3</sup>) 167 measured by spectrophotometry (Shimadzu UV-1800). Pigments were extracted using pure acetone. The 168 supernatant was evaporated under nitrogen, and extracts were subsequently redissolved in 2 ml of pure acetone 169 (method adapted from Schneider at al. 2018). For the calculation of Bphe concentrations, we used the molar 170 extinction coefficient for Bphe a by Fiedor et al. (2002). For TChl, we applied the molar extinction coefficient for 171 chlorophylls and chlorophyll derivatives by Jeffrey et al. (1975). The performance of the proxy-to-proxy linear 172 regression models was assessed using the coefficient of determination (R<sup>2</sup>) and the root mean square error of 173 prediction (RMSEP) (Butz et al., 2015) run in R (R Core Team, 2015). The calibration model for TChl showed an 174  $R^2$  of 0.91 (p < 0.001) and a RMSEP ~8 % (Fig. S1a). The calibration model for Bphe showed an  $R^2$  of 0.95 (p < 175 0.001) and a RMSEP ~6 % (Fig. S1b). The Shapiro-Wilk and the Kolmogorov-Smirnov tests of the residuals 176 showed that they are most likely normally distributed, suggesting that inferences can be made with both models. 177

178 HPLC analysis was conducted on the same 46 samples used for the proxy-to-proxy calibration. Chlorophyll, 179 chlorophyll derivatives and carotenoids were measured using ion pairing reverse-phase (Mantoura and Llewellyn, 180 1983; Hurley, 1988). The system used a UV-VIS detector set at 460 nm and 656 nm for carotenoids and 181 chloropigments, respectively. The results were corrected for water content and expressed as nmol g OM-1 (Züllig, 182 1982; Guilizzoni et al., 1983; Lami et al., 1994). According to Jeffrey et al. (2011), Guilizzoni and Lami (2002), 183 chlorophyll a,  $\beta\beta$ -carotene, pheophytin a, and pheophytin b are considered as indicators of total algal biomass. 184 Chlorophyll b and lutein are associated with green algae. B-carotene, dinoxanthin (pyrophytes), diadinoxanthin 185 (siliceous algae), fucoxanthin (diatoms), diatoxanthin (chrysophytes) and alloxanthin (cryptophytes) are related to 186 brown algae. Echinenone and zeaxanthin are associated to most taxa of blue-green algae, and myxoxanthophyll 187 and canthaxanthin to colonial and filamentous cyanobacteria (Leavitt and Hodgson, 2001). K-myxol (4-keto-188 myxol-2'-methylpentoside) is associated with N-fixing cyanobacteria (Anabaena flos-aquae) (Kosourov et al., 189 2016). Pheophorbide a is a degradation product of Chl a transformed by microbial processes and used as 190 considered asan indicator of grazing (Bianchi and Findlay, 1991; Cartaxana et al., 2003). In the phototrophic 191 bacteria community, BChl a is common to all anoxygenic phototrophic purple bacteria. Okenone (Chromatium 192 sp.) is associated with purple sulfur bacteria (PSB), whereas spheroidene and spheroidenone (Rhodopseudomonas 193 sphaeroides) are related to purple nonsulfur bacteria (PnSB). Both groups are able to oxidize sulfide. Yet, PSB 194 store any S<sup>0</sup> formed intracellularly, whereas PnSB do so outside the cell (Madigan and Jung, 2009). The main 195 difference between the two groups is that PSB are strong photoautotrophs, whereas PnSB are physiologically 196 versatile and can grow well both phototrophically and in darkness via fermentation or anaerobic respiration 197 (Madigan and Jung, 2009). R. sphaeroides are also excellent N-fixing bacteria. Oxygen tolerance varies among 198 species, with R. sphaeroides being able to grow under vigorous aeration. Spheroidenone is produced by R.

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sphaeroides only when even small amounts of oxygen are present (Züllig, 1989). Hence, the presence of spheroidenone is used as an indication of better oxygen conditions, whereas the presence of spheroidene with parallel absence of spheroidenone is used as an indication of meromictic conditions (Züllig, 1989; Guilizzoni and Lami, 2002). Isorenieratene is associated with GSB (*Chlorobium sp.*). GSB have low light requirements and can cope with low light availability, occupying deeper layers in stratified lakes (Montesinos et al., 1983). Hence, a dominance of GSB over PSB is used as an indicator of a deeper oxic–anoxic boundary (Montesinos et al., 1983; Itoh et al., 2003).

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207 Total organic carbon (TOC) was determined by Loss on Ignition (LOI; Heiri et al., 2001). Total carbon (TC) and 208 total nitrogen (TN) were measured with a CNS-Analyzer (Elementar vario EL cube). Total inorganic carbon (TIC) 209 was calculated by the difference between TC and TOC (Enters et al., 2010). The TOC/TN ratio was used to infer 210 changes in OM sources (Meyers, 2003). The lithogenic flux was calculated based on the residual calculation after 211 removing the organic matter and carbonate fraction by LOI.

213 Statistical analysis was performed in R (R Core Team, 2015). To define the sedimentary lithotypes we performed 214 an hierarchical unconstrained clustering on the geochemical proxies (XRF data: Ti, Ca, Si/Ti, Si, S, Fe, Mn, Mn/Fe; 215 HSI: TChl, Bphe; TOC, TIC, TN, TOC/TN, Fig. 3) using the Euclidean distance matrix and the ward.D2 clustering 216 method (Murtagh and Legendre, 2014). On the same dataset, we performed a PCA analysis with the samples 217 grouped based on the unconstrained clustering to investigate the relationships between the lithotypes and the 218 geochemical variables (Fig. S2). The data were log transformed and scaled before statistical analysis. We 219 performed a redundancy analysis (RDA) using the Vegan package (Oksanen et al., 2016) in R to relate the pigment 220 matrix i.e. HPLC- and HSI-inferred pigment concentrations (Hellinger-transformed variables) to the 221 environmental variables i.e. temperature (Heikkilä and Seppä, 2010), arboreal pollen (AP), non-arboreal pollen 222 (NAP) (Kinder et al., 2019; Marcisz et al., 2020) and lithogenic flux (log transformed variables). The elements 223 were plotted using scaling 2 (see Borcard et al., 2011, pp. 166–167). This analysis was followed by a permutation 224 test in R to test for significance in the redundancy analysis (Legendre and Legendre, 1998; Borcard et al., 2011). 225 The zones of pigment data were defined by constrained clustering using the Bray distance and ward.D2 linkage 226 method in R.

### 227 4. Results and interpretation

#### 228 4.1 Chronology

229 The age-depth model (Fig. 2) reveals a basal age of ca. 9500 cal BP. The model shows a stationary distribution, 230 matching prior and posterior accumulation rates, and a smooth sediment accumulation as indicated by its memory 231 or variability (Fig. 2). Three radiocarbon samples (Fig. 2, in red) have calibrated ages that do not fit with the 95 % 232 confidence interval. Based on the lithology and the much older ages, these samples were considered as containing 233 reworked carbon and were excluded from the Bacon model. The sediment sequence is entirely laminated 234 throughout the Holocene showing regular continuous sedimentation without any hiatus. In the lowermost section 235 (1257-1120 cm), sedimentation rates (SR) are relatively high (0.5 cm y<sup>-1</sup>) and the mean age error (95% confidence 236 interval) is ca. ±160 years. Numerous event layers and slumps characterize the part between 1120 cm and 800 cm 237 where the SR is ca. 0.2 cm y<sup>-1</sup> and the mean age error is ca. ±200 years. From 800 cm to the top, the sediment is 238 continuously varved and the SR is 0.1 cm y<sup>-1</sup> (0.2 cm y<sup>-1</sup> in the last 500 years). The mean age error in this section

is ca. ±140 years. The ages at the top 10 cm of the core (data shown in Fig 4b) were calculated by extrapolation of

the radiocarbon chronology to the sediment surface. A stratigraphic correlation with the <sup>210</sup>Pb dated cores from

241 <u>Butz et al. (2016) showed an age error of ±5 years for this section.</u>

#### 242 4.2 Lithotypes and biogeochemical proxies

243 Figure 3 shows the biogeochemical data that defined four sedimentary lithotypes A-D. Fig. S3 (supplementary 244 material) shows the RGB images and the biogeochemical composition of selected close-ups within the sediment 245 sequence. Lithotype A and B appear in segments between ca. 9500-6800 cal BP (Fig. 3). Lithotype A, at the 246 bottom part (9500-9200 cal BP), consists of light greenish grey (GLEY 2 7/2) fine sand and continues with pale 247 yellow (2.5Y 7/3) and grey (2.5Y 5/1) laminations with light greenish grey silty lenticular bedding. This part is 248 characterized by high detrital inputs (Ti, lithogenic flux), moderate carbonate content (Ca, TIC), low production 249 and biogenic silica (HSI-TChl, Si/Ti) and low TOC. Low HSI-Bphe and S, and higher Mn/Fe ratios indicate 250 effective oxygenation of bottom waters. From ca. 9200-8500 cal BP, lithotype B is introduced and is characterized 251 by slightly higher production (HSI-TChl) and biogenic silica (Si/Ti); carbonates (TIC, Ca), TOC and TN contents 252 increase, whereas higher S, Fe and HSI-Bphe, and lower Mn/Fe ratios indicate the development of anoxic (sulfidic) 253 conditions. Between ca. 8500-6800 cal BP, lithotype A continues with varved sediments; starting with biogenic 254 pale yellow (2.5Y 7/3) and grey (2.5Y 5/1) varves with intercalated reddish brown (2.5YR 5/4) and reddish black 255 (2.5YR 2.5/1) laminations rich in clastic material and iron oxides. In the second half of this part, varves are less 256 well-preserved with several intercalated clastic-rich laminations. Based on color, layer thickness, and grain size 257 we interpret these intercalated layers as event (flood) deposits. In this period, lithotype A is characterized by high 258 detrital input (Ti, lithogenic flux); primary production (HSI-TChl) remains unchanged and carbonates (Ca, TIC) 259 show increased variability. Biogenic silica (Si/Ti), TOC and Fe slightly decrease. S decreases, HSI-Bphe is very 260 low or absent and Mn/Fe increases, suggesting better oxygen conditions.

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Lithotype C occurs between ca. 6800–500 cal BP and consists mainly of light grey (2.5YR) and dark grey (2.5YR 4/1) fine biogenic varves, with some dispersed event layers that occur only at the beginning of this period until ca. 6000 cal BP. This period is characterized by low erosional input (Ti, lithogenic flux), gradually increasing production (HSI-TChI) and TOC content, fluctuating biogenic silica (Si/Ti) and constantly high carbonates content (Ca, TIC). S counts are minimal. HSI-Bphe is mostly present suggesting the development of anoxic conditions in the hypolimnion. Mn/Fe seems to fluctuate, with higher values when HSI-Bphe is lower and vice versa.

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Lithotype D occurs from ca. 500 cal BP to the present and consists of biogenic pale yellow (2.5Y 7/3), grey (2.5Y
5/1) and dark grey (2.5Y 4/1) calcareous biogenic varves. This period is characterized by instances of higher
detrital input (Ti) and several intercalated event (flood) layers. Mn counts also increase. Primary production (HSITChl), TOC and TN reach maximum levels, whereas biogenic silica and carbonates (Ca, TIC) decrease. HSI-Bphe

273 reach maximum values at the top suggesting persistent anoxia in this part. The Mn/Fe ratio and HSI-Bphe show

274 opposite fluctuations indicating phases of better oxygen conditions when Bphe is absent.

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#### 275 4.3 HPLC pigment stratigraphy

Figure 4 presents the pigment dataset of individual chlorophylls and carotenoids measured by HPLC in the Holocene (Fig. 4a), and for the last 50 years (Fig. 4b). The pigments are grouped according to their taxonomic relation and the zones are defined by constrained clustering, which yielded boundaries that are similar to those of the sediment lithotypes (Fig. 3).

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In zone I (ca. 9500–9200 cal BP), pigment concentrations are very low. Chromophytes are more abundant than green algae, especially cryptophytes (alloxanthin) and chrysophytes (fucoxanthin). Blue–green algae (echinenone, zeaxanthin) are present in low concentrations. Grazing (pheophorbide *a*) is low. In the purple bacteria group, *Chromatium* species (okenone, PSB) are absent, whereas *R. sphaeroides* (spheroidene and spheroidenone, PnSB) are both present in low concentrations. *Chlorobium sp.* (isorenieratene, GSB) are present in traces.

In zone II (ca. 9200–6700 cal BP), pigment concentrations increase overall. Green algae (chlorophyll *b*, lutein) still have low concentrations, whereas chromophytes ( $\beta$ -carotene) become more abundant especially pyrophytes (dinoxanthin) and chrysophytes (diatoxanthin) that show a distinctive local maximum around 7300 cal BP. Colonial filamentous cyanobacteria (canthaxanthin) appear in this zone. Grazing (pheophorbide *a*) starts increasing around 8300 cal BP. *Chromatium sp.* (okenone, PSB) is mostly absent. *R. sphaeroides* (spheroidene and spheroidenone, PnSB) have moderate concentrations, whereas *Chlorobium sp.* (isorenieratene, GSB) reach a maximum around 7300 cal BP.

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295 In zone III (6700-500 cal BP), most pigments concentration increases gradually. Green algae (chlorophyll b) 296 increase significantly. Chromophytes remain abundant. Diatoms and other siliceous algae (diadinoxanthin, 297 fucoxanthin), and cryptophytes (alloxanthin) show a local maximum around 2000 cal BP. Blue-green algae 298 (echinenone, zeaxanthin) increase gradually. More colonial filamentous cyanobacteria (myxoxanthophyll) appear 299 around 2300 cal BP and, together with zeaxanthin, reach a maximum around 2000 cal BP. N-fixing cyanobacteria 300 (k-myxol) appear at ca. 5000 cal BP. Chromatium sp. (okenone, PSB) appear in this zone and increase gradually. 301 R. sphaeroides (spheroidene and spheroidenone, PnSB) also show a gradual increase, whereas Chlorobium sp. 302 (isorenieratene, GSB) decrease to minimum concentrations.

303

Zone IV (500 cal BP to present), is characterized by a further gradual increase of most pigments, reaching unprecedented maximum concentrations at the top. In more detail, Fig. 4b shows the distribution of pigment concentrations in the last 50 years. Most pigments reach maximum values around 1997 CE. *Chromatium sp.* (okenone, PSB) have high concentrations, whereas *R. sphaeroides* are present producing only spheroidene and almost no spheroidenone. *Chlorobium sp.* (isorenieratene, GSB) show only trace concentrations around 1997 CE.

#### 309 4.4 The relationships between land use, temperature, and pigment stratigraphy

We applied a redundancy analysis (RDA) to examine the response of our HPLC- and HSI-inferred pigment dataset
to land use changes (arboreal pollen: AP, and non-arboreal pollen: NAP; Kinder et al., 2019; Marcisz et al., 2020),
annual mean temperature variability (Heikkilä and Seppä, 2010) and catchment surface processes (lithogenic flux).
Figure 5 shows the RDA ordination output in a triplot with the explanatory variables (in blue) and response (in

B14 red) variables (in red), as well as the samples divided into the four distinct zones defined by constrained clustering

315 (see Sect. 4.3). The numerical output shows that the first two axis (RDA 1 20.95 % and RDA 2 11.25 %) explain 316 36 % of the variation (unadjusted values). The  $R^2_{adj}$  for the constrained ordinations suggests that this model 317 explains ca. 29 % of the variation in the data. The permutation test on the unconstrained ordinations indicates that 318 the first two axis are significant (p<0.001; Table S1) and represent the data adequately.

319

320 The RDA triplot (Fig. 5) shows that AP and NAP play an important role in the distribution of the pigment data 321 along the first axis (RDA 1). Lithogenic flux and temperature drive pigment variability along the second axis 322 (RDA 2). Lithogenic flux is strongly correlated with siliceous algae (fucoxanthin, diadinoxanthin) and blue-green 323 algae (echinenone), as well as enhanced aquatic primary production (HSI-TChl) by green algae (lutein) and 324 cryptophytes (alloxanthin,  $\beta$ -carotene). Lithogenic flux is clearly anticorrelated with PSB (okenone, HSI-Bphe) 325 and Chl a. AP is mainly correlated with GSB pigments (isorenieratene) indicating a deeper oxic-anoxic boundary, 326 and PnSB (spheroidene and spheroidenone) that suggest a more effective oxygenation of the water column. AP is 327 also correlated with variables indicating the presence of chromophyte (brown) algae, pyrophytes (dinoxanthin), 328 chrysophytes (diatoxanthin), as well as some blue-green algae (zeaxanthin). Higher lithogenic input and AP drive 329 pigment variability in zones I and II. Temperature seems to be correlated with higher production of some green 330 algae (Chl b, pheophytin b), increased cyanobacteria abundance ( $\beta\beta$ -carotene,  $\beta$ -carotene) and colonial-331 filamentous cyanobacteria (myxoxanthophyll, canthaxanthin). Temperature seems to drive pigment variability 332 mainly in zone III. NAP is correlated with PSB production (BChl a, HSI-Bphe and okenone), overall higher 333 primary production (Chl a, pheophytin a), higher grazing (pheophorbide a), and N-fixing cyanobacteria (k-myxol). 334 NAP drives pigment variability in zone IV.

#### 335 5. Discussion

## 5.1 Combining sedimentological and biogeochemical data to infer past lake production and bottom water oxygenation

338 The 12.5 m long and almost entirely varved sediment record of Lake Jaczno continuously spans the last ca. 9500 339 cal yr BP (Fig. 2). The chronology is robust and exclusively based on terrestrial macrofossils. The lithology of 340 Lake Jaczno (Fig. 3) revealed the deposition of frequent event layers between 8500-7000 cal BP, which likely 341 reflect a regional catchment/climatic signal as similar features have been observed, for the same period, in the 342 nearby Lake Szurpiły (Kinder et al., 2020). The physical characteristics of the catchment favored the transport of 343 lithogenic material into the lake (Fig. 3), thereby possibly affecting the density stratification, light availability, and 344 subsequently the phototrophic community dynamics. A proper assessment of these changes requires high-345 resolution data that is impossible to reach using HPLC data alone. Yet, the combination of high-resolution (µm-346 scale) calibrated HSI bulk data for TChl and Bphe, combined with scanning XRF and compound specific HPLC 347 data, provides a unique opportunity for paleoproduction and paleooxygenation reconstructions at sub-seasonal 348 scale for multi-millennial-long records (Butz et al., 2017; Makri et al., 2020). This approach is directly applicable 349 to diverse lacustrine (Butz et al., 2017; Schneider et al., 2018; Makri et al., 2020; Sanchini et al., 2020) and 350 potentially marine environments (Hubas et al., 2011, 2013) with uncertain past redox state changes.

351

The calibration of the RABD<sub>673</sub> and RABD<sub>845</sub> to absolute pigment concentrations of green pigments (chlorophylls
 and diagenetic products) and Bphe (*a* and *b*) respectively, revealed robust calibration statistics (Fig. S1,

354 supplementary material) with very low uncertainties (ca. 6–8 %) comparable to other studies (Butz et al., 2017;

Formatted: English (United States) Formatted: English (United States) 355 Schneider et al., 2018; Makri et al., 2020; Sanchini et al., 2020). Between ca. 9200 and 7000 cal BP, the calibration 356 model of the RABD<sub>673</sub> for green pigments calculates negative concentrations (Fig. 3). This offset can be produced 357 by matrix effects, i.e. the variability of the reflectance of the sediment matrix or substances that absorb in the same 358 range as chlorophylls and their diagenetic products (590-730 nm) (Makri et al., 2020). Interestingly, GSB 359 (isorenieratene) peak between 9200 and 7000 cal BP (Fig. 4). GSB contain bacteriochlorophyll c, d, and e that 360 absorb in the same range as chlorophylls and chlorophyll derivatives (Oren, 2011). This could indicate that a part 361 of the RABD<sub>673</sub> calibration error may be due to the increased GSB abundance. Nonetheless, the calibration 362 statistics reveal an overall error of less than 8 %.

#### 363 5.2 Holocene production dynamics and chemocline evolution

364 The presence of anoxygenic sulfur bacteria throughout our record combined with chlorophylls, carotenoids and 365 geochemical evidence, suggests that euxinic conditions prevailed in Lake Jaczno for most of the past 9500 years. 366 Nonetheless, the changing composition of photosynthetic sulfur bacteria indicates persisting but variable euxinia. 367 Figure 6 summarizes the Holocene evolution of the relative abundance of PSB, PnSB and GSB, Chromatium 368 (okenone) and Clorobium (isorenieratene), the content of spheroidene and spheroidenone pigments produced by 369 R. sphaeroides, and the high-resolution calibrated HSI-TChl and Bphe, with respect to lithogenic flux, climate 370 variability (annual mean temperature; Heikkilä and Seppä, 2010) and human impact (land use and vegetation 371 cover; Kinder et al., 2019; Marcisz et al., 2020).

#### 372 5.2.1 Low trophic levels with a deep oxic-anoxic boundary

373 In the period from 9500 to 6700 cal BP, which corresponds to pigment zones I and II, the phototrophic bacteria 374 population is dominated by GSB (Fig. 6). A small percentage of PnSB (R. sphaeroides) is present and seems to 375 produce both spheroidene and spheroidenone during this time. Chromatium (okenone, PSB) is almost completely 376 absent. Considering that R. sphaeroides produces spheroidenone only when even small amounts of oxygen is 377 present (Züllig, 1989) we suggest that, in this period, euxinic conditions were already present but the strength or 378 extent of anoxia was likely weak. HSI-Bphe that corresponds to purple bacteria is very low. Anoxia is mainly a 379 function of lake stratification and productivity. HSI-TChl, which indicates total primary production, is still at low 380 levels (Fig. 6). Indeed, the stratigraphy of individual pigments indicates low to moderate in-lake production, which 381 mainly consists of chromophyte (brown) algae and some colonial cyanobacteria (canthaxanthin) (Fig. 4), which is 382 also confirmed in the RDA analysis (Fig. 5). Brown siliceous algae are well adapted and tolerant algae species that 383 thrive in oligotrophic conditions in symbiosis with other algae species and bacteria (Bird and Kalff, 1986; Wetzel, 384 2001). Similar observations of algae composition were made in Lake Peipsi (Tõnno et al., 2019; Estonia) and Lake B85 Lazduny (Sanchini et al., 2020) Lazduny (Sanchini et al., 2020; NE Poland).

386

Temperature gradually increased and a closed forest canopy with pine/birch and later elm/hazel/alder persisted in the catchment (Fig. 6) (Gałka, 2014). These provided shelter from wind and increased the nutrient pools in the catchment soils (Bajard et al., 2017). The closed forest canopy, combined with the deep and relatively small basin (relative depth 3.01 %), favors the establishment of a naturally anoxic hypolimnion (Zolitschka et al., 2015). Yet, it seems that enhanced permanent stratification was still not established in the lake. This phase of GSB dominance corresponds to a period of high lithogenic flux or high-energy sedimentation (Fig. 3, 6), as confirmed in the RDA

893 analysis (Fig. 5). Turbidity currents and underflows can increase turbidity and nutrient availability and , but can

**B94** also-cause sporadic ventilation of bottom waters. Higher suspended matter and/or algal growth would decrease light availability in the oxic–anoxic boundary. Since GSB and PnSB are more tolerant to low light intensities than PSB (Biebl and Pfennig, 1978; Parkin and Brock, 1980; Madigan and Jung, 2009), a dominance of GSB and presence of spheroidene and spheroidenone in the sediments is expected under these conditions. Similar observations were made in Lake Cadagno (Wirth et al., 2013). GSB often inhabit the lowermost part of stratified water bodies due to their efficient light capture (Manske et al., 2005; Imhoff, 2014). Higher abundance of GSB could also indicate a deep oxic–anoxic boundary in the lake (Itoh et al., 2003; Antoniades et al., 2009).

#### 401 5.2.2 Gradually increasing trophy levels with a shallower oxic-anoxic boundary

402 The period from 6700 to 500 cal BP, which corresponds to pigment zone III, is characterized by a gradual shift in 403 the phototrophic bacterial community to higher PSB abundance, especially after ca. 2000 cal BP (Fig. 6), GSB are 404 present, inhabiting the anoxic layers below PSB and seem to fluctuate as a function of the primary production in 405 the oxic layer (HSI-TChl) and related light availability (Montesinos et al., 1983). When production was higher in 406 the oxic layers, Chromatium (okenone, PSB) increased and Chlorobium (isorenieratene, GSB) decreased. This is 407 also confirmed by the individual pigment stratigraphy (Fig. 4). Green algae (chlorophyll b, lutein) and N-fixing 408 cyanobacteria (k-myxol) increase markedly since ca. 5500 cal BP, indicating a higher lake trophy than before, 409 driven most probably by lake ontogeny and a gradual increase of nutrient availability. The appearance of N-fixing 410 cyanobacteria at that time agrees with this interpretation. Prolonged periods of anoxia leading to intense recycling 411 of phosphorous from the sediments would decrease the N:P ratio in the water column promoting nitrogen fixation 412 by N-fixing algae (Howarth et al., 1999; Vitousek et al., 2002). Similar trends in lake trophy evolution are reported 413 from nearby Lake Szurpiły (Kinder et al., 2019) and Lakes Albano and Peipsi (Lami et al., 2000; Guilizzoni and 414 Lami, 2002; Tõnno et al., 2019). An increase of Chromatium (okenone, PSB) over Chlorobium (isorenieratene, 415 GSB) with increasing lake trophy has been reported from other lakes, e.g. Lake Albano in Italy (Lami et al., 1994), 416 Little Round Lake in Canada (Brown et al., 1984), and Lake Hamana in Japan (Itoh et al., 2003). R. sphaeroides 417 (PnSB) are also present producing both spheroidene and spheroidenone, suggesting phases of effective aeration of 418 bottom waters (Züllig, 1989). 419

420 The catchment is continuously densely forested and human impact is very low (Fig. 6). The RDA analysis points 421 to a temperature driven pigment variability in this zone, but mainly for cyanobacteria abundance (Fig. 5). 422 Cyanobacteria can benefit from higher water temperature, yet nutrient inputs have in most cases a much stronger 423 and synergetic effect (Lürling et al., 2018). Temperature variability did not seem to have affected lake stratification 424 directly. However, seasonality, precipitation and windiness play an important role in lake circulation and are not 425 reflected in the annual mean temperature variability. Hence, the role of climate may be underestimated. The oxic-426 anoxic stratification was enhanced in this period but permanent perennial anoxia was still not established as 427 indicated also by the low HSI-Bphe concentrations. The increase in PSB abundance suggests a shallower oxic-428 anoxic boundary (Itoh et al., 2003). It appears that during most of the Holocene, anoxia was largely influenced by 429 primary production and lithogenic flux. The case of Lake Jaczno is different from e.g Lake Łazduny (Masurian 430 Lake District, NE Poland; Sanchini et al., 2020), where erosional input is negligible and anoxia was mainly a 431 function of primary production and forest cover.

#### 432 5.2.3 20th century eutrophication, shallow oxic-anoxic boundary and meromixis

433 In the period from 500 cal BP to the present, which corresponds to pigment zone I, the phototrophic sulfur bacteria 434 composition changed to an almost complete dominance of purple bacteria (Fig. 6). Between 500-200 cal BP, HSI-435 Bphe and the absolute concentrations of PSB (okenone,) and PnSB (spheroidene and spheroidenone) are at a 436 minimum, but dominate the phototrophic bacteria community since GSB are completely absent (Fig. 4, 6). Lake 437 production (HSI-TChl) also decreases while lithogenic flux increases (Fig. 6). These suggest an oxic rather than 438 anoxic phase during this period, with some intervals of weak euxinia. Increased Mn accumulation during this time 439 (Fig. 3) supports the indications of rather oxygenated bottom waters.

440

441 Between 200 cal BP to the present, when human impact starts to increase in the catchment (Fig. 5), PSB increase 442 as well. The pPresence of spheroidene and only trace concentrations of spheroidenone (PnSB) and isorenieratene 443 (GSB) suggest increasing and gradually persisting anoxia. Intensive agriculture in the last 100 years and the 444 use of fertilizers, combined with exceptionally warm summers after 1990 CE (Czernecki and Miętus, 2017; 445 IMGW-PIB, 2017)\_ increased primary production (HSI-TChl) substantially to unprecedented levels in the 1990s, 446 relative to the Holocene baseline. This is also reflected in the individual pigment stratigraphy (Fig. 4). Bphe reaches 447 maximum levels suggesting persisting anoxia and mostly meromictic conditions in the lake, especially since the 448 1970s when gradual afforestation in the catchment is observed. This is also supported by the HPLC-inferred 449 composition of phototrophic bacteria (Fig. 3).

450 In this period, the high-resolution HSI-Bphe record indicates that the intervals of lowest AP in the catchment 451 coincide with absence of Bphe, indicating oxic bottom waters. Bphe increases again only when AP and the tree 452 canopy recovers (Fig. 6), with a parallel absence of spheroidenone (PnSB), suggesting meromictic conditions. 453 Butz et al. (2016, 2017) showed that these intervals of low AP and low or absent Bphe in the sediments were 454 accompanied by strong pulses of terrigenous material from the catchment. The role of human impact with regard 455 to anoxia and interrelated catchment processes (deforestation/afforestation and nutrient inputs) has also been 456 shown in other lakes with diverse timing of human impact onset. For example, Lake Moossee (Makri et al., 2020) 457 and Soppensee (Lotter, 1999) on the Swiss Plateau, Lakes Albano and Nemi in Italy (Guilizzoni et al., 2002), Lake 458 Zazari in Greece (Gassner et al., 2020) with an early Mid-Holocene human impact, and Lake Szurpiły (Kinder et 459

al., 2019) in the vicinity of Lake Jaczno with a late human impact, mainly in the last 500 years.

#### 460 6. Conclusions

461 In this study, we used a multiproxy approach, combining high-resolution HSI pigment data with lower resolution 462 HPLC-inferred concentrations of specific algal pigments, and geochemical data to investigate algal community 463 composition and its relationship with aquatic production and water column oxygenation in a 9500-years sediment 464 record from NE Poland. Land use changes, vegetation cover and climate variability were also taken into account. 465 Our aim was to examine factors that determine trophic state changes and lake stratification, in a lake system with 466 stable catchment vegetation and low human impact until very recent times.

467

468 The Holocene sedimentary pigment and geochemical record of Lake Jaczno revealed distinct changes in lake 469 trophy and stratification states, mainly driven by the catchment evolution, lithogenic flux, nutrient input and 470 subsequent increase in primary production. The lake had a first phase (9500-6700 cal BP) of low production that 471 consisted mainly of brown algae in the oxic zone, yet an early immediate establishment of weak euxinic conditions 472 in a deep water column dominated by GSB in its anoxic zone. Increased suspended loads, turbidity currents and 473 underflows seem to have increased turbidity and restricted the proliferation of PSB at the deep oxic-anoxic 474 boundary. Between 6700-500 cal BP, primary production increased gradually with higher contributions of green 475 algae and cyanobacteria, following lake ontogeny in a continuously densely forested catchment. The oxic-anoxic 476 boundary became gradually shallower with a shift from GSB to PSB. The composition of phototrophic bacteria 477 and the presence of spheroidene and spheroidenone (PnSB) in the sediments suggest pronounced yet intermittent 478 euxinia in the lake. Between 500 cal BP to the present, lake trophy increases dramatically, especially in the last 479 100 years, due to intensified human impact. Eutrophication accompanied by catchment deforestation and 480 subsequent afforestation after land abandonment were the main driving forces for the establishment of permanently 481 anoxic and meromictic conditions in the modern lake.

482

483 This study highlights the great potential of calibrated and validated HSI measurements combined with HPLC data.

484 Lake Jaczno provided a rare site to explore the mechanisms that can potentially induce changes in lake mixing,

185 <u>lake production and sustained persisting bottom water anoxia in times from minimum to intensive human impact</u>

486 ,-in a naturally stratified lake system. Our findings, together with findings from other lakes across Europe, can

487 greatly expand our understanding on these major environmental problems while providing a tailored toolset for

488 implementing effective remediation techniques in the future.

## 489 Data availability

490 The data will be made is available at PANGAEA-BORIS https://doi.org/10.5194/bg-2020-362.

#### 491 Author contributions

492 Stamatina Makri: Investigation, Data Curation, Formal analysis, Writing - Original Draft, Visualization. <u>Andrea</u>
 493 <u>Lami: Investigation, Writing - Review & Editing. Luyao Tu: Investigation, Writing - Review & Editing.</u>

494 Lami: Investigation, Writing - Review & Editing. Wojciech Tylmann: Writing - Review & Editing. Hendrik

495 Vogel: Writing - Review & Editing, Martin Grosjean: Conceptualization, Methodology, Writing - Review &

496 Editing, Supervision, Funding acquisition.

#### 497 Competing interests

498 The authors declare that they have no conflict of interest.

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794 Figure 1: a) Localization of Lake Jaczno. b) Lake bathymetry (modified from Poraj-Górska et al., 2017) and coring position c) Slopes and land use maps of the catchment (modified from Poraj-Górska et al., 2017) d) Seasonal limnological parameters in 2013 CE (Butz et al., 2016).



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Bacon (Blaauw and Christen, 2011; Blaauw et al., 2020); the excluded outliers are shown in red. The grey dotted lines indicate the 95 % ( $2\sigma$ ) probabilities. The grey horizontal areas indicate event layers (>3 cm) excluded from the model. The horizontal dashed line marks the boundary of a higher sedimentation rate (model parameter). The upper left panel shows the log objective vs. MCMC iteration that indicates a



stationary distribution. The middle and right panels indicate the distributions (prior in green, posterior in
 grey) for the accumulation rate and the memory, respectively.





Figure 3: Selected biogeochemical proxies that defined the four sedimentary lithotypes A–D (in different color) after unconstrained clustering and PCA analysis (Fig. S2). On the right: sediment lithology based on

visual examination.





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Figure 4: Chlorophyll, chlorophyll derivatives, carotenoids and bacterial pigments concentrations measured by HPLC a) for the entire Holocene, and b) for the last 50 years. The zones are defined by constrained hierarchical clustering. The different colors indicate different algal groups based on the pigments' taxa affiliation. The occasional red scale on top marks the significantly higher concentrations of these pigments in the last 50 years.

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Fig 5: RDA triplot showing the explanatory variables (AP, NAP, temperature and lithogenic flux) in blue,

855 and the response variables (HPLC- and HSI-inferred pigment concentrations) in red. The samples are

856 grouped according to the pigment zones (Fig. 4a).

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#### 858

Figure 6: Holocene summary of the relative abundance of purple bacteria (sum of PSB and PnSB) and GSB, *Chromatium* (okenone, PSB) and *Clorobium* (isorenieratene, GSB), the content of spheroidene and spheroidenone pigments produced by *R. sphaeroides* (PnSB), and the high-resolution calibrated HSI-TChl and HSI-Bphe concentrations. Top: indication of lithogenic flux and general evolution of the chemocline. Bottom: AP/NAP percentages (Kinder et al., 2019; Marcisz et al., 2020) with archaeological evidence of human impact, and the annual mean temperature variability (Heikkilä and Seppä, 2010).

#### Table 1: Radiocarbon age results and calibrated ages. Uncertainties for <sup>14</sup>C ages refer to 68 % probabilities

 $(1\sigma),$  whereas ranges of calibrated ages refer to 95 % probabilities (2 $\sigma$ ). Outlier samples are marked with

an asterisk. Indet: indeterminable, dicot: dicotyledonous.

Sample ID	Material	C mass	Age ${}^{14}C$	Age	Age range	Graphite
		(µg C)	BP	(cal BP) <sup>a</sup>	$(cal BP)^b$	/Gas
BE-10957.1.1	Betula alba fruit, woody scale, Pinus	104	132±64	142	0–284	gas
	sylvestris needle base					
BE-10958.1.1	Betula alba fruit scale, woody scale,	219	482±44	755	679–904	graphite
	dicot leaf fragment					
BE-10959.1.1	Pinus sp. periderm, coniferous wood	118	872±55	790	694–912	graphite
	and periderm fragment, Betula alba					
	fruit fragments, coniferous scales					
BE-10960.1.1	Pinus sp. periderm, Betula alba fruit	64	1460±67	1364	1283–1522	gas
	fragments, conifer scale, Pinus sp.					
	periderm, Betula alba fruit fragments					
BE-10961.1.1	Betula alba fruit fragments, conifer	19	1781±127	1706	1410–1987	gas
	scale, Betula alba fruit, semi-charred					
	periderm					
BE-10962.1.1	Alnus glutinosa fruit, Betula alba	268	2321±39	2341	2180-2458	graphite
	fruit fragments, needle/leaf indet,					
	male anthere indet					
BE-10963.1.1	Betula alba fruit fragments, Pinus sp.	73	2677±69	2801	2545-2959	gas
	periderm, male anthere indet, Betula					
	alba fruit fragments, Pinus sp.					
	periderm, conifer scales					
BE-10964.1.1	Betula alba fruit fragments, Pinus sp.	74	3229±72	3458	3259–3633	gas
	periderm, male anthere indet, Betula					
	alba fruit fragments					
BE-10965.1.1	Alnus glutinosa fruit fragment, Betula	130	3758±60	4125	3927–4383	graphite
	alba fruit fragments, conifer scales,					
	dicot leaf fragments					
BE-10966.1.1	Male anthere indet, dicot leaf	399	4322±36	4887	4836–4972	graphite
	fragments, conifer scales, indet scale,					
	wood indet					
BE-10967.1.1	Dicot leaf fragments, indet scale,	428	4860±37	5601	5491–5650	graphite
	male anthere indet					

BE-10968.1.1	Dicot leaf fragments, wood remains	348	5144±39	5906	5753–5989	graphite	
BE-10969.1.1	Dicot leaf fragments, indet periderm, wood remains	183	5998±57	6839	6678–6977	graphite	
BE-10970.1.1	Deciduous woody scale	365	6153±41	7062	6942–7166	graphite	
BE-10971.1.1	<i>Betula alba</i> fruit fragments, <i>Pinus sp.</i> periderm, conifer scale, wood indet	111	6699±79	7567	7439–7674	graphite	
*BE-10972.1.1	<i>Pinus sylvestris</i> needle fragments, wood indet	58	8291±99	9279	9029–9475	gas	
BE-10973.1.1	Dicot leaf fragments, deciduous periderm, wood indet	996	8018±22	8896	8778–9007	graphite	
BE-10974.1.1	Betula alba fruit fragments, <i>Pinus</i> sylvestris needle fragments, dicot leaf fragments	117	8094±91	9019	8651–9287	gas	
*BE-10975.1.1	Pinus sylvestris needle fragments, Betula alba fruit fragments, indet periderm	280	8715±54	9677	9548–9887	graphite	
*BE-10976.1.1	Dicot. leaf fragments, male anthere indet, conifer needle tip, indet periderm	308	12446±69	14580	14198–14994	graphite	
BE-10977.1.1	Dicot leaf fragments, <i>Pinus sp.</i> periderm, woody scale	999	8388±22	9440	9318–9479	graphite	
872 ª	Median probability (Stuiver and Reimer	, 1993)					
b Calibrated age range with the IntCal 13 calibration curve (Stuiver and Reimer, 1993; Reimer et al.,							
874 2	2013)						
875							