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Key words: lake restoration; implementation plan; PAC dosage estimation; planktonic community structure; calcite precipitation; time-delayed response

Abstract

Feldberger Haussee (NE Germany) was polluted for almost a century. During the late 1970s, the nutrient input reached a maximum of approximately 1.9/11.5 g TP/TN m\textsuperscript{-2} yr\textsuperscript{-1}. As a result, the lake became a hypertrophic ecosystem and had largely lost its recreational value. In 1980, the sewage discharge was stopped, decreasing the external loading by approximately 90%. Because of vast amounts of phosphorus stored in the sediment, the lake remained highly eutrophic until 1985 with a TP concentration of ca. 1 mg L\textsuperscript{-1}. To accelerate recovery, biomanipulation was applied from 1985 – 2002 but was successful to only a minor extent. Eventually, due to sediment sequestration and discharge to downstream lakes the TP spring maximum (2006 – 2010) dropped to 0.112 - 0.078 mg L\textsuperscript{-1}. However, given the trend, it was obvious that it would take another 10 – 15 years for the concentration to approach the desired mesotrophic level. Thus, it was suggested to inactivate the surplus phosphorus by treating the lake with poly-aluminium chloride (PAC) as precipitant. To ensure good water quality, the objective was to decrease concentrations below 0.035 mg TP L\textsuperscript{-1}, while optimising the amount of PAC applied (as much as needed, but as little as possible). As a prerequisite, the status of the lake was carefully studied; external phosphorus loading and the amount of mobile phosphorus stored in the sediment being of specific interest. Laboratory experiments and field
observations eventually resulted in an estimated dosage of 27 g Al m$^{-2}$ (molar Al/P 12).

Following the treatment in April 2011, prime water quality parameters showed two opposing trends: (1) TP concentration immediately dropped below the restoration target ($\leq 0.025/0.035$ mg L$^{-1}$), primary production and phytoplankton biomass declined substantially. (2) However, water clarity did not improve for another four years. The likely reason for the delay was the structure of the phytoplankton community. It was dominated by cyanobacteria with the potential to trigger intensive calcite precipitation and thus impair transparency. In spring 2016, the cyanobacteria suddenly disappeared and transparency increased significantly. We speculate that these changes of the planktonic community shifted the ratio of assimilation and respiration in favour of the latter. This allowed an increase of free CO$_2$* (dissolved CO$_2$ & dissociated carbonic acid) altering the carbonate buffering system and thus halting the formation of calcite crystals. Also, the phytoplankton, now represented by small readily ingestible taxa, promoted a flourishing Daphnia population inflicting heavy grazing losses, resulting in clear water stages (2015 June, 4.20 m; 2016, August 3.70 m; 2017 August, 4.5 m). We conclude that the drastic decrease of phosphorus availability in concert with structural and functional changes of the plankton community eventually improved the water quality of Haussee significantly. The lake is now in a mesotrophic status; well in accordance with the aim of the restoration project.

1. Introduction

Although the basic principles of lake remediation and restoration are essentially clear (e.g. Sas et al., 1989, Cooke et al., 2005, Lürling et al., 2016), the results of the applied measures can be disappointing. Reasons for failure are typically a lack of site-specific information and understanding of the processes involved (Schauser et al., 2003, Mackay et al., 2014, Spears et al., 2014). Five specific issues are of central interest in this respect: (1) the water balance of the lake under consideration, (2) the nutrient budget, (3) the chemistry with special regard to the phosphorus content and binding forms in the sediment, and (4) the structure of the biological community. Finally, (5) if chemical nutrient inactivation is intended, an effective precipitation agent for phosphorus has to be chosen and a lake-specific quantity applied to rapidly, significantly and sustainably improve water quality.

Concerning the water quality management of lakes, there is a long-standing basic rule: Reduction of external loading (remediation) has priority over lake-internal measures (restoration; Vollenweider 1976, Uhlmann 1985). More precisely, while remediation
measures in the drainage basin are suitable for polymictic, shallow lakes with high water renewal rates, thermally stratified lakes with long-lasting water residence time require a combination of both load reduction and in-lake restoration efforts (Uhlmann 1982, Sas 1989, Schauer et al., 2003). Nevertheless, quite a number of studies have been published where this principle was either neglected or there was no effective solution to reduce the external nutrient input. Thus, the resulting improvement of water quality was either transient or fell short of expectations (e.g. Phillips et al., 2005, Egemose et al., 2011, Lang et al., 2016).

Even though of critical importance for any kind of remediation and restoration measure, to establish a reliable nutrient budget can be a challenge. This applies especially to seepage lakes because both surface runoff and groundwater inflow can only be estimated with limited precision (Holzbecher et al., 1999), even though a substantial proportion of external nutrient loading may enter by this pathway (Meinikmann et al., 2015). Also, data are not always available on atmospheric deposition, even though it sometimes constitutes a significant proportion of external loading, (Blake & Downing 2009). If urban settlements are located in the drainage basin, information on the surface runoff and nutrient concentration of the stormwater sewers is required (Lathrop et al., 1998).

Besides decreasing the external nutrient load below an acceptable, lake-specific level (Vollenweider 1976, Nürnberg 1984, OECD 1986), the central objective of any kind of in-lake restoration targeting nutrients is to reduce the phosphorus (P) concentration in the water column rapidly, significantly and sustainably below an appropriate threshold (Janse et al. 2008). P inventories of lakes consistently reveal that the bulk is stored in the sediment, which hence constitutes a potential major P source (Søndergaard et al., 2013); whereby the P content varies both vertically (Gonsiorczyk et al., 1998) and horizontally (Noges & Kisand 1999). However, the total P content of the sediment is not a good predictor of mobile P because only the latter has the potential to be released into the water column (Hupfer et al., 2016). The task, therefore, is to reliably estimate the permanently bound P fractions, the mobile fractions, and the fractions still undergoing diagenetic transformations (Psenner & Pucsko 1988, Hupfer & Lewandowski 2005). Thus, a realistic assessment of the different P fractions is of paramount importance to determine the specific quantity of precipitant to guarantee a long-lasting success of the measure (Wauer et al., 2009).
Given a sound evaluation of the lake under consideration and the availability of a well-designed management concept, the P concentration of the water can rapidly approach the anticipated values (Huser et al., 2016), but the biological community is likely to change less rapidly. Specifically, the phytoplankton community of nutrient-rich lakes is frequently dominated by cyanobacteria which might continue to significantly impair the water quality (Mischke & Nixdorf 2003). Because of several specific traits, such as accessory pigments for effective light harvesting (Kaiblinger et al., 2007) or the ability to replenish internal P pools while resting on the sediment surface (Istvánovics et al., 1993), cyanobacteria may predominate for considerable periods even after a drastic reduction of the external P input followed by a substantial decrease of P concentrations in the water (hysteresis behaviour of lakes; Gächter & Imboden 1985).

Even though the ultimate causes are still a matter of debate (Dolman et al. 2012), it seems evident that P concentrations of <30-50 µg TP L$^{-1}$ impair the growth of cyanobacteria (Lathrop et al., 1998). Although the role of N/P ratios is less clear (Dolman & Wiedner 2015), there is ample reason to believe that during limiting growth conditions, low ratios might favour cyanobacteria in general and nitrogen-fixing species (Nostocales) in particular (Nixdorf et al., 2013). Since P inactivation results in a substantial rise of N/P ratio, cyanobacteria are supposed to dwindle as the dominating group within the phytoplankton community (Downing et al., 2001).

From a management point of view, the choice of an appropriate precipitant and the quantity to be applied are largely a matter of the chemistry of the lake to be treated and the amount of P to be inactivated (Huser et al., 2016). Meanwhile, there is a variety of precipitants on the market, but regardless of their specifics all are essentially based on iron, aluminium or lanthanum (Lürling et al., 2016). However, there are at least three good reasons for giving preference to precipitants with aluminium as the active element: (1) They are highly efficient (Cooke et al., 2005) (2) in comparison to iron salts, the resulting P complex is not sensitive to redox conditions (Zampara & Zacharias 2014), and (3) the price is relatively low (Mackay et al., 2014). Finally, there is no significant risk of toxicity if applied properly (Pacioglou et al., 2016).

In April 2011, Feldberger Haussee (NE Germany, hereafter referred to as Haussee), a stratified, eutrophic hard-water lake, was subject to P inactivation using poly-aluminium...
chloride (PAC) as precipitant. For various reasons, the lake has been studied for almost a
century. Therefore, its pristine status and eutrophication history in terms of a number of
physical, chemical and biological characteristics are well documented (e.g. Thienemann,
1925, Uhlmann 1961, Koschel et al. 1981, Kasprzak et al., 2007). A substantial proportion of
this information could be used to establish a sound remediation and restoration program to
strive for a ‘mesotrophic lake’ as the restoration objective (TP spring maximum, summer
mixed layer average <0.035 mg L\(^{-1}\), Chla summer mixed layer average <0.010 mg L\(^{-1}\), Secchi
transparency, summer average > 2.5 m; LAWA 2014). Our purpose was to apply an
optimised dose of PAC (i.e. as much as needed, but as little as possible) which would
facilitate a rapid, significant and sustained improvement of the water quality for at least 10 –
15 years.

Nevertheless, in spite of our efforts to precisely plan the restoration measure and contrary to
our expectations, Haussee remained remarkably turbid for another four years. In general
terms, the reason was a considerable temporal difference by which chemical and biological
traits of the lake responded to the Al-treatment. Specifically, while TP dropped immediately
and significantly below the anticipated concentration level, cyanobacteria continued to
dominate the phytoplankton community until late winter 2015; whereupon they abruptly
collapsed and never recovered. The on-going high turbidity, however, was primarily caused
by massive calcite precipitation events during spring and summer both before and after the
treatment. By 2015 these events had decreased substantially. Here, we present the results of
the restoration project with close scrutiny of the above quoted five criteria. We evaluate the
results of the intervention and detail the underlying mechanisms with respect to the restoration
of this formerly heavily-polluted lake.

2. Methods
2.1. Site description
Haussee is located about 90 km north of Berlin within Germany’s Baltic lake region
(53°20´10”N, 13°26´03”E, 88 m AMSL). The lake basin was formed during the last
continental glaciation some 12,000 years ago and is today situated at the transition between
temperate maritime and temperate continental climates (Fraedrich et al., 2001). The
catchment area of 7.12 km\(^2\) was shaped by a terminal moraine with hills up to a height of 150
m AMSL. Haussee is a seepage lake essentially fed by groundwater and rainfall (Trömel
1964). However, on average ca. 250,000 m\(^3\) of storm water runoff from the neighbouring
The town of Feldberg discharges into the lake annually. Although this is only 3% of the lake’s volume, it currently represents 42% of the total external phosphorus input (0.064 g TP m$^{-2}$ yr$^{-1}$). Haussee is connected by a channel with two downstream, low-nutrient lakes (Breiter and Schmaler Luzin). Some characteristics of the lake are outlined in Table 1, Fig. 1, 14 (supplemental material).

The drainage basin shows a mosaic of different land use with forests (33%), residential areas (22%), lakes (20%) and farmland (16%) being the most important. Till and sandy soils prevail (>50%). Earlier estimates of the water residence time ranged between 2.5 and 5 years (Barby 1967). Our own calculations using a general hydrological water balance model (Holzbecher et al., 1999, p. 39, equation 1) resulted in a long-term (1974 - 2014) average of 8.9 (3.0 SD) years. In contrast to the common method of hydrological balances, which includes precipitation, groundwater inflow, and evaporation, this estimate is exclusively based on discharge measurements. The result is a ‘phosphorus-relevant’ residence time. The town of Feldberg is located adjacent to the southern shore and has approximately 2,000 residents. During summer, Feldberg and the surrounding lakes are water recreation hotspots, attracting thousands of weekenders and holidaymakers.

2.2. Eutrophication history

Haussee’s long history of eutrophication began in 1888 when a dairy factory started to discharge raw sewage into the lake (Richter 1986). Nevertheless, in the middle of August 1924, Thienemann (1925) found the water quality of the lake still to be excellent, with a Secchi transparency of 5 m and a hypolimnetic concentration of dissolved oxygen between 1.5 - 4.5 mg L$^{-1}$. Only a decade later, also in August, Ohle (1934) encountered a clearly deteriorated lake, with an anoxic hypolimnion, accumulation of hydrogen sulphide and a Secchi transparency of only 1.3 m. In the 1950s, the town of Feldberg built and later enlarged a central municipal water supply system including a sewage treatment plant. The sewage, however, was treated only with a percolating filter, which removed most of the organic load but discharged the bulk of the N and P into the lake. As a result, Haussee progressively became a hypertrophic ecosystem (Koschel et al., 1985). By the end of the 1970s, the external nutrient input amounted to 1.9 g P m$^{-2}$ yr$^{-1}$ and 11.5 g N m$^{-2}$ yr$^{-1}$, respectively (Hahmann et al., 1977). As a consequence of this heavy pollution, besides other severe shortcomings, the lake’s recreational value declined, especially for all water-related activities and posed a
serious threat of eutrophication to the low-nutrient lakes Breiter and Schmaler Luzin downstream.

In 1980, the sewage discharge was suddenly stopped, decreasing the external nutrient loading by approximately 90%, raising hopes for a quick recovery. However, the water quality did not improve significantly. Instead, because of the extraordinarily high amounts of P accumulated in the sediment, the lake remained eutrophic with a constant TP concentration of approximately 1 mg L\(^{-1}\) until 1985. In order to accelerate improvement, biomanipulation (introduction of piscivores, removal of planktivores) was applied from 1985 – 2002, but was successful only to a minor extent (Kasprzak et al., 2007). The central problem was a shift in the phytoplankton community structure from small, easily-grazed green algae to large filamentous cyanobacteria which could not be handled by herbivorous zooplankton (Kasprzak et al., 1993). Eventually, as a result of continuing sequestration into the sediment and discharge to downstream lakes, the volume-weighted, mean annual TP concentration by 2010 had dropped to 0.072 mg L\(^{-1}\). Although the trend was towards a continuing decrease, the equilibrium concentration calculated by different models (Vollenweider 1976, OECD 1982, Nürnberg 1984) was estimated to range between 0.043 and 0.059 mg TP L\(^{-1}\), given the present external loading of 199 kg TP yr\(^{-1}\). Thus, without additional restoration measures, water quality traits typical for mesotrophic lakes could not be achieved (TP, spring maximum, summer mixed layer average <0.035 mg L\(^{-1}\), Chl\(\alpha\) summer mixed layer average <0.010 mg L\(^{-1}\), Secchi transparency, summer average > 2.5 m; LAWA 2014). It was therefore decided to treat the lake using poly-aluminium chloride (PAC) as a precipitant in order to rapidly and significantly accelerate recovery and to sustain good water quality.

2.2. Limnological survey

Sampling campaign: Samples (2006 – 2017) were collected during the entire year at the deepest site of the lake (Fig. 1), except when unsafe ice coverage or temperatures below freezing point prevented from doing so. While a fortnightly schedule was maintained from May – September, monthly samples were taken during the remainder of the year. Vertical profiles of water temperature, oxygen concentration, and pH were measured using multi-parameter probes (YSI, Ohio, USA). Depending on temperature profiles, composite water samples of the mixed layer were taken from the surface, 2.5 m, and 5 m. A sample from 7.5 m was considered representative for the hypolimnion.
Chemical analysis: Total phosphorus (TP), total nitrogen (TN) and chlorophyll a (Chla) were analysed spectrophotometrically according to standard protocols (DIN EN ISO 15681-1:2005-05, DIN EN ISO 13395:1996-12, DIN 38412-16:1985-12). TP and TN were measured after wet digestion of unfiltered subsamples in an autoclave (potassium peroxodisulfate, TP 30 min., 134 °C; TN 40 min., 121 °C, FOSS FIAstar 5000 analyser, Hillerød, Denmark). Chla was estimated by filtration of aliquots through membranes (pore size 1.2 µm, Schleicher & Schüll, Dassel, Germany) which were immediately frozen at -20 °C until further analysis. Extraction was performed by adding 5 ml of 99.8 % analytical grade acetone. To enhance extraction efficiency, filters were homogenised and subsequently stored in darkness for 12 – 24 hrs. Samples were then centrifuged (15 min, 3,000 rpm) and the absorbance of the supernatant was recorded at three different wavelengths (630, 665 and 750 nm, UV/VIS Lambda 2, Perkin Elmer, Überlingen, Germany). Concentration was calculated according to Strickland and Parsons (1968).

Alkalinity was measured by titration (DIN EN ISO 9963-1:1996-02, Titrando 888, Metronom, Filderstadt, Germany). The concentration of CaCO$_3$ (calcite) was determined by filtering aliquots through membranes (cellulose acetate, pore size 0.45 µm, Sartorius, Göttingen) which were stored in a desiccator until further analysis. Calcite was then dissolved in 10 % hydrochloric acid and the released CO$_2$ was measured using an infrared gas analyser (Infralyt 50 Saxon, Junkalor, Dessau, Germany; see Proft 1984). The calcite saturation index (SI) was calculated using a model established by Hepperle and Krienitz (1997; available online at http://www.sequentix.de/software_winiap.php).

The concentration of soluble aluminium (Al) was estimated applying a protocol published by Wauer et al., (2004), which ensured the detection of all potentially reactive forms of Al. Aliquots of 100 mL were filtered through membranes (cellulose acetate, pore size 0.45 µm, Sartorius, Göttingen) and acidified with 1 mL HCl. The principal reagent for the complexation of Al was pyrocatechol violet. Samples were finally measured using a flow-injection analyser (FIA-LAB II Flow Analyser, MLE Dresden GmbH, Germany). The Al content of two seston size fractions (>50 µm, >90 µm) and selected groups of benthic organisms were analysed following a protocol suggested by Wauer & Teien (2010).

Plankton analysis: Phytoplankton was obtained from the same water samples as for chemical analysis and preserved in Lugol’s solution. Subsamples were filled into differently-sized
sedimentation chambers and allowed to settle overnight (Utermöhl 1958). Then a minimum of 400 settling units were counted under an inverted microscope at 100 – 400x magnification. Biovolume was calculated according to Hoehn et al., (1998, Table 3, p. 60 - 64) and converted into carbon units \(FM \times 0.2 = DM \times 0.5 = C\), Winberg et al. 1971). Secchi transparency was determined using a white disc of 25 cm in diameter.

Crustacean plankton was collected by vertical net hauls from 6.5 m (mean depth of the lake) to the surface using a plankton net of 90 µm mesh size (Hydrobios, Kiel, Germany). The net had a cone-shaped cap, an opening of 0.27 m², a length of 1.2 m and a filtration efficiency of approximately 1 (estimated using a flow-meter). Each sample was preserved in 4 % formalin–sugar solution (Haney and Hall 1973). Using sedimentation chambers, three subsamples containing a total of at least 100 individuals of the dominant group (except for nauplii) were counted in an inverted microscope at 60x magnification. Mean length was estimated by measuring 15 individuals of each group using a computer-aided microscopy system (TSO-VID-MESS-HY, Pulsnitz, Germany). Dry mass was calculated based on published length–weight relationships (Bottrell et al., 1976, Kasprzak 1984) and converted into carbon units \(DM \times 0.5 = C\), Winberg et al., 1971).

Activity parameters: Primary production was quantified as a ‘production potential’ meaning that instead of a vertical set of bottles, only one sample collected from 1 m was exposed at the same depth. For the measurement 2 x 250 mL of water (light and dark bottle) were collected, inoculated with 1 mL of \(^{14}\)C-bicarbonate solution (specific activity 26.3 \(10^6\) dpm mL\(^{-1}\)) and incubated for 4 hrs in situ. Incubation was stopped by addition of 1 mL formalin. Thereafter, 10 mL subsamples were filtered onto cellulose membranes (0.65 µm, Sartorius Göttingen, Germany). Radioactivity was measured in a liquid scintillation counter (Perkin Elmer, Tri-Carb 2810 TR, Akron, Ohio, USA) for 4 hours or until the standard deviation of counts remained below 5 % of the average. Calculation of daily primary production followed the protocol of Köhler et al., (1999).

Bacterial protein production (BPP) was determined by incorporation of \(^{14}\)C-leucine (Simon & Assam 1989) as modified by Grossart et al., (2006). Triplicates and a formalin-preserved control were incubated with \(^{14}\)C-Leu (213 mCi mmol L\(^{-1}\); Hartmann Analytic GmbH, Germany) at a final concentration of 165 nM, which ensured saturation of the uptake systems of both free-living (FL) and particle-attached (PA) bacteria. Incubation was performed in the
dark at *in situ* temperature for 1.5 h. After preservation with 2 % formalin, samples were filtered onto 5.0 µm (PA bacteria) nitrocellulose membranes (Sartorius, Göttingen, Germany) and the collected filtrate was filtered on 0.2 µm (FL bacteria) nitrocellulose filters (Sartorius, Göttingen, Germany). All filters were extracted with ice-cold 5 % trichloroacetic acid (TCA) for 5 min. Thereafter, filters were rinsed twice with ice-cold 5 % TCA, once with ethanol (50 % v/v), and dissolved in ethyl acetate for measurement by liquid scintillation counting (Perkin Elmer, Tri-Carb 2810 TR, Akron, Ohio, USA). Standard deviation of triplicate measurements was usually <15 %. The amount of incorporated $^{14}$C-Leu was converted into BPP by using an intracellular isotope dilution factor of 2. A conversion factor of 0.86 was used to convert the produced protein into carbon (Simon & Azam, 1989).

**Sediment analysis:** To quantify sediment phosphorus (P) and to account for both horizontal and temporal differences, samples were taken (2010-2013, 2015 – 2017) using a gravity corer (UWITEC, Mondsee, Austria) at different stations with special reference to the deepest locations of the basins (Fig. 1). The cores were subsequently sectioned into 1 – 5-cm slices for further analysis. To estimate mobile P ($P_{\text{mobile}}$), different P-binding forms were acquired by applying a sequential P extraction protocol of Psenner & Pucsko, (1988) as modified by Hupfer et al., (1995). $P_{\text{mobile}}$ was calculated as the sum of P binding forms, potentially contributing to P release; *i.e.* loosely adsorbed P ($NH_4Cl$-P), redox-sensitive P (BD-P), and organic-bound P (NaOH, non-reactive P). The proportion of the specific fractions was determined spectrophotometrically by applying a standard protocol (DIN EN ISO 15681-1:2005-05, Machery-Nagel, Nanocolor 505D, Düren, Germany; see Gonsiorczyk et al., 1998). To measure the SRP concentration of the pore water, aliquots of sediment samples were centrifuged for 5 min (13,000 g at 4 °C). The supernatant was subsequently filtered through cellulose-nitrate membranes (0.45 µm) and further processed as outlined for the extraction method.

**Phosphorus budget:** Haussee’s present external nutrient sources are the storm water sewer of the adjacent town of Feldberg, atmospheric deposition, surface runoff from the drainage basin and groundwater input. For the estimation of external nutrient inputs, only phosphorus was considered. Since the storm water sewer lacks a gauging station, it was impossible to calculate the influx by measuring the hydraulic loading multiplied by a concentration estimate. Thus, a protocol suggested by Behrendt et al., (1999) was applied. The estimated size of paved or otherwise sealed areas within the urban fringe of the town of Feldberg connected to the storm
water sewer adds up to a total of 41 ha. The long-term (1977 - 2014) average annual rainfall was 600 mm, which equals an aggregated water volume of ca. 250,000 m$^3$ yr$^{-1}$. Since Feldberg is located on a hill with steep slopes, it can safely be assumed that with some minor losses the bulk of the runoff is immediately diverted into the lake. Depending on the temporal distribution of rainfall, the runoff TP concentration was estimated during the years of 2001, 2006, 2007 and 2009 ($n = 113$). Finally, by multiplying the calculated runoff with the average TP concentration, the annual nutrient input was obtained.

A similar approach was applied to estimate the phosphorus inflow from the ground water. Using the above mentioned general hydrological water balance equation (Holzbecher et al. 1999) the annual groundwater inflow was calculated (660,000 m$^3$ yr$^{-1}$). Unfortunately, there are no groundwater wells in the drainage basin of the lake to measure the phosphorus concentration. Therefore, 12 wells located in a neighbouring catchment area were used as a substitute. During the years 2001 – 2008, the TP concentration was measured quarterly. By multiplying the calculated groundwater inflow with the average concentration of the wells, the loading was estimated. For atmospheric deposition and the remaining drainage basin runoff, literature data were used (LAWA 1998).

2.3. Modelling approach

To calculate Haussee’s phosphorus (P) mass balance, a model proposed by Gächter & Imboden (1985) modified by Hupfer & Scharf (2002) was used (One-Box-Model). Symbols are specified and explained in Table 2. The TP equilibrium concentration at given external phosphorus loading was obtained by the equation:

$$TP_{stat} = \frac{TP_{in}}{\beta + \tau \times \sigma}$$

(1)

TP concentration at a specific year ($t$) before reaching equilibrium concentration was computed as:

$$TP(t) = (TP_0 - TP_{stat}) \times e^{-\left(\frac{\beta}{\tau + \sigma}\right) \times t} + TP_{stat}$$

(2)

The annual average of the stratification factor $\beta$ corresponds to:

$$\beta = \frac{TP_{out}}{TP_{lake}}$$

(3)
The annual net sedimentation rate $\sigma$ was calculated as:

$$\sigma = \frac{NS}{TP_{take}}$$  \hspace{1cm} (4)

For comparison the following empirical models were additionally used:

$$TP_{stat} = \frac{TP_{in}}{1 + \sqrt{t}}$$  \hspace{1cm} Vollenweider, 1976  \hspace{1cm} (5)

$$TP_{stat} = 1.55 \cdot \left( \frac{TP_{in}}{1 + \sqrt{t}} \right)^{0.82}$$  \hspace{1cm} OECD, 1982  \hspace{1cm} (6)

$$TP_{stat} = \frac{TP_{Lin}}{q_s} \cdot \left( 1 - \frac{15}{18 + q_s} \right)$$  \hspace{1cm} Nürnberg, 1984  \hspace{1cm} (7)

2.4. Statistics

Statistical tests (principal components, t-tests, correlation, and linear regression) comprise the results of before (2006 – 2010) and after (2011 – 2017) the Al treatment. To eliminate within-season temporal autocorrelation, individual measurements were aggregated to seasonal means (March – October; except for CaCO$_3$, where data were only available from May – September). Changing variability of response variables was assessed by seasonal standard deviations of all measurements within one season. Then both mean values and seasonal standard deviations before and after the treatment were compared. Because we were interested in both change of mean values and change of variation, t-tests for unequal variances (Welch 1938) were consistently used. However, because of their nature, lake restoration measures represent a complex unrepeated experiment. Therefore, single $p$-values need to be interpreted with care ‘to assess the reliability of descriptive statistics and as a way to better inform the reader’ (Davies & Gray 2015).

The reaction of a complex, dynamic system to a manipulative event is simultaneously distributed over a series of response variables, resulting in either alpha-error inflation and false positives (cf. Garcia 2004) or overly conservative testing (Moran 2003) if sequential Bonferroni corrections (Holm, 1979) are applied. Therefore, we used a principal components and redundancy analysis (PCA, RDA, cf. Legendre & Legendre 2012) first to check for the overall reaction of the system (as a multivariate ‘omnibus’ test, cf. Garcia 2004) before testing single response variables. Significance of the overall effect was assessed by a permutation test of the RDA results, with CaCO$_3$, oxygen saturation, pH, calcite saturation index, Secchi
depth, biomass of total phytoplankton and filamentous cyanobacteria as the response, and the
time period before and after the treatment as a single environmental variable (constraint). All
tests were performed using the R environment for statistical computing (R Core Team, 2016)
and the vegan package (Oksanen et al., 2016) for the multivariate analysis.

2.5. Precipitation chemical
To remove phosphorus from the water column, to minimize release from the sediment and to
bind the incoming quantity from the drainage basin and atmospheric deposition, PAC (PAX-18 ®; http://www.pwthielemann.de/download/sicherheitsdatenblatt.html) was used as precipitant spread
onto the surface of the lake from a floating platform. To ensure the application of aliquot
amounts both with respect to water depth and position, the platform was equipped with a GPS
system and an echo-sounder. PAX-18 is an extremely acidic chemical (pH 1) which may
significantly decrease the pH of the lake under treatment. Thus, during application, pH was
frequently measured at different locations and depth (n = 64). The average pH ranged around
7.8 ±0.3SD (min. 7.0, max. 8.3), which means that the interval of no risk for Al-toxicity (6<
pH < 9) was safely maintained (Cook et al., 2005). Also, Al may form toxic species in high
alkalinity lakes if the pH is high (Anderson 2004). However, data collected during the
treatment did not indicate any problem. Nevertheless, the separate basins of the lake were
processed sequentially to allow fish to escape the treated areas (Exley 2000).

The P inventory of the sediment and the water body revealed a stock of 2 g P_{mobile} m^{-2}, or 2
metric tons for the entire lake. Based on the estimated external loading rate, another 2 metric
tons is expected to enter the lake within the next decade. Incubation experiments of sediment
samples indicated that an Al/P ratio of at least 4.5 (12 g Al m^{-3}) was necessary to sustainably
bind P_{mobile} in the sediment. To inactivate the continuing P input from the catchment area, it
was concluded that the same quantity should additionally be deposited in the sediment. To
stay on the safe side, the dose was slightly increased to 27 g Al m^{-2}; which comes close to the
general suggestions of Vincente et al. (2008). The whole treatment lasted from April 11 - 21,
2011. The total amount of Al applied was 21 metric tons.

3. Results
Modelling: The long-term response of Haussee’s water quality traits after the 90 % load
reduction in 1980 is characterised by two opposing trends (Fig. 2). Although the TP
concentration of the mixed layer over time dropped by more than an order of magnitude, Chla
and water clarity did not respond accordingly. Given the present external TP loading of 199 kg yr\(^{-1}\) \((TP_{in} = 0.230 \text{ mg L}^{-1})\), the equilibrium concentration calculated based on equations 1, 5 – 7 would range between 0.043 – 0.059 mg L\(^{-1}\), which is clearly above the intended threshold concentration of 0.035 mg TP L\(^{-1}\). A detailed study applying a One-Box-Model (see Methods section) resulted in four separate scenarios (Fig. 3). For Scenario A, the stratification factor \(\beta\) (0.776), the residence time \(\tau\) (8.9 yrs.) and \(TP_{in}\) (0.230 mg L\(^{-1}\)) were held constant, while the net sedimentation coefficient \(\sigma\) was allowed to linearly increase from 0.173 – 0.510 \(\text{yr}^{-1}\) during 12 consecutive years (see discussion section for reasoning and Tab. 4 in supplementary material). If no additional treatment was implemented, it would take the TP concentration this many years to approach the calculated equilibrium level \(TP_{lake}\) of 0.043 mg TP L\(^{-1}\), which is again above the upper threshold concentration (0.035 mg L\(^{-1}\)) considered to apply to mesotrophic lakes. If only TP in the water column was to be precipitated (Scenario B), the concentration would immediately drop to approximately 0.025 mg L\(^{-1}\). However, because of continuing external loading \((TP_{in} = 0.230 \text{ mg L}^{-1})\) the values would return to the equilibrium level within 3 – 4 years. If a surplus of Al would be deposited in the sediment allowing an increase of \(\sigma\) to 0.95 \(\text{yr}^{-1}\) followed by a gradual drop to 0.510 \(\text{yr}^{-1}\) over the course of 25 years (Scenario C), the concentration should again drop rapidly to 0.025 mg L\(^{-1}\). Subsequently, however, it would remain below the threshold for mesotrophic lakes (0.035 mg TP L\(^{-1}\)) for at least 25 years. Finally (Scenario D), to reach an annual average TP concentration of 0.025 mg L\(^{-1}\) solely by decreasing external loading, \(TP_{in}\) would have to be decreased from 0.230 to 0.133 mg L\(^{-1}\) (43 %).

The P inventory indicated that there was 1.5 t of P\(_{mobile}\) (2 g m\(^{-2}\)) in the sediment \((Z \geq 2.0 \text{ m})\) and another 0.5 t in the water column. Moreover, based on the present external TP input of 199 kg yr\(^{-1}\), a further 2.0 t P is likely to be discharged into Haussee within the next decade. Therefore, to keep \(TP_{lake}\) significantly and sustainably below 0.035 mg TP L\(^{-1}\) (see Fig. 3, Scenario C) an aluminium dosage of 27 g Al m\(^{-2}\) (2.72 mg Al m\(^{-3}\)) was applied. This equals an atomic Al/P ratio of 12 if related to the P stock within the sediment and the water column. Including the external loading of 2 t would decrease the ratio to 6. Figure 4 shows the concentration of soluble Al during the years 2010 – 2012. Depending on sampling depth, the values increased to 0.142 – 0.228 mg L\(^{-1}\) for a short period after the treatment in April 2011, but dropped rapidly during the second half of the year. In 2012, the concentration resembled the pre-treatment level. However, the Al content of two different seston size fractions remained elevated until November 2011. Variable results were found for selected groups of
the zoobenthos. Shortly after the treatment, all taxa revealed an enhanced contamination followed by a decreasing trend, but remarkable differences were found between groups. While caddisflies and dragonflies had the highest content, the contamination of snails and mussels remained low.

**Sediment response:** In response to the treatment, over time there was a general tendency of the metal-oxide bound (i.e. Al-bound) phosphorus of the sediment to increase. While this fraction was only 0.3 g TP kg\(^{-1}\) DW (Fig. 5A) in March 2011, the maximum concentration had increased to 1.3 g TP kg\(^{-1}\) DW by April 2016. The peak that formed between 2011 and 2016 has since been buried by almost 4 cm of freshly deposited sediment. In 2017 no further increase of Al-bound P was detected. A clear change was also recorded in pore water SRP (Fig. 5B). Depending on sediment depth, the concentration in August 2010 varied between 1.0 – 2.9 mg P L\(^{-1}\) but was clearly lower in October 2016 (0.13 - 1.15 mg P L\(^{-1}\)). Compared to previous years, a slight increase of SRP concentration occurred in 2017 in the uppermost 3 - 4 cm, but SRP in the water immediately above the sediment surface was still very low (0.003 mg L\(^{-1}\)).

**PCA, RDA:** The Al application had a clear overall impact on almost all water quality parameters. A principal component analysis (PCA) using a set of relevant variables standardized prior to analysis showed a clear correlation structure with 82 % of the variance in the first two axes (Fig. 6, Tab. 3). While CaCO\(_3\), total phytoplankton, oxygen saturation and filamentous cyanobacteria (Hormogonales) were positively correlated with one another, Secchi transparency was negatively related to these variables. The years before and after Al treatment were clearly separated by large differences in phytoplankton biomass, oxygen saturation and CaCO\(_3\) (Fig. 6, shaded polygons). While phytoplankton biomass, oxygen saturation and CaCO\(_3\) were high before and low afterwards, the opposite was found for Secchi transparency. Redundancy analysis (RDA) of the same data set with pre- and post-Al treatment periods as explanation variable attributed 45 % of the total variance to the treatment period (permutation test, significant at p < 0.01); i.e. almost half of the standardized total variation of the annual average values of the considered variables can be ascribed to the treatment.

**Phosphorus, nitrogen:** During the five years before the aluminium treatment, TP concentration in the mixed layer ranged between 0.019 and 0.119 mg L\(^{-1}\) showing the typical
seasonal fluctuations (Fig. 7A) with their peaks and troughs mirrored by concentrations in the hypolimnion (Fig. 7B). This pattern clearly changed after the treatment in April 2011: the TP concentration in the mixed layer remained well below the restoration target of 0.035 mg TP L\(^{-1}\). Any noticeable seasonal rhythm had vanished. During thermal stratification, there was a minor P accumulation in the deep water, but it was irrelevant relative to the situation before 2011. Since May 2011, the volume-weighted, annual mean TP concentration of the lake never exceeded 0.025 mg L\(^{-1}\). The median SRP concentration both in the mixed layer and in the hypolimnion (7.5 m) was 0.001 mg L\(^{-1}\) (max. 0.013, min. 0.001 mg L\(^{-1}\)). In contrast, TN showed substantial fluctuations both before and after the treatment, but there was no trend in concentration (Fig. 7C). Nevertheless, as a result of the TP reduction, TN/TP ratios clearly increased. While the average ratio was 23.7 (10.1 SD) before the treatment, it rose to 58.2 (24.1 SD) afterwards (Fig. 7D).

**Activity parameters:** Although prior to Al treatment, primary production measurements were only available in 2010, a substantial reduction was obvious thereafter (Fig. 8A). While the average for 2010 (May – October) was 0.449 mg C L\(^{-1}\) day\(^{-1}\) (0.121 SD), the grand average for 2011 – 2017 was 0.141 mg C L\(^{-1}\) (0.052 SD). While planktonic bacterial protein production before the treatment amounted to 0.097 mg C L\(^{-1}\) day\(^{-1}\) (Fig. 8B), the grand mean afterwards was 0.065 mg C L\(^{-1}\) day\(^{-1}\). However, the variability of the results remained high even after the treatment (0.044/0.034 SD). Both the ratio of BPP/PP and the respective SDs had considerably increased from 21 (9.7 SD) % to 49 (33.9 SD) %, (Fig. 8C).

**Phytoplankton:** The 68 % reduction of primary production rate was reflected in the biomass of total phytoplankton and filamentous cyanobacteria (Fig. 9A/B, seasonal means March - October). While the grand mean of phytoplankton biomass during the period 2006 - 2010 was 0.80 mg C L\(^{-1}\), it significantly dropped to 0.30 mg C L\(^{-1}\) following the treatment (Welch-test, t = 3.3, p = 0.023, df = 5.0). Likewise, SD of the readings significantly decreased from 0.47 to 0.15 (Welch test of seasonal standard deviations, t = 4.8, p = 0.006, df = 4.8), indicating that the variance dropped because phytoplankton maxima were significantly reduced after the treatment. Also, the grand mean of seasonal (April – October) Chla concentration dropped from 0.018 (0.012 SD) mg L\(^{-1}\) prior to the treatment to 0.011 (0.006 SD) mg L\(^{-1}\) afterwards (data not plotted). However, the results regarding the filamentous cyanobacteria were less clear. Although there was an obvious trend towards lower standing stocks (0.44/0.11 mg C L\(^{-1}\)), the average biomass recorded after the aluminium treatment did not significantly decrease...
(t = 2.0, p = 0.11, df = 4.6). The same applies to the proportion of cyanobacteria within total phytoplankton (42/28 %, t = 1.1, p = 0.31, df = 9.6, data not plotted). In contrast, the average seasonal SD dropped significantly from 0.40 to 0.07 (t = 3.6, p = 0.018, df = 4.5) pointing to much lower peak values. The community composition of cyanobacteria, however, did not change substantially (Fig. 9C). In 11 out of 12 years, *Pseudanabaena limnetica* dominated (≥ 45 % of total cyanobacterial biomass), accompanied by *Aphanizomenon* sp. (9 – 45 %). Finally, during early spring of 2015, the filamentous cyanobacteria nearly disappeared from the plankton and never recovered.

**pH, O₂, carbon buffering system, water clarity:** The average pH remained almost constant (8.57/8.43, Fig. 10A) regardless of the treatment, but the SD decreased significantly (0.43/0.27, t = 3.2, p = 0.018, df = 5.8), pointing to a lower photosynthetic activity by the phytoplankton after the treatment. Also, the average oxygen saturation of the mixed layer did not change significantly (105/105 %, Fig. 10B), but the SD decreased significantly (28/16, t = 4.5, p = 0.005, df = 5.5), *i.e.* the oxygen oversaturation as a consequence of algal photosynthesis was less.

The average calcite saturation index showed a significant decline (Fig. 11A, 7.69/5.30, t = 3.6, p = 0.005, df = 9.9) and the same applied to the difference in SD (5.64/2.94, t = 3.29, p = 0.018, df = 5.8). However, the average calcite concentration did not reveal a significant reduction, although the difference between the pre- and post-treatment period was obvious (Fig. 11B). The SD, however, dropped (1.16/0.64, Welch test of standard deviation, t = 3.3, p = 0.009, df = 8.8); *i.e.* the concentration maxima substantially decreased. Very little calcite was detected in 2015/17 (0.14/0.48 mg L⁻¹), but in 2016 the concentration was slightly higher again (0.81 mg L⁻¹). Secchi transparency slightly increased from 1.4 m to 2.0 m but the difference was not significant (Fig. 11C). The same was true for the SD (0.66/0.60). However, from 2015 - 2017 the average seasonal (March – October) water clarity increased to 2.1 – 2.9 m. The maximum values recorded were 4.2/3.7/4.5 m.

**Planktonic crustaceans:** The biomass of two dominant groups of planktonic crustaceans and total biomass are depicted in Fig. 12. The response of *Daphnia* sp. was ambiguous. For 2 – 3 years both before and after the Al treatment, their biomass was low but eventually increased between 2013 and 2017. Nevertheless, neither average nor SD was significantly different. A significant difference was found concerning the group of cyclopoid copepods (*Mesocyclops*,...
Thermocyclops, Cyclops, 0.079/0.045 mg C L\(^{-1}\), \(p = 0.05, \text{df} = 5.64\). However, the SD was not significantly smaller. Whereas total crustacean biomass did not change significantly, the SD did (0.13/0.05, \(p = 0.03, \text{df} = 4.44\)). Small cladocerans as a group (*Bosmina, Ceriodaphnia, Diaphanosoma*) revealed a significant decrease both regarding average annual biomass (0.019/0.010 mg C L\(^{-1}\), \(p = 0.011, \text{df} = 9.9\)) and SD (0.029/0.012, \(p = 0.019, \text{df} = 5.3\); data not plotted).

Water clarity, CaCO\(_3\) phytoplankton biomass: Finally, a multiple linear regression showed that both phytoplankton and CaCO\(_3\) had a diminishing impact on Secchi transparency (Fig. 13) and explained 60 % of its variance (\(r^2 = 0.604, p < 0.001, \text{df} = 2/15\)). However, the slopes of the standardized predictor variables indicated a 1.7-fold higher influence of CaCO\(_3\) on Secchi transparency as compared to phytoplankton (slope = -0.31/-0.18). The interaction term between CaCO\(_3\) and phytoplankton was not significant (\(p = 0.72\)) and can thus be neglected.

4. Discussion

General trends: The collective information obtained from our study documents that except for water clarity all anticipated restoration goals were achieved within a reasonable period. Although delayed by 4 years, even transparency clearly increased eventually. Thus, as intended, Haussee’s overall water quality substantially improved and is now in a range typical for mesotrophic lakes (LAWA 2014). During the seven years subsequent to the Al treatment, the volume-weighted, mean annual TP concentration (< 0.025 mg L\(^{-1}\)) remained well below the restoration target (0.034 mg L\(^{-1}\)). This is of paramount importance for the sustainability of the management measure. Although the dose of 27 g Al m\(^{-2}\) was relatively low (Cooke et al., 2005), the drastically reduced TP values indicate that the calculated amount of aluminium necessary to inactivate the phosphorus released from the sediment and introduced through external loading was sufficient. All water quality parameters indicated a clearly reduced metabolic activity of the whole planktonic community. Nevertheless, the future persistence of improvement primarily depends on how reliably the Al dosage was calculated and, consequently, how the sediment P-binding capacity develops in the long term. This applies especially to a robust assessment of potentially mobile P in the upper sediment layer and to the parameters implemented in the one-box model (\(TP_{in}, \beta, \tau, \sigma\)), because in part the Al dose was calculated based on these results.
Phosphorus budget, sediment, modelling: The P content of sediments is a site-specific attribute particularly impacted by the trophic status of a given lake (Gonsiorczyk et al., 1998) modified both by horizontal patches and vertical gradients (Grüneberg et al., 2015). Moreover, depending on the P-binding forms, the mobile fraction ($P_{\text{mobile}}$) of the sediment TP may considerably fluctuate (Hupfer et al., 1995). Also, Wauer (2006) and Hupfer et al., (2016) pointed out that the fractionation method may substantially overestimate the pool of potentially mobile P. Nevertheless, an independent test applying the gradient method (Hupfer & Scharf 2002) resulted in a similar content of approximately 2 g $P_{\text{mobile}}$ m$^{-2}$, (Gonsiorczyk, unpublished data) confirming a reliable quantification.

Given the present external P-loading rate of approximately 199 kg yr$^{-1}$ (151 mg P m$^{-2}$ yr$^{-1}$), the calculated equilibrium TP concentration of Haussee would range between 0.043 and 0.059 mg L$^{-1}$, depending on the model used (Vollenweider, 1976, OECD 1982, Nürnberg 1984, Schauer et al. 2003, see Methods section, equations 1, 6 – 8). According to the LAWA (2014) scheme of classification, the lake would thus retain a slightly eutrophic status. However, Gächter & Imboden (1985, see methods section, equation 1) indicated that in response to reduced external loading, the equilibrium concentration $TP_{\text{stat}}$ depends on $TP_{\text{in}}$, the stratification factor $\beta$, the water residence time $\tau$ and the net-sedimentation coefficient $\sigma$. While $\tau$ of seepage lakes is likely to be more or less constant, $\beta$ may increase or decrease depending on whether the concentration differences between the mixed layer and the deep water shrink or increase (Hupfer & Scharf 2002). Since the sediments of the majority of lakes act as P-sinks rather than P-sources over prolonged periods (Sas 1989), $\sigma$ is likely to increase up to a threshold which corresponds to the actual external loading and the chemical constitution of the sediment (Gonsiorczyk et al., 1998, Grüneberg et al., 2011).

Concerning the Haussee, $\beta$ both before and after the Al treatment fluctuated around 0.753 (0.123 SD) without any noticeable trend. In contrast, $\sigma$ calculated based on annual average TP concentrations and net sedimentation linearly increased from 0.166 yr$^{-1}$ in 2007 to 0.256 yr$^{-1}$ in 2010 ($r^2 = 0.95$). This indicates that the ‘natural’ (without any treatment) P-binding capacity of the sediment was still growing and the lake had not yet reached steady-state conditions. Given the present external nutrient loading ($TP_{\text{in}} = 230 \mu g L^{-1}$), the calculated maximum $\sigma$ at a steady-state concentration of 0.043 $\mu g$ TP L$^{-1}$ would be 0.51 yr$^{-1}$ (Tab. 4, supplementary material). Brett & Benjamin (2008, p. 202, Tab. 4, hypothesis 4) concluded that for a specific $TP_{\text{in}}$ the magnitude of $\sigma$ is an inverse function of $\tau$. Applied to the residence
(8.9 yrs.), $\sigma$ would approach 0.35 yr$^{-1}$. The difference between these two values demonstrates that $\sigma$ is hard to estimate and subject to a remarkable level of uncertainty. If, however, the value of 0.51 yr$^{-1}$ is assumed to be realistic for $\sigma$, then the extra binding capacity provided by the PAC overdose could raise $\sigma$ to 0.95 yr$^{-1}$ (as supported by the constantly low TP concentrations shown in Fig. 7A/B). The initial extra capacity in $\sigma$ of 0.44 yr$^{-1}$, decreasing over time, would inactivate a total of ca. 2 t of P, either coming from the drainage basin or ascending from deeper sediment layers (Fig. 3, Scenario C; Tab. 4, supplementary material). The extra binding capacity is likely to be exhausted 30 years after the treatment. Whether this elevated binding capacity will truly remain for this many years is unclear because several factors are hard to control (Hupfer & Scharf 2002). Some of the most important are: ‘aging’ of the aluminium flock by binding organic substances or silicate (Vincente et al., 2008), burial of the active Al-layer by new sediment (Lewandowski et al., 2003), and the intensity of diagenetic processes within the uppermost sediment layers (Huser et al., 2011). Regardless of these possible impairments the continuously low TP concentration during the past seven years and the other improved water quality parameters indicate a sufficient and sustained effect of our measure up to the present, verifying the amount of PAC used for the treatment.

Phytoplankton biomass, community structure: Filamentous cyanobacteria have dominated Haussee's phytoplankton since 1985 (Krienitz et al., 1996, IGB unpublished data). Although the biomass of filamentous cyanobacteria clearly decreased after Al-treatment, their continuing overall high proportion within total phytoplankton from 2011 - 2014 (18 – 61 %) was unexpected. However, during spring 2015 they suddenly vanished almost completely from the plankton, and in 2016/17 their biomass approached zero. Cyanobacteria are known to be highly resource-efficient. This is true for their light-harvesting properties (Mc Causland et al., 2002), P acquisition (Barbiero & Kann 1994) and the uptake of dissolved inorganic carbon (Merz 1992). Although the impact of the N/P ratio on their growth is still a matter of debate (Dolman & Wiedner 2015), there is ample evidence for the P concentration to be of prime importance. Lathrop et al., (1998) showed that the likelihood of severe cyanobacterial blooms diminishes when the external P loading is adequately reduced. Also, empirical studies suggest that cyanobacterial dominance is less likely when the summer epilimnetic TP concentration is below 0.035 – 0.055 mg L$^{-1}$ (Dolman et al., 2012).
After May 2011, the annual average volume-weighted TP concentration was < 0.025 mg L\(^{-1}\). Except for rare instances in early spring and autumn, the SRP supply was almost always exhausted. Thus, as suggested by the drastic decline of planktonic primary production, P shortage was very likely the reason for impaired growth of both phytoplankton as a whole but also cyanobacteria in particular. Ptačník et al., (2008) concluded that with growing diversity, any phytoplankton community is increasingly capable of effectively utilising the whole spectrum of available resources, which in turn means that the dominance of a single species or group of species by monopolarising resources is unlikely. From May to September 2015 the phytoplankton of Haussee was characterised by a diverse community of cryptophytes (25.7 \%), chrysophytes (21.4 \%) and dinophytes (21.2 \%). A similar situation was encountered in 2016/17 but with a higher proportion of chlorophytes (27 \%). The drastic increase of TN/TP from 23.7 (10.1 SD) to 58.2 (24.1 SD) in response to Al-treatment may have assisted the complete alteration of the phytoplankton community structure (Teubner et al., 1999).

As a result of their elongated cell shape and accessory pigments, filamentous cyanobacteria are known to be superior competitors for light (Mc Causland et al. 2001). Though differences exist between species, this physiological peculiarity is shared by many species’ (Mischke & Nixdorf 2003). Conversely, Scheffer et al., (1997) showed that, relative to eukaryotic taxa, cyanobacteria suffer a competitive disadvantage if more light penetrates deeper into the water column. Haussee’s euphotic depth increased from 4.0 m in 2011 – 2014 (May – September) to 6.3 m in 2015 – 2017, which might also have contributed to terminating the prevalence of filamentous cyanobacteria.

**Carbon buffering system, calcite:** Following Al treatment, the grand averages (2006 – 2010/2011 – 2017) of pelagic calcite concentration did not change significantly; although in 2015/17 little calcite was detected. Calcite precipitation is both a long-known and common phenomenon of hard-water lakes (Koschel et al., 1983). Despite being a complex biogeochemical process (Kelts & Hsü 1978), the major prerequisites are a sufficiently high calcium-carbonate alkalinity, elevated pH and a low concentration of free CO\(_2\)\(^*\) (dissolved CO\(_2\) plus dissociated H\(_2\)CO\(_3\)). Koschel et al., (1997) hypothesized that the proportion of CO\(_2\) uptake by photosynthesis and CO\(_2\) release by respiration are of central relevance for the position of the carbonate buffering system of lakes and thus for calcite precipitation. Furthermore, Maberly (1996) demonstrated that during thermal stratification neither the
replenishment from the atmosphere nor the supply from hypolimnetic resources is of
considerable importance for the CO$_2$ balance of the mixed layer.

Although photosynthesis by any phytoplankton community has the potential to decrease CO$_2$
concentration and thus to increase pH, Koschel et al., (1987) observed that intense calcite
precipitation is frequently associated with a high abundance of cyanobacteria. It seems that at
least some taxa may have the rare physiological ability to not only exhaust the CO$_2$ supply
(Shapiro 1997), but also to take-up and decompose bicarbonate and subsequently release OH$^-$
ions (Merz 1992). As a consequence, the pH in a narrow layer near the cell wall can be higher
than in the ambient water, favouring calcite precipitation by increasing the carbonate super-
saturation (Dittrich et al., 2003). Moreover, because calcite precipitation in lakes is always
heterogeneously nucleated, it takes a surface to induce crystal growth (Küchler-Krischun &
Kleiner 1990). It has been shown that, at high cell densities, the cell surface of cyanobacteria,
and especially picocyanobacteria, provides an ideal matrix to initiate micro-crystals which
then detach and continue to grow (Dittrich & Obst 2004).

From 2006 to 2017 Haussee’s average mixed layer pH of 8.5 (0.35 SD) was always in the
alkaline range with little variability (CV 4.1 %). In comparison, the CO$_2^*$ concentration of
1.67 (1.96 SD) mg L$^{-1}$ remained low on average but was considerably variable (CV 117 %).
Proft & Stutter (1993) demonstrated that beyond a threshold pH of approximately 7.5, the
calcite saturation index (SI) progressively increases. Koschel et al., (1997) indicated that for
intensive calcite precipitation the CO$_2^*$ concentration should be < 1 mg L$^{-1}$. Looking at the
respective data from 2006 to 2017, it turns out that at pH < 8.25, very little calcite (< 0.2 mg
CaCO$_3$ L$^{-1}$) was precipitated. When the pH increased beyond this threshold, results varied
between 0 and 4.1 mg CaCO$_3$ L$^{-1}$. The opposite applies to CO$_2^*$ concentration, with 1.25 mg
L$^{-1}$ being the upper threshold for high but variable calcite concentrations (data not plotted).
We, therefore, speculate that minor differences both in pH and CO$_2^*$, as impacted by the
delicate balance between planktonic photosynthesis and respiration governed by the structure
of the planktonic community might be the ultimate reason for whether or not calcite is
precipitated.

By 2015, filamentous, non-edible cyanobacteria had almost completely been replaced by
readily-edible phytoplankton species. The CO$_2^*$ concentration of 1.70 (1.36 SD) mg L$^{-1}$ was
relatively high and in June the abundance of *Daphnia* sp. increased to 153 individual L$^{-1}$,
resulting in low phytoplankton biomass and a maximum water clarity of 4.20 m. Thus, relative to previous years the planktonic community during summer 2015 was more ‘heterotrophic’; i.e. the CO\(_2\) balance might have been inclined in favour of production rather than uptake, which may have halted the precipitation of calcite.

In summary, we conclude that the anticipated goals of our restoration measure have been accomplished. Since the present external P-loading rate is apparently tolerable relative to the binding capacity of the sediment, there is reason to believe that the improved water quality will be sustained for the foreseeable future. A number of published examples indicate that if properly conducted, Al-treatments can remain effective for \(\geq 10 – 15\) years (e.g Cooke et al., 2005, Huser et al., 2011, Gonsiorczyk et al., 2015). Nevertheless, our study also shows that even if a project is well designed and implemented, unexpected effects can be encountered and patience is required. Haussee has been heavily polluted for at least two decades (Koschel & et al., 1985). In retrospect, it is no surprise that the adaptation time of various water quality parameters differed by several years. Gächter & Imboden (1985) and Carpenter (1999) concluded that lakes follow a different trajectory depending on whether loading is increasing or decreasing. In some cases, it might be necessary to drastically reduce both the external P-loading and sediment release well below a lake-specific threshold in order to reach the restoration goal (hysteresis behaviour). Lake Feldberger Haussee and the related project of remediation and restoration represent a nice example for that conclusion.

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The authors are very grateful to a number of scientists, technicians, committed amateur researchers and colleagues from the water authorities. Although it officially was never dubbed this way, without their joint action over 35 years the comprehensive project ‘Remediation and Restoration of the Upper Feldberg Lakes’ would have never become reality. However, the list would be too long to name all of them individually. Some of them are no longer alive. Nevertheless, our special gratitude goes to our co-operation partner, the Ministry of Agriculture and Environment of the Bundesland Mecklenburg-Vorpommern, for continuing interest in our work and for significant financial support. We are especially grateful to Dr. Jürgen Mathes and Ilona Korczynski. For 25 years they kindly supported our attempts to significantly and sustainably improve the water quality of the Upper Feldberg Lakes. Without their help, we would never have succeeded. Thanks also to Julianne Rolf, Eugene Welch and Tom Shatwell for significantly improving language and style of the paper.
References


Table 1: Topographical, morphological, hydrological and chemical characteristics of Feldberger Haussee (Koschel et al. 1981, Koschel et al. 1985, IGB unpublished data).

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<tr>
<th>Criterion</th>
<th>Measured/calculated parameter</th>
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<tr>
<td>Drainage basin (ha)</td>
<td>712</td>
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<tr>
<td>Lake surface (ha)</td>
<td>132</td>
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<tr>
<td>Mean depth (m)</td>
<td>5.8</td>
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<tr>
<td>Maximum depth</td>
<td>12.5</td>
</tr>
<tr>
<td>Volume (m$^3$ 10$^6$)</td>
<td>7,695</td>
</tr>
<tr>
<td>Discharge (m$^3$ 10$^6$ yr$^{-1}$)</td>
<td>0.861</td>
</tr>
<tr>
<td>1) Water residence time (yrs.)</td>
<td>8.9 (±3.0 SD)</td>
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<tr>
<td>Thermal stratification</td>
<td>May – September</td>
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<tr>
<td>External nutrient loading (mg P m$^{-2}$ yr$^{-1}$)</td>
<td>151</td>
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<tr>
<td>Storm water sewer (mg P m$^{-2}$ yr$^{-1}$)</td>
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<td>Ground water (mg P m$^{-2}$ yr$^{-1}$)</td>
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<td>Atmospheric deposition (mg P m$^{-2}$ yr$^{-1}$)</td>
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<tr>
<td>Drainage basin run-off (mg P m$^{-2}$ yr$^{-1}$)</td>
<td>28</td>
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<tr>
<td>2) Annual average TP concentr. (mg P L$^{-1}$)</td>
<td>0.087 ±0.011 SD</td>
</tr>
<tr>
<td>3) Annual average TN concentr. (mg N L$^{-1}$)</td>
<td>1.183 ±0.321 SD</td>
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</table>

1) phosphorus-relevant residence time (see methods section)
2) calculated for the years 2006 – 2010, volume-weighted, seasonal-integrated means
3) arithmetic average of the years 2006 – 2010
<table>
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<th>Abbreviation</th>
<th>Unit</th>
<th>Explanation</th>
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<td>$TP_{stat}$</td>
<td>(mg L$^{-1}$)</td>
<td>equilibrium TP concentration as related to external nutrient loading (restoration target)</td>
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<td>$TP_0$</td>
<td>(mg L$^{-1}$)</td>
<td>in-lake TP concentration prior to treatment</td>
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<td>$TP_{lake}$</td>
<td>(mg L$^{-1}$, kg)</td>
<td>in-lake TP concentration, or average annual TP content</td>
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<tr>
<td>$TP_{out}$</td>
<td>(kg yr$^{-1}$)</td>
<td>annual TP export</td>
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<tr>
<td>$TP(t)$</td>
<td>(mg L$^{-1}$)</td>
<td>mean annual in-lake TP concentration at year ($t$) subsequent to treatment</td>
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<tr>
<td>$TP_{in}$</td>
<td>(mg L$^{-1}$)</td>
<td>TP inflow concentration, sum of annual external TP input divided by hydraulic loading (see Tab. 1)</td>
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<td>$TP_{Lin}$</td>
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<td>areal external TP loading</td>
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<td>$q_s$</td>
<td>(m yr$^{-1}$)</td>
<td>areal hydraulic loading</td>
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<td>$\sigma$</td>
<td>(yr$^{-1}$)</td>
<td>TP net-sedimentation coefficient</td>
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<tr>
<td>$\beta$</td>
<td>-</td>
<td>TP stratification factor</td>
</tr>
<tr>
<td>$\tau$</td>
<td>(yrs)</td>
<td>water residence time$^1$</td>
</tr>
<tr>
<td>$V$</td>
<td>($m^3$ $10^6$)</td>
<td>lake volume</td>
</tr>
<tr>
<td>$NS$</td>
<td>(kg yr$^{-1}$)</td>
<td>TP net sedimentation (annual difference of external input and output by discharge)</td>
</tr>
</tbody>
</table>

$^1$ phosphorus-relevant residence time (see methods section)
Table 3: Principal component analysis (PCA) and redundancy analysis (RDA) with grouping before/after 2006 as a single constraint, and corresponding permutation test (3999 replicates) of the data collected from 2006 – 2016. Higher principal components (5 to 9) explained less than 6% to the overall variance and were omitted.

<table>
<thead>
<tr>
<th>PCA</th>
<th>PC1</th>
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<th>PC3</th>
<th>PC4</th>
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<tr>
<td>Criterion</td>
<td>Eigenvalue</td>
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<td>Cumulative proportion</td>
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<td>0.551</td>
<td>0.551</td>
<td>0.551</td>
</tr>
<tr>
<td></td>
<td>2.646</td>
<td>0.2658</td>
<td>0.816</td>
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</tr>
<tr>
<td></td>
<td>0.727</td>
<td>0.073</td>
<td>0.889</td>
<td>0.932</td>
</tr>
<tr>
<td></td>
<td>0.435</td>
<td>0.043</td>
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</table>

<table>
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<tr>
<th>RDA</th>
<th>Variance</th>
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<th>Rank</th>
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<td>1.0000</td>
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<tr>
<td></td>
<td>Constrained (grouping before/after 2011)</td>
<td>4.5276</td>
<td>0.4518</td>
</tr>
<tr>
<td></td>
<td>Unconstrained</td>
<td>5.4824</td>
<td>0.5482</td>
</tr>
<tr>
<td></td>
<td>Permutation test (3999 permutations)</td>
<td>F=8.24</td>
<td>P=0.002</td>
</tr>
</tbody>
</table>
Table 4 (supplementary material): Time series of in-lake TP concentration (TP\textsubscript{lake}) and TP retention of the sediment (TP\textsubscript{retention}) as impacted by the net sedimentation coefficient (σ) implemented for Scenario C (Fig. 3). σ\textsubscript{natural} 2004 – 2010, linear increase as regressed upon field observations from 2006 - 2010; 2011 - 2016 – predicted based on this regression. The threshold value of 0.510 was calculated using equation (1) in the methods section resolved for σ and is considered the ‘natural maximum’ that could be reached without any treatment (see below). σ\textsubscript{treatment} 2006 -2010, as with σ\textsubscript{natural}, 2011 – 2015, a hypothetical increase to 0.950 as a result of PAC application, 2016 – 2039, linear decrease towards the ‘natural maximum’ as a consequence of continuing external P input and a gradual loss of binding capacity of the applied PAC.

<table>
<thead>
<tr>
<th>Year</th>
<th>σ\textsubscript{natural}</th>
<th>σ\textsubscript{treatment}</th>
<th>σ\textsubscript{difference}</th>
<th>TP\textsubscript{lake} (mg L\textsuperscript{-1})</th>
<th>TP\textsubscript{retention} (kg yr\textsuperscript{-1})</th>
<th>TP\textsubscript{retention} (kg accumulated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2004</td>
<td>0.173</td>
<td>0.173</td>
<td>0.000</td>
<td>97.7</td>
<td>389.8</td>
<td>389.8</td>
</tr>
<tr>
<td>2005</td>
<td>0.202</td>
<td>0.202</td>
<td>-0.308</td>
<td>95.6</td>
<td>372.2</td>
<td>334.5</td>
</tr>
<tr>
<td>2006</td>
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<td>0.230</td>
<td>-0.280</td>
<td>91.8</td>
<td>354.6</td>
<td>306.1</td>
</tr>
<tr>
<td>2007</td>
<td>0.258</td>
<td>0.258</td>
<td>-0.252</td>
<td>86.8</td>
<td>336.9</td>
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</tr>
<tr>
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<td>0.287</td>
<td>-0.224</td>
<td>81.3</td>
<td>319.2</td>
<td>251.4</td>
</tr>
<tr>
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<td>0.315</td>
<td>-0.195</td>
<td>75.7</td>
<td>291.4</td>
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</tr>
<tr>
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<td>0.343</td>
<td>-0.167</td>
<td>70.1</td>
<td>263.5</td>
<td>156.6</td>
</tr>
<tr>
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<td>0.579</td>
<td>64.9</td>
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<tr>
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</tr>
<tr>
<td>2016</td>
<td>0.510</td>
<td>0.950</td>
<td>0.435</td>
<td>40.1</td>
<td>96.1</td>
<td>-3.3</td>
</tr>
<tr>
<td>2017</td>
<td>0.510</td>
<td>0.950</td>
<td>0.435</td>
<td>40.1</td>
<td>96.1</td>
<td>-3.3</td>
</tr>
<tr>
<td>2018</td>
<td>0.510</td>
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<td>0.435</td>
<td>40.1</td>
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<td>2019</td>
<td>0.510</td>
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<td>96.1</td>
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<td>2024</td>
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<td>96.1</td>
<td>-3.3</td>
</tr>
</tbody>
</table>

\[
\sigma = \left( \frac{\text{TP}_{\text{in}}}{\text{TP}_{\text{stat}}} - \beta \right) \frac{1}{\tau} = \left( \frac{230}{43} - 0.779 \right) \frac{1}{8.9} = 0.51 a^{-1}; \text{TP}_{\text{in}}, \text{TP}_{\text{stat}}, \sigma, \beta, \tau \text{ as outlined in the results section and Table 2.}
\]
Fig. 1: Feldberger Haussee, location and bathymetric map (courtesy of Mecklenburg-Vorpommern Ministry of Agriculture and Environment, Schwerin, Germany). White marks indicate the places where sediment cores (x) and water samples (●) were taken.
Fig. 2: Boxplots indicating the eutrophication history of Feldberger Haussee as exemplified by TP, Chla (mixed layer) and water clarity (Secchi transparency); results comprise the period from March – October; □ average, ● minimum/maximum, — median, box 25/75 % quartile, whisker 1/99 % percentile.
Fig. 3: Analysis of the phosphorus budget applying a One-Box-Model (Gächter & Imboden 1985, see methods section, Table 2). The situation in 2006 is considered the starting point; $TP_\in - 0.230\, \text{mg L}^{-1}$, $\tau - 8.9$ yrs., $\beta - 0.776$; Scenario A – no treatment, $\sigma$ linearly increasing from 0.173 to 0.510 yr$^{-1}$ within 12 years (see Tab. 3, supplementary material), Scenario B – phosphorus precipitation from the water only, $\sigma$ linearly increasing from 0.173 to 0.510 yr$^{-1}$ within 12 years, Scenario C – phosphorus precipitation from the water with additional sediment P inactivation, $\sigma$ linearly increasing from 0.173 - 0.510 yr$^{-1}$ within 7 years and a step-like increase to 0.95 yr$^{-1}$ during year 8 as a result of precipitation agent overdosing. During the subsequent 25 years, $\sigma$ is allowed to slowly drop to 0.510 yr$^{-1}$. Scenario D – to sustain an annual average TP concentration of 0.025 mg L$^{-1}$ solely by decreasing the external loading with a linear increase of $\sigma$ from 0.173 to 0.510 yr$^{-1}$ within 12 years, $TP_\in$ would need to remain below 0.133 mg L$^{-1}$, which corresponds to a 58 % reduction of the present input. Reasons for the selection of various $\sigma$ are detailed in the discussion section. For comparison, the annual average volume-weighted $TP_{\text{lake}}$ concentrations are presented.
Fig. 4: Concentration and content of aluminium before during and after the treatment; dissolved Al (top), seston size fractions (central) and selected groups of zoobenthos (bottom); whiskers indicate standard deviation.
Fig. 5: Sediment content of metal oxide bound phosphorus and SRP concentration in pore water before and after the Al-treatment.
Fig. 6: Principal Component Analysis (PCA) of standardized data to test for the overall system response comprising the seasonal (March – October) average values (points) of selected response variables (arrows). The years before and after the treatment form clearly separated clusters (shaded areas, permutation test for RDA, \( p = 0.0025 \)).
Fig. 7: Time series of TP concentration in the mixed layer (A) and in 7.5 m (B); TN concentration in the mixed layer (C) and TN/TP proportion (D). The horizontal line in panel A depicts the upper threshold of TP mixed layer concentration (0.035 mg L\(^{-1}\)) for mesotrophic lakes (LAWA 2014). The black mark indicates the time of the Al-treatment.
Fig. 8: Boxplots of planktonic primary production (A), bacterial protein production (B) and the ratio of BPP/PP (C). Both PP and BPP were measured from May – October (n = 6). No estimates are available before 2010; □ average, ● minimum/maximum, — median, box 25/75 % quartile, whiskers 1/99 % percentile.
Fig. 9: Boxplots of biomass (March – October, \( n = 7 – 13 \)) of total phytoplankton (A), filamentous cyanobacteria (B) and the structure of the cyanobacterial community (C) in the mixed layer. The genus *Dolichospermum* was formerly known as *Anabaena*. The empty space in 2016 means no filamentous cyanobacteria were detected; □ average, ● minimum/maximum, — median, box 25/75 % quartile, whiskers 1/99 % percentile.
Fig. 10: Boxplots of pH and oxygen saturation of the mixed layer (March – October, n = 7 – 18); □ average, ● minimum/maximum, – median, box 25/75 % quartile, whiskers 1/99 % percentile.
Fig. 11: Boxplots of calcium saturation index (A; March - October, mixed layer, n = 7 - 15), CaCO$_3$ concentration (B; only available from May - September, mixed layer, n = 10 - 15) and water clarity (C; Secchi transparency, March – October, n = 9 - 17); □ average, ● minimum/maximum, ─ median, box 25/75 % quartile, whisker 1/99 % percentile.
Fig. 12: Boxplots of the biomass (May – October) of *Daphnia* sp., cyclopoid copepods and total crustacean plankton sampled from 0 – 6.5 m (average depth of Feldberger Haussee, n = 7 – 11); □ average, ● minimum/maximum, — median, box 25/75 % quartile, whiskers 1/99 % percentile.
Fig. 13: Multiple linear regression with annual means of the vegetation period (May – September) of Secchi transparency (SD) as a function of calcite concentration (CaCO$_3$) and phytoplankton biomass (PB). Regression equation with standardized explanation variables: 

$$SD = 2.87 - 0.88 \text{CaCO}_3 - 0.58 \text{Phytoplankton}; r^2 = 0.60 (F = 11.47 \text{ with } 2 \text{ and } 15 \text{ d.f.}, p < 0.001).$$
Fig.: 14 (supplemental material): Scatter plot (2006 – 2017) of water temperature, oxygen saturation and pH within the mixed layer and in the hypolimnion.