

## Varve formation in the acidic (pH 2.7) pit lake 111 (Lusatia, Germany)

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### Abstract

Sediments from the north basin of Lake 111, a small but very well studied lake resulting from lignite mining in Lusatia, show a pronounced fine layering. This layering can be found in several lignite pit lakes, but mechanisms to explain it have not been investigated with respect to the specific hydrology and chemistry of acid pit lakes.

The north basin of Lake 111 is flat-bottomed, dimictic, and bioturbation can be neglected. Physical and chemical characteristics, sedimentation rates and composition of settling material have been monitored over two years and large thin sections of sediment cores were analysed microscopically to identify fine sediment layering as annual.

Total sedimentation rate was highest in winter, partly due to storms, while sedimentation of particulate organic matter showed peaks in May. Sedimentation of chrysophyte cysts occurred mainly in summer and autumn. Regular bands of chrysophyte cysts were detected, and comparison with the documented history of the lake substantiated that the observed lamination formed annually. To the best of our knowledge, this is the first report on varve formation in an extremely acidic lake which is not governed by fumaroles at the lake bottom.

Key words: acid pit lake, sediment, varve formation, chrysophyte

### Introduction

Pit lakes or mining lakes form in many parts of the world as a consequence of opencast mining. In many cases, sulfide minerals in the dumps are oxidized upon contact with air, producing metal oxides and sulfuric acid. After mining the open pits fill by re-ascending groundwater or rainwater, which flush the acid and metals from the dumps into the lake water. This results in severe acidification of these lakes (pH 2-3) and high sulfate and metal concentrations. Such lakes are extreme ecosystems with respect to their chemical composition and their biocoenoses, which are practically devoid of higher organisms and poor in zooplankton species (Rodrigues et al. 2009, Belyaeva and Deneke 2013) and show low phytoplankton diversity and primary production (Lessmann and Nixdorf 2013). The most widespread phytoplankton genera comprise Chrysophyceae of the genus *Ochromonas*, Chlorophyceae of the genus *Chlamydomonas*, and Bacillariophyceae of the genus *Eunotia*. Their primary production is limited both by phosphorus and inorganic carbon (Lessmann and Nixdorf 2013), which is a consequence of high iron concentrations and extreme acidity.

Annual/seasonal laminations (varves) may form in lake sediments in the absence of significant water movement, bioturbation or gas bubbling. They reflect seasonal changes in sedimenting material. In lakes with a large catchment or with unstable soils in the catchment, the seasonal variation in sediment supply leads to clastic laminations, while a seasonal cycle of production and sedimentation brings about biogenic laminations (O'Sullivan 1983). Phytoplankton production can be traced in the sediment record using diatom frustules and chrysophyte stomatocysts (e.g. Hobbs et al. 2010). Lakes with high internal carbonate loading often possess calcareous laminations, which are triggered by rising temperature and algal uptake of CO<sub>2</sub>. In humic lakes, ferrogenic lamination caused by seasonal Fe(II) oxidation may occur (O'Sullivan 1983). Counting and analysis of varves can be used to estimate the

age of certain sediment layers and to elucidate specific situations or gradual development in the past of a lake and its catchment. However, this approach has apparently not been applied for mine pit lakes so far.

A fine layering has been reported to be common in sediments of Lusatian pit lakes (Friese et al. 2013), but the processes governing its formation have not been studied yet. Since calcite precipitation, a typical process causing sediment lamination (Scharf et al. 2009) cannot occur in an acidic, carbonate-free lake, it remained an open question if the laminations represented annual cycles (varves) that can be used for age determination of acidic pit lakes. Pit lakes are often situated in remote areas and not regularly monitored. A means to determine the age of sediment layers would allow to elucidate distinct events and processes in the past of these lakes or in their catchments, such as physical disturbance events, progress of landscape reclamation, or land use changes. Seasonal lamination of sediments has been documented for the very acidic and dimictic crater lake Katanuma (Satake and Saijo 1978), but the underlying mechanism requires the presence of fumaroles at the lake bottom.

Lake 111 is a small acidic (pH 2.7) pit lake in Lusatia, East Germany (51°29' north, 13°38' east). It started to form after closure of the lignite mine Agnes which was operated between 1929 and 1958 (Koschorreck 2013). Because of its high sulfate concentrations (1050-1600 mg L<sup>-1</sup>) and the absence of surface inflows or outflows the lake served as a model site for testing passive bioremediation and the application of in-lake sulfate-reducing bioreactors (Koschorreck 2013), so its bathymetry as well as water and sediments have been thoroughly studied. The north basin is flat-bottomed, has a maximum depth of 6 m and is dimictic. Lake 111 water is low in nutrients and carbon (table 1). Its phytoplankton community is restricted to unicellular flagellates of the genera *Chlamydomonas* (Chlorophyta) and *Ochromonas* (Chrysophyta) which are present through the whole growing season (Kamjunke et al. 2004). Lake sediments are also acidic (pH 2.7-3), and sediment cores regularly showed a finely laminated structure, especially in the upper centimeters (Wendt-Potthoff et al. 2010; Friese et al. 2013).

**Table 1** Water chemistry of Lake 111 between 1999 and 2008. Data were compiled by Koschorreck (2013) using 143 to 287 single measurements. TIC total inorganic carbon, TOC total organic carbon.

Parameter	Unit	Value	Parameter	Unit	Value
KB <sub>8.2</sub>	mmol L <sup>-1</sup>	17 ± 2	Cu	µg L <sup>-1</sup>	6.4
Ca <sup>2+</sup>	mg L <sup>-1</sup>	219 ± 33	Ni	µg L <sup>-1</sup>	200
Mg <sup>2+</sup>	mg L <sup>-1</sup>	30	NH <sup>4+</sup> -N	mg L <sup>-1</sup>	2.8 ± 0.5
Na <sup>+</sup>	mg L <sup>-1</sup>	7 ± 1	NO <sub>3</sub> <sup>-</sup> -N	mg L <sup>-1</sup>	0.3 ± 0.1
Fe	mg L <sup>-1</sup>	171 ± 70	Total P	mg L <sup>-1</sup>	0.009
Al	mg L <sup>-1</sup>	38 ± 5	Si	mg L <sup>-1</sup>	17.9
Mn	mg L <sup>-1</sup>	3.1 ± 0.4	TIC	mg L <sup>-1</sup>	6.1 ± 9.2
Zn	mg L <sup>-1</sup>	1.08	TOC	mg L <sup>-1</sup>	2.1 ± 1.8

The aim of the present study was to clarify whether the laminations represent varves. As the key to understanding varve formation is the study of modern lake processes (Tylmann et al. 2012), we combined the microscopic analysis of thin sections of a sediment core with sediment trap studies over 28 months from August 2006 to January 2009, and with documented facts about the history of this young anthropogenic lake.

## Methods

Sediments were obtained in September 2002 by gravity coring (Uwitec, Mondsee, Austria). Cores sampled with pre-cut liners fastened with waterproof tape were sectioned vertically in the field for documentary purposes. One half of a 51 cm long sediment core was transported intact to the laboratory within the plastic liner and then embedded for thin sectioning following Röhrig and Scharf (2006). Briefly, samples were dehydrated by immersion in acetone. Then acetone was replaced by Palatal, a polyester resin. The resin was allowed to harden for approximately two weeks and finally cured at 60°C for 48 h. Large thin sections were prepared by Thomas Beckmann (Dünnschlifflabor

Schwülper-Lagesbüttel, Germany). Thin sections were analyzed using a Zeiss Axiolab microscope with a Nikon (Coolpix 990) camera for documentation.

Sedimentation rates were determined using two parallel sediment traps (Uwitec, Mondsee, Austria) which were exchanged approximately every two weeks from August 2006 to December 2008. Aliquots of the homogenized sediment trap contents were fixed with Lugol's solution. The sediment trap flasks were kept refrigerated and the remaining material was analyzed the following day. The contents were again carefully homogenized before filtration. Pre-washed and weighed membrane filters (ME24) were used to determine total sediment mass from 150 mL of sediment trap material. Pre-combusted glass fibre filters were used to determine particulate organic carbon (POC) from 200 mL of sediment trap material. All filters were dried for 2 h at 60°C. POC was determined with a TOC analyzer (Vario EL, Elementar, Germany). The sediment from the traps was also regularly inspected by light microscopy using 400 x magnification, and photographs were taken using an AxioVision camera and software (Zeiss, Germany).

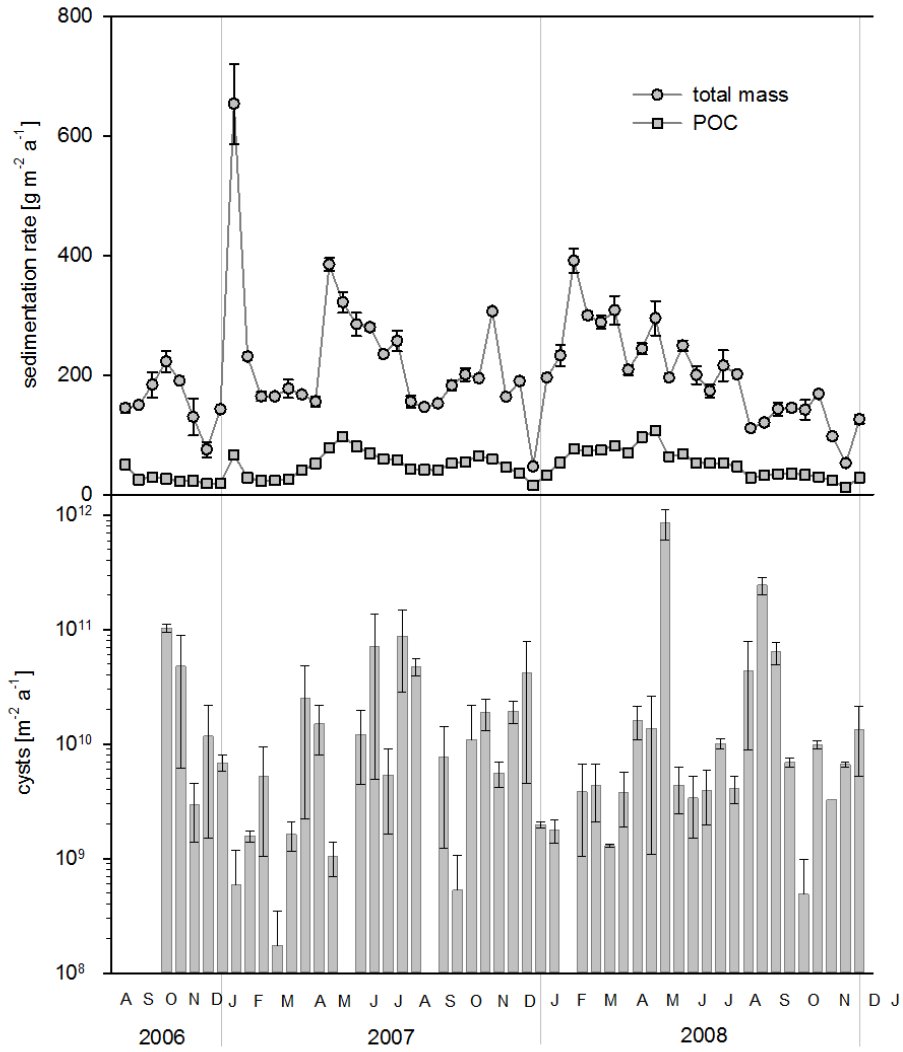
To facilitate counting of chrysophyte stomatocysts in sediment trap material, organic matter from Lugol-fixed samples was removed by incubation and boiling with H<sub>2</sub>O<sub>2</sub> and subsequent potassium dichromate treatment. After three washing steps with water, samples were again fixed with Lugol's solution. Chrysophyte cysts were then counted using sedimentation chambers and an inverted microscope.

## Results and Discussion

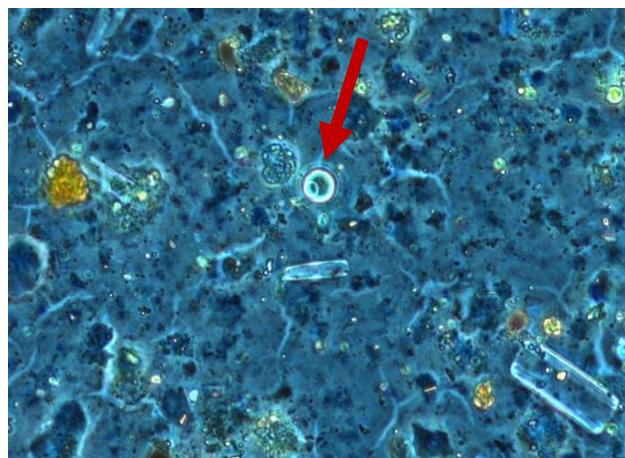
Regarding recent sedimentation, a yearly cycle of gross sedimentation rate and POC content of the sedimenting material was evident (fig.1), with maxima of gross sedimentation rate in winter and summer and highest POC sedimentation in the summer. Minima of gross sedimentation occurred in late autumn. After the severe winter storm Kyrill on January 18 and 19, 2007, the sedimentation rate was 1.5fold higher than the other maxima. Living specimens from January 31 also contained empty cysts in addition to those with still visible cell contents, which indicates sediment resuspension. However, dump erosion may have been of key importance, as the eastern and southern shore of Lake 111 are still poorly covered by vegetation. Chrysophyte cysts were detected almost throughout the year and their counts had maxima in spring and late summer (fig. 1), but counts were also high around 10<sup>10</sup> cysts m<sup>-2</sup> a<sup>-1</sup> at the end of the year. This appears unusual, however, maxima of cyst deposition in other lakes have been observed both in autumn (Smol 1988) as well as in winter or late spring/early summer (O'Sullivan 1983). Cysts in Lake 111 were 5-7 µm in diameter, their surfaces appeared rather smooth, and their collar was not pronounced (fig. 2), however, electron microscopy would be needed to substantiate details. Given the limitations of light microscopy, the overall morphology agreed reasonably with stomatocysts of known *Ochromonas* species (Holen 2014), and no other chrysophyte genera were detected in Lake 111 during several years of study (Kamjunke et al. 2004, Koschorreck 2013).

Fresh sediment was soft, fine-grained and layered to a depth of approximately 22 cm. Greenish-yellow and brownish bands with varying thicknesses alternated (fig. 3).

Large thin sections of the sediment confirmed the lamination up to 22.3 cm. Yellow bands appeared gel-like and did not contain clastic material, while the brownish bands were more dense. The high iron concentrations of the sediments (Wendt-Potthoff et al. 2010, Friese et al. 2013) suggest that the gel-like material may consist of amorphous iron minerals. Below 22.3 cm few limnic remains were detected, but the mineral matrix contained lignite particles, fly ash spherules, splinters of charcoal and gypsum crystals (fig. 4). Surprisingly, no pollen grains were seen in the whole core. Presumably they had been mineralized in the extreme chemical matrix of the sediment, or they are masked by the optical properties of the polyester resin and/or the wall of the pollen grains. Sedimentological patterns underlying glacial varves result from regular seasonal processes at the front of a glacier. In contrast, the structures of Lake 111 sediments formed by sand and silt layers are caused by the management of the lake or extreme weather events. Limnochemical and -physical processes may explain layering, but they may occur several times in a year. Moreover, calcite and siderite precipitation can be excluded in the present chemical status of the lake. Other biological proxies are diatom frustules and chrysophyte cysts, the latter being more stable against chemical attack (Hobbs et al. 2010).



**Figure 1** Sedimentation rates of total solids, particulate organic carbon (POC) and numbers of chrysophyte cysts.



**Figure 2** Appearance of a chrysophyte cyst in sediment trap material after treatment with  $\text{H}_2\text{O}_2$  and potassium dichromate.

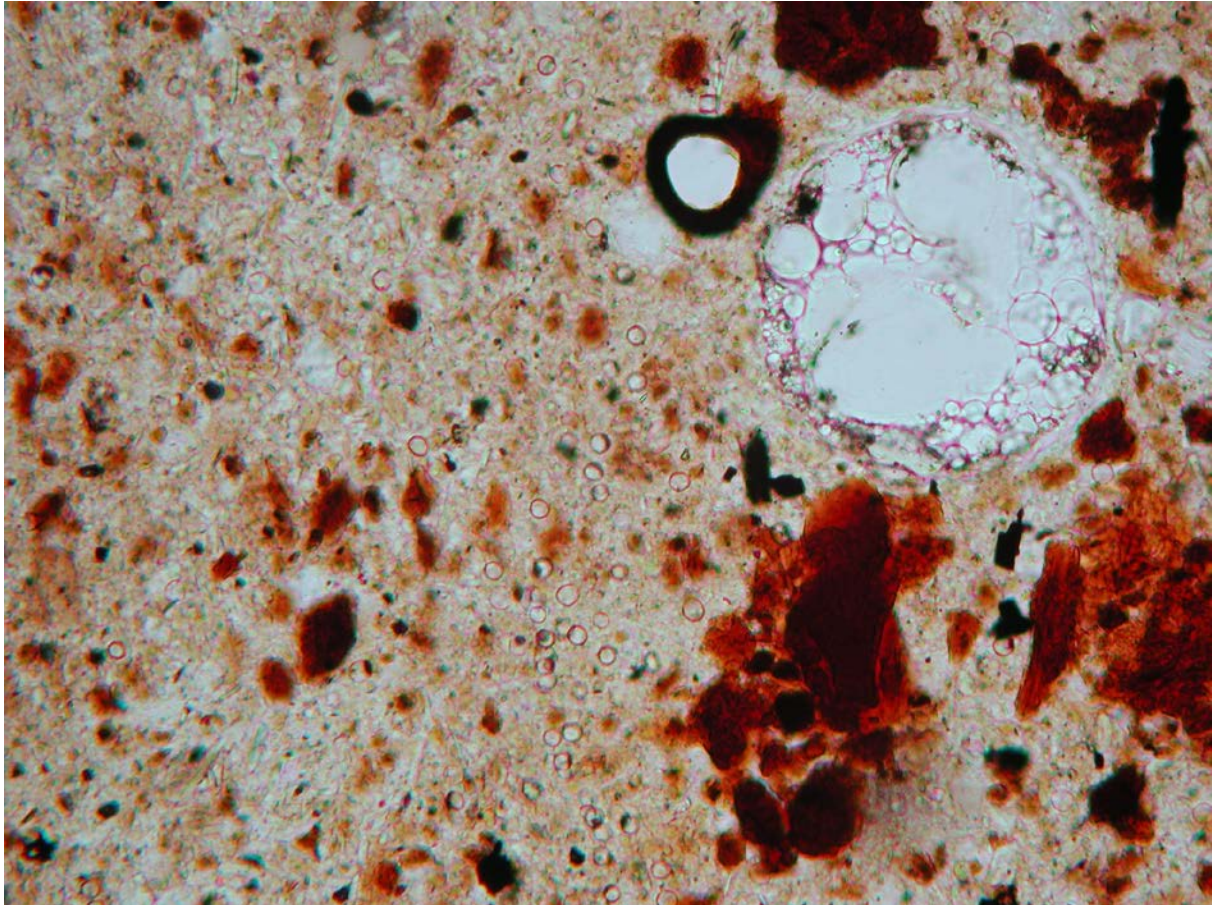
Indeed, rather well preserved frustules of the genus *Eunotia* and severely etched "ghosts" of *Navicula*, *Cymbella* and *Melosira* were detected, especially in the top 5 cm. Deeper in the sediment, they did not form clear and regular layers, and their numbers declined. This may be partly due to chemical degradation in the extreme chemistry of the sediment. Bands of chrysophyte cysts were found more regularly close to or in the yellow bands. In some cases, chrysophyte cysts were "missing", or it was unclear if two thin bands originated in the same year. There is one report indicating that *Ochromonas* might have been absent from Lake 111 in 1995, however, the authors could not rule out methodical problems (Wollmann et al. 2000). As chrysophyte cysts are typically better preserved in the sediment than diatom frustules, we assume that if only diatoms are detected in a defined layer, chrysophyte cysts have not been formed in the respective period. The formation of more than a single chrysophyte band is probably explained by intermittent intense sedimentation of other material.



**Figure 3** Vertically cut sediment core from Lake 111 with laminations.

Assuming that formation of chrysophyte cyst bands formed annually in the sediment of Lake 111, the age of the sediment layers can be explained as follows:

The top 3 cm appear to be disturbed during sampling, probably due to the high water content and softness of the material. Down to 4.9 cm depth, the deposits of 4-5 years can be found. Further downwards to 6.8 cm, approximately 7 years are counted (altogether 11-12 years). The section between 6.8 and 8.2 cm represents 4 years. Between 9 and 10 cm depth, some uncertainty exists because chrysophyte cyst layers appear to occur in pairs. Taking this into account, the top 11 cm of sediment represent 23-26 years. Further downward, 4 cysts layers were detected until 12.7 cm, and another 0 to 2 unclear bands until 16.1 cm followed by 3 layers down to 16.6 cm (30-33 years in total). After another cyst band between 1.6. and 20.4 cm (summing up to 31-34 years), the sediment matrix was still layered but contained more plant particles and also diatoms. In one case the diatoms formed a band and were accompanied by scattered chrysophyte cysts. The seasonality remained unclear, as also signs of bioturbation were evident. We know that chironomid larvae colonize modern Lake 111 sediments (Rodrigues et al. 2009) and that their burrowing activity might be detected until 4 m water depth (Lagauzère et al. 2011). Maybe the water level was lower at that time, as the lake gradually filled with groundwater and precipitation is low in Lusatia. One or two additional years may be counted until 22.3 cm. The limnic regime must have been different below, and the contents of lignite, charcoal, glassy particles which probably represent fly ash, and gypsum crystals increased. These remains are associated with active mining in the area. Altogether, counting the chrysophyte cyst layers as annual laminations gives at least 32-36 years. Below, another 10 years of limnic sedimentation are estimated, giving at total lake age of 42-46 years at the time of sediment coring (2006). This corresponds well with the documented mine closure in 1958, assuming that it took at least two years to form a lake in the north basin of former mine Agnes.



**Figure 4** Microscopic image of a layer with chrysophyte stomatocysts, a fly-ash spherule and coal splinters.

## Conclusions

Chrysophyte cyst layers in the sediment thin sections combined with the available information on the recent sedimentation and history of the lake clearly indicate that the fine laminations in Lake 111 sediment represent varves. To our knowledge, this is the first verification of varves in an extremely acidic pit lake. The cysts can be assigned to *Ochromonas* sp., since it was the only chrysophyte genus detected in Lake 111 and other acid pit lakes. Cyst formation was apparently not restricted to a defined season, as in many other lakes, but occurred more steadily with a bimodal maximum during summer. Only in some cases paired cyst layers were also seen in the sediment record. More detailed analysis of the sedimentation regime (e.g. iron sedimentation, re-dissolution processes) will be necessary to understand how the living planktonic cysts in the sediment trap finally form defined fossil layers in the lake sediment.

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