

Restoration of a eutrophic hard-water lake by applying an optimised dosage of polyaluminium chloride (PAC)

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1	Restoration of a eutrophic hard-water lake by applying an optimised dosage of poly-
2	aluminium chloride (PAC)
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15	Key words: lake restoration; implementation plan; PAC dosage estimation; planktonic
16	community structure; calcite precipitation; time-delayed response
17	
18	Abstract
19	Feldberger Haussee (NE Germany) was polluted for almost a century. During the late 1970s,
20	the nutrient input reached a maximum of approximately 1.9/11.5 g TP/TN m ⁻² yr ⁻¹ . As a
21	result, the lake became a hypertrophic ecosystem and had largely lost its recreational value. In
22	1980, the sewage discharge was stopped, decreasing the external loading by approximately
23	90%. Because of vast amounts of phosphorus stored in the sediment, the lake remained highly
24	eutrophic until 1985 with a TP concentration of ca. 1 mg L ⁻¹ . To accelerate recovery,
25	biomanipulation was applied from $1985 - 2002$ but was successful to only a minor extent.
26	Eventually, due to sediment sequestration and discharge to downstream lakes the TP spring
27	maximum (2006 – 2010) dropped to 0.112 - 0.078 mg L^{-1} . However, given the trend, it was
28	obvious that it would take another $10 - 15$ years for the concentration to approach the desired
29	mesotrophic level. Thus, it was suggested to inactivate the surplus phosphorus by treating the
30	lake with poly-aluminium chloride (PAC) as precipitant. To ensure good water quality, the
31	objective was to decrease concentrations below 0.035 mg TP L ⁻¹ , while optimising the amount
32	of PAC applied (as much as needed, but as little as possible). As a prerequisite, the status of
33	the lake was carefully studied; external phosphorus loading and the amount of mobile
34	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). 35 Following the treatment in April 2011, prime water quality parameters showed two opposing 36 trends: (1) TP concentration immediately dropped below the restoration target ($\leq 0.025/0.035$ 37 mg L^{-1}), primary production and phytoplankton biomass declined substantially. (2) However, 38 water clarity did not improve for another four years. The likely reason for the delay was the 39 structure of the phytoplankton community. It was dominated by cyanobacteria with the 40 potential to trigger intensive calcite precipitation and thus impair transparency. In spring 41 2016, the cyanobacteria suddenly disappeared and transparency increased significantly. We 42 speculate that these changes of the planktonic community shifted the ratio of assimilation and 43 respiration in favour of the latter. This allowed an increase of free CO_2^* (dissolved CO_2 & 44 dissociated carbonic acid) altering the carbonate buffering system and thus halting the 45 formation of calcite crystals. Also, the phytoplankton, now represented by small readily 46 47 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 48 49 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 50 51 Haussee significantly. The lake is now in a mesotrophic status; well in accordance with the aim of the restoration project. 52

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1. Introduction

Although the basic principles of lake remediation and restoration are essentially clear (e.g. Sas 55 et al., 1989, Cooke et al., 2005, Lürling et al., 2016), the results of the applied measures can 56 be disappointing. Reasons for failure are typically a lack of site-specific information and 57 understanding of the processes involved (Schauser et al., 2003, Mackay et al., 2014, Spears et 58 al., 2014). Five specific issues are of central interest in this respect: (1) the water balance of 59 the lake under consideration, (2) the nutrient budget, (3) the chemistry with special regard to 60 the phosphorus content and binding forms in the sediment, and (4) the structure of the 61 biological community. Finally, (5) if chemical nutrient inactivation is intended, an effective 62 precipitation agent for phosphorus has to be chosen and a lake-specific quantity applied to 63 rapidly, significantly and sustainably improve water quality. 64

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66 Concerning the water quality management of lakes, there is a long-standing basic rule:

67 Reduction of external loading (remediation) has priority over lake-internal measures

68 (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,
Schauser 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 77 establish a reliable nutrient budget can be a challenge. This applies especially to seepage lakes 78 because both surface runoff and groundwater inflow can only be estimated with limited 79 precision (Holzbecher et al., 1999), even though a substantial proportion of external nutrient 80 loading may enter by this pathway (Meinikmann et al., 2015). Also, data are not always 81 available on atmospheric deposition, even though it sometimes constitutes a significant 82 83 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 84 85 stormwater sewers is required (Lathrop et al., 1998).

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Besides decreasing the external nutrient load below an acceptable, lake-specific level 87 (Vollenweider 1976, Nürnberg 1984, OECD 1986), the central objective of any kind of in-88 lake restoration targeting nutrients is to reduce the phosphorus (P) concentration in the water 89 column rapidly, significantly and sustainably below an appropriate threshold (Janse et al. 90 2008). P inventories of lakes consistently reveal that the bulk is stored in the sediment, which 91 hence constitutes a potential major P source (Søndergaard et al., 2013); whereby the P content 92 varies both vertically (Gonsiorczyk et al., 1998) and horizontally (Noges & Kisand 1999). 93 94 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, 95 therefore, is to reliably estimate the permanently bound P fractions, the mobile fractions, and 96 the fractions still undergoing diagenetic transformations (Psenner & Pucsko 1988, Hupfer & 97 Lewandowski 2005). Thus, a realistic assessment of the different P fractions is of paramount 98 importance to determine the specific quantity of precipitant to guarantee a long-lasting 99 success of the measure (Wauer et al., 2009). 100

Given a sound evaluation of the lake under consideration and the availability of a well-102 designed management concept, the P concentration of the water can rapidly approach the 103 anticipated values (Huser et al., 2016), but the biological community is likely to change less 104 rapidly. Specifically, the phytoplankton community of nutrient-rich lakes is frequently 105 106 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 107 effective light harvesting (Kaiblinger et al., 2007) or the ability to replenish internal P pools 108 while resting on the sediment surface (Istvánovics et al., 1993), cyanobacteria may 109 110 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 111

- 112 lakes; Gächter & Imboden 1985).
- 113

114 Even though the ultimate causes are still a matter of debate (Dolman et al. 2012), it seems evident that P concentrations of $<30-50 \ \mu g \ TP \ L^{-1}$ impair the growth of cyanobacteria 115 (Lathrop et al., 1998). Although the role of N/P ratios is less clear (Dolman & Wiedner 2015), 116 there is ample reason to believe that during limiting growth conditions, low ratios might 117 118 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, 119 cyanobacteria are supposed to dwindle as the dominating group within the phytoplankton 120 community (Downing et al., 2001). 121

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From a management point of view, the choice of an appropriate precipitant and the quantity to 123 be applied are largely a matter of the chemistry of the lake to be treated and the amount of P 124 to be inactivated (Huser et al., 2016). Meanwhile, there is a variety of precipitants on the 125 market, but regardless of their specifics all are essentially based on iron, aluminium or 126 127 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 128 129 (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 130 al., 2014). Finally, there is no significant risk of toxicity if applied properly (Pacioglou et al., 131 2016). 132 133

134 In April 2011, Feldberger Haussee (NE Germany, hereafter referred to as Haussee), a

135 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 136 century. Therefore, its pristine status and eutrophication history in terms of a number of 137 physical, chemical and biological characteristics are well documented (e.g. Thienemann, 138 1925, Uhlmann 1961, Koschel et al. 1981, Kasprzak et al., 2007). A substantial proportion of 139 this information could be used to establish a sound remediation and restoration program to 140 strive for a 'mesotrophic lake' as the restoration objective (TP spring maximum, summer 141 mixed layer average <0.035 mg L⁻¹, Chla summer mixed layer average <0.010 mg L⁻¹, Secchi 142 transparency, summer average > 2.5 m; LAWA 2014). Our purpose was to apply an 143 144 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 -145 146 15 years. 147

148 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 149 150 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 151 152 and significantly below the anticipated concentration level, cyanobacteria continued to dominate the phytoplankton community until late winter 2015; whereupon they abruptly 153 collapsed and never recovered. The on-going high turbidity, however, was primarily caused 154 by massive calcite precipitation events during spring and summer both before and after the 155 treatment. By 2015 these events had decreased substantially. Here, we present the results of 156 the restoration project with close scrutiny of the above quoted five criteria. We evaluate the 157 results of the intervention and detail the underlying mechanisms with respect to the restoration 158 of this formerly heavily-polluted lake. 159

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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 km² 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 m³ of storm water runoff from the neighbouring

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⁻²). Haussee is connected by a channel with two downstream, low-nutrient lakes (Breiter and

173 Schmaler Luzin). Some characteristics of the lake are outlined in Table 1, Fig. 1, 14

174 (supplemental material).

175

The drainage basin shows a mosaic of different land use with forests (33 %), residential areas 176 (22 %), lakes (20 %) and farmland (16 %) being the most important. Till and sandy soils 177 prevail (>50 %). Earlier estimates of the water residence time ranged between 2.5 and 5 years 178 (Barby 1967). Our own calculations using a general hydrological water balance model 179 (Holzbecher et al., 1999, p. 39, equation 1) resulted in a long-term (1974 - 2014) average of 180 8.9 (3.0 SD) years. In contrast to the common method of hydrological balances, which 181 includes precipitation, groundwater inflow, and evaporation, this estimate is exclusively based 182 on discharge measurements. The result is a 'phosphorus-relevant' residence time. The town 183 of Feldberg is located adjacent to the southern shore and has approximately 2,000 residents. 184 During summer, Feldberg and the surrounding lakes are water recreation hotspots, attracting 185 186 thousands of weekenders and holidaymakers.

187 188

2.2. Eutrophication history

Haussee's long history of eutrophication began in 1888 when a dairy factory started to 189 discharge raw sewage into the lake (Richter 1986). Nevertheless, in the middle of August 190 1924, Thienemann (1925) found the water quality of the lake still to be excellent, with a 191 Secchi transparency of 5 m and a hypolimnetic concentration of dissolved oxygen between 192 1.5 - 4.5 mg L⁻¹. Only a decade later, also in August, Ohle (1934) encountered a clearly 193 194 deteriorated lake, with an anoxic hypolimnion, accumulation of hydrogen sulphide and a 195 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, 196 however, was treated only with a percolating filter, which removed most of the organic load 197 but discharged the bulk of the N and P into the lake. As a result, Haussee progressively 198 became a hypertrophic ecosystem (Koschel et al., 1985). By the end of the 1970s, the external 199 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., 200 1977). As a consequence of this heavy pollution, besides other severe shortcomings, the 201 lake's recreational value declined, especially for all water-related activities and posed a 202

serious threat of eutrophication to the low-nutrient lakes Breiter and Schmaler Luzindownstream.

205

In 1980, the sewage discharge was suddenly stopped, decreasing the external nutrient loading 206 by approximately 90 %, raising hopes for a quick recovery. However, the water quality did 207 208 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 209 approximately 1 mg L⁻¹ until 1985. In order to accelerate improvement, biomanipulation 210 (introduction of piscivores, removal of planktivores) was applied from 1985 – 2002, but was 211 212 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 213 214 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 215 216 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 217 equilibrium concentration calculated by different models (Vollenweider 1976, OECD 1982, 218 Nürnberg 1984) was estimated to range between 0.043 and 0.059 mg TP L⁻¹, given the present 219 external loading of 199 kg TP yr⁻¹. Thus, without additional restoration measures, water 220 quality traits typical for mesotrophic lakes could not be achieved (TP, spring maximum, 221 summer mixed layer average $<0.035 \text{ mg L}^{-1}$, Chla summer mixed layer average $<0.010 \text{ mg L}^{-1}$ 222 ¹, Secchi transparency, summer average > 2.5 m; LAWA 2014). It was therefore decided to 223 treat the lake using poly-aluminium chloride (PAC) as a precipitant in order to rapidly and 224 significantly accelerate recovery and to sustain good water quality. 225 226 227 2.2. Limnological survey

Sampling campaign: Samples (2006 - 2017) were collected during the entire year at the 228 deepest site of the lake (Fig. 1), except when unsafe ice coverage or temperatures below 229 freezing point prevented from doing so. While a fortnightly schedule was maintained from 230 May – September, monthly samples were taken during the remainder of the year. Vertical 231 profiles of water temperature, oxygen concentration, and pH were measured using multi-232 parameter probes (YSI, Ohio, USA). Depending on temperature profiles, composite water 233 samples of the mixed layer were taken from the surface, 2.5 m, and 5 m. A sample from 7.5 m 234 235 was considered representative for the hypolimnion.

Chemical analysis: Total phosphorus (TP), total nitrogen (TN) and chlorophyll a (Chla) were 236 analysed spectrophotometrically according to standard protocols (DIN EN ISO 15681-1:2005-237 05, DIN EN ISO 13395:1996-12, DIN 38412-16:1985-12). TP and TN were measured after 238 wet digestion of unfiltered subsamples in an autoclave (potassium peroxodisulfate, TP 30 239 min., 134 °C; TN 40 min., 121 °C, FOSS FIAstar 5000 analyser, Hillerød, Denmark). Chla 240 was estimated by filtration of aliquots through membranes (pore size 1.2 µm, Schleicher & 241 Schüll, Dassel, Germany) which were immediately frozen at -20 °C until further analysis. 242 Extraction was performed by adding 5 ml of 99.8 % analytical grade acetone. To enhance 243 244 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 245 246 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 247 248 Strickland and Parsons (1968).

249

250 Alkalinity was measured by titration (DIN EN ISO 9963-1:1996-02, Titrando 888, Metronom, Filderstadt, Germany). The concentration of CaCO₃ (calcite) was determined by filtering 251 252 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 % 253 hydrochloric acid and the released CO₂ was measured using an infrared gas analyser (Infralyt 254 50 Saxon, Junkalor, Dessau, Germany; see Proft 1984). The calcite saturation index (SI) was 255 calculated using a model established by Hepperle and Krienitz (1997; available online at 256 http://www.sequentix.de/software winiap.php). 257

258

The concentration of soluble aluminium (Al) was estimated applying a protocol published by 259 Wauer et al., (2004), which ensured the detection of all potentially reactive forms of Al. 260 Aliquots of 100 mL were filtered through membranes (cellulose acetate, pore size 0.45 µm, 261 Sartorius, Göttingen) and acidified with 1 mL HCl. The principal reagent for the 262 263 complexation of Al was pyrocatechol violet. Samples were finally measured using a flowinjection analyser (FIA-LAB II Flow Analyser, MLE Dresden GmbH, Germany). The Al 264 content of two seston size fractions (>50 μ m, >90 μ m) and selected groups of benthic 265 organisms were analysed following a protocol suggested by Wauer & Teien (2010). 266 267

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

270 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.
- 275

Crustacean plankton was collected by vertical net hauls from 6.5 m (mean depth of the lake) 276 to the surface using a plankton net of 90 µm mesh size (Hydrobios, Kiel, Germany). The net 277 had a cone-shaped cap, an opening of 0.27 m^2 , a length of 1.2 m and a filtration efficiency of 278 approximately 1 (estimated using a flow-meter). Each sample was preserved in 4 % formalin-279 280 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 281 282 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-283 VID-MESS-HY, Pulsnitz, Germany). Dry mass was calculated based on published length-284 weight relationships (Bottrell et al., 1976, Kasprzak 1984) and converted into carbon units 285 $(DM \times 0.5 = C, Winberg et al., 1971).$ 286

287

Activity parameters: Primary production was quantified as a 'production potential' meaning 288 that instead of a vertical set of bottles, only one sample collected from 1 m was exposed at the 289 same depth. For the measurement 2 x 250 mL of water (light and dark bottle) were collected, 290 inoculated with 1 mL of 14 C-bicarbonate solution (specific activity 26.3 10⁶ dpm mL⁻¹) and 291 incubated for 4 hrs in situ. Incubation was stopped by addition of 1 mL formalin. Thereafter, 292 10 mL subsamples were filtered onto cellulose membranes (0.65 µm, Sartorius Göttingen, 293 Germany). Radioactivity was measured in a liquid scintillation counter (Perkin Elmer, Tri-294 Carb 2810 TR, Akron, Ohio, USA) for 4 hours or until the standard deviation of counts 295 remained below 5 % of the average. Calculation of daily primary production followed the 296 297 protocol of Köhler et al., (1999).

298

Bacterial protein production (BPP) was determined by incorporation of ¹⁴C-leucine (Simon &

- Assam 1989) as modified by Grossart et al., (2006). Triplicates and a formalin-preserved
- 301 control were incubated with ¹⁴C-Leu (213 mCi mmol L⁻¹; Hartmann Analytic GmbH,
- 302 Germany) at a final concentration of 165 nM, which ensured saturation of the uptake systems
- 303 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 304 filtered onto 5.0 µm (PA bacteria) nitrocellulose membranes (Sartorius, Göttingen, Germany) 305 and the collected filtrate was filtered on 0.2 µm (FL bacteria) nitrocellulose filters (Sartorius, 306 Göttingen, Germany). All filters were extracted with ice-cold 5 % trichloroacetic acid (TCA) 307 for 5 min. Thereafter, filters were rinsed twice with ice-cold 5 % TCA, once with ethanol (50 308 % v/v), and dissolved in ethyl acetate for measurement by liquid scintillation counting (Perkin 309 Elmer, Tri-Carb 2810 TR, Akron, Ohio, USA). Standard deviation of triplicate measurements 310 was usually <15 %. The amount of incorporated ¹⁴C-Leu was converted into BPP by using an 311 intracellular isotope dilution factor of 2. A conversion factor of 0.86 was used to convert the 312

- 313 produced protein into carbon (Simon & Azam, 1989).
- 314

Sediment analysis: To quantify sediment phosphorus (P) and to account for both horizontal 315 316 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 317 318 locations of the basins (Fig. 1). The cores were subsequently sectioned into 1 - 5-cm slices for further analysis. To estimate mobile P (P_{mobile}), different P-binding forms were acquired by 319 320 applying a sequential P extraction protocol of Psenner & Pucsko, (1988) as modified by Hupfer et al., (1995). P_{mobile} was calculated as the sum of P binding forms, potentially 321 contributing to P release; *i.e.* loosely adsorbed P (NH₄Cl-P), redox-sensitive P (BD-P), and 322 organic-bound P (NaOH, non-reactive P). The proportion of the specific fractions was 323 determined spectrophotometrically by applying a standard protocol (DIN EN ISO 15681-324 1:2005-05, Machery-Nagel, Nanocolor 505D, Düren, Germany; see Gonsiorczyk et al., 1998). 325 To measure the SRP concentration of the pore water, aliquots of sediment samples were 326 centrifuged for 5 min (13,000 g at 4 °C). The supernatant was subsequently filtered through 327 cellulose-nitrate membranes (0.45 μ m) and further processed as outlined for the extraction 328 329 method.

330

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 $\text{m}^3 \text{ yr}^{-1}$. Since
- 340 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.
- 345

346 A similar approach was applied to estimate the phosphorus inflow from the ground water.

- 347 Using the above mentioned general hydrological water balance equation (Holzbecher et al.
- 1999) the annual groundwater inflow was calculated (660.000 $\text{m}^3 \text{ yr}^{-1}$). Unfortunately, there
- 349 are no groundwater wells in the drainage basin of the lake to measure the phosphorus
- 350 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).
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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:

361

$$TP_{stat} = \frac{TP_{in}}{\beta + \tau \times \sigma} \tag{1}$$

362 TP concentration at a specific year (*t*) before reaching equilibrium concentration was363 computed as:

$$TP(t) = (TP_0 - TP_{stat}) \times e^{\left[-\left(\frac{\beta}{\tau} + \sigma\right) \times t\right]} + TP_{stat}$$
⁽²⁾

364

365 The annual average of the stratification factor β corresponds to:

$$\beta = \frac{TP_{out}}{TP_{lake}}\tau\tag{3}$$

 (\mathbf{n})

366

367 The annual net sedimentation rate σ was calculated as:

$$\sigma = \frac{NS}{TP_{lake}} \tag{4}$$

368

369 For comparison the following empirical models were additionally used:

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

$$TP_{stat} = 1.55 \cdot \left(\frac{TP_{in}}{1 + \sqrt{\tau}}\right)^{0.82} \qquad \text{OECD, 1982} \tag{6}$$

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

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- 371

2.4. Statistics

372 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-373 374 season temporal autocorrelation, individual measurements were aggregated to seasonal means (March – October; except for CaCO₃, where data were only available from May – 375 376 September). Changing variability of response variables was assessed by seasonal standard deviations of all measurements within one season. Then both mean values and seasonal 377 378 standard deviations before and after the treatment were compared. Because we were interested 379 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 380 represent a complex unrepeated experiment. Therefore, single *p*-values need to be interpreted 381 with care 'to assess the reliability of descriptive statistics and as a way to better inform the 382 reader' (Davies & Gray 2015). 383

384

The reaction of a complex, dynamic system to a manipulative event is simultaneously 385 distributed over a series of response variables, resulting in either alpha-error inflation and 386 false positives (cf. Garcia 2004) or overly conservative testing (Moran 2003) if sequential 387 Bonferroni corrections (Holm, 1979) are applied. Therefore, we used a principal components 388 389 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 390 single response variables. Significance of the overall effect was assessed by a permutation test 391 of the RDA results, with CaCO₃, oxygen saturation, pH, calcite saturation index, Secchi 392

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.

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2.5. Precipitation chemical

To remove phosphorus from the water column, to minimize release from the sediment and to 399 bind the incoming quantity from the drainage basin and atmospheric deposition, PAC (PAX-400 401 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 402 403 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 404 405 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 406 407 7.8 ± 0.3 SD (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 408 409 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 410 processed sequentially to allow fish to escape the treated areas (Exley 2000). 411

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The P inventory of the sediment and the water body revealed a stock of 2 g P_{mobile} m⁻², or 2 413 metric tons for the entire lake. Based on the estimated external loading rate, another 2 metric 414 tons is expected to enter the lake within the next decade. Incubation experiments of sediment 415 samples indicated that an Al/P ratio of at least 4.5 (12 g Al m⁻³) was necessary to sustainably 416 bind P_{mobile} in the sediment. To inactivate the continuing P input from the catchment area, it 417 was concluded that the same quantity should additionally be deposited in the sediment. To 418 stay on the safe side, the dose was slightly increased to 27 g Al m⁻²; which comes close to the 419 general suggestions of Vincente et al. (2008). The whole treatment lasted from April 11 - 21, 420 2011. The total amount of Al applied was 21 metric tons. 421

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3. Results

424 *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

426 concentration of the mixed layer over time dropped by more than an order of magnitude, Chla

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 β (0.776), the residence time τ (8.9 yrs.) and TP_{in} (0.230 mg L⁻¹) were held constant, while the net sedimentation coefficient σ was allowed to linearly increase from 0.173 – 0.510 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 σ to 0.95 yr⁻¹ followed by a gradual drop to 0.510 yr⁻¹ over the course
- 443 of 25 years (Scenario C), the concentration should again drop rapidly to 0.025 mg L^{-1} .
- 444 Subsequently, however, it would remain below the threshold for mesotrophic lakes (0.035 mg
- 445 TP L^{-1}) for at least 25 years. Finally (Scenario D), to reach an annual average TP
- 446 concentration of 0.025 mg L⁻¹ solely by decreasing external loading, TP_{in} would have to be 447 decreased from 0.230 to 0.133 mg L⁻¹ (43 %).
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The P inventory indicated that there was 1.5 t of P_{mobile} (2 g m⁻²) in the sediment (Z \ge 2.0 m) 449 and another 0.5 t in the water column. Moreover, based on the present external TP input of 450 199 kg yr⁻¹, a further 2.0 t P is likely to be discharged into Haussee within the next decade. 451 Therefore, to keep TP_{lake} significantly and sustainably below 0.035 mg TP L^{-1} (see Fig. 3, 452 Scenario C) an aluminium dosage of 27 g Al m⁻² (2.72 mg Al m⁻³) was applied. This equals an 453 atomic Al/P ratio of 12 if related to the P stock within the sediment and the water column. 454 Including the external loading of 2 t would decrease the ratio to 6. Figure 4 shows the 455 concentration of soluble Al during the years 2010 - 2012. Depending on sampling depth, the 456 values increased to $0.142 - 0.228 \text{ mg L}^{-1}$ for a short period after the treatment in April 2011, 457 but dropped rapidly during the second half of the year. In 2012, the concentration resembled 458 the pre-treatment level. However, the Al content of two different seston size fractions 459 remained elevated until November 2011. Variable results were found for selected groups of 460

and water clarity did not respond accordingly. Given the present external TP loading of 199

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.

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Sediment response: In response to the treatment, over time there was a general tendency of the 466 metal-oxide bound (i.e. Al-bound) phosphorus of the sediment to increase. While this fraction 467 was only 0.3 g TP kg⁻¹ DW (Fig. 5A) in March 2011, the maximum concentration had 468 increased to 1.3 g TP kg⁻¹ DW by April 2016. The peak that formed between 2011 and 2016 469 has since been buried by almost 4 cm of freshly deposited sediment. In 2017 no further 470 471 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 1.0 472 -2.9 mg P L^{-1} but was clearly lower in October 2016 (0.13 - 1.15 mg P L⁻¹). Compared to 473 previous years, a slight increase of SRP concentration occurred in 2017 in the uppermost 3 - 4 474 cm, but SRP in the water immediately above the sediment surface was still very low (0.003 475 $mg L^{-1}$). 476

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PCA, RDA: The Al application had a clear overall impact on almost all water quality 478 parameters. A principal component analysis (PCA) using a set of relevant variables 479 standardized prior to analysis showed a clear correlation structure with 82 % of the variance 480 in the first two axes (Fig. 6, Tab. 3). While CaCO₃, total phytoplankton, oxygen saturation 481 and filamentous cyanobacteria (Hormogonales) were positively correlated with one another, 482 Secchi transparency was negatively related to these variables. The years before and after Al 483 treatment were clearly separated by large differences in phytoplankton biomass, oxygen 484 saturation and CaCO₃ (Fig. 6, shaded polygons). While phytoplankton biomass, oxygen 485 saturation and CaCO₃ were high before and low afterwards, the opposite was found for Secchi 486 transparency. Redundancy analysis (RDA) of the same data set with pre- and post-Al 487 treatment periods as explanation variable attributed 45 % of the total variance to the treatment 488 period (permutation test, significant at p < 0.01); *i.e.* almost half of the standardized total 489 variation of the annual average values of the considered variables can be ascribed to the 490 treatment. 491

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493 *Phosphorus, nitrogen:* During the five years before the aluminium treatment, TP

494 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 495 hypolimnion (Fig. 7B). This pattern clearly changed after the treatment in April 2011: the TP 496 concentration in the mixed layer remained well below the restoration target of 0.035 mg TP L⁻ 497 ¹. Any noticeable seasonal rhythm had vanished. During thermal stratification, there was a 498 minor P accumulation in the deep water, but it was irrelevant relative to the situation before 499 2011. Since May 2011, the volume-weighted, annual mean TP concentration of the lake never 500 exceeded 0.025 mg L⁻¹. The median SRP concentration both in the mixed layer and in the 501 hypolimnion (7.5 m) was 0.001 mg L^{-1} (max. 0.013, min. 0.001 mg L^{-1}). In contrast, TN 502 showed substantial fluctuations both before and after the treatment, but there was no trend in 503 concentration (Fig. 7C). Nevertheless, as a result of the TP reduction, TN/TP ratios clearly 504 increased. While the average ratio was 23.7 (10.1 SD) before the treatment, it rose to 58.2 505 (24.1 SD) afterwards (Fig. 7D). 506

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Activity parameters: Although prior to Al treatment, primary production measurements were 508 only available in 2010, a substantial reduction was obvious thereafter (Fig. 8A). While the 509 average for 2010 (May – October) was 0.449 mg C L^{-1} day⁻¹ (0.121 SD), the grand average 510 for 2011 - 2017 was 0.141 mg C L⁻¹ (0.052 SD). While planktonic bacterial protein 511 production before the treatment amounted to $0.097 \text{ mg C } \text{L}^{-1} \text{ day}^{-1}$ (Fig. 8B), the grand mean 512 afterwards was 0.065 mg C L^{-1} day⁻¹. However, the variability of the results remained high 513 even after the treatment (0.044/0.034 SD). Both the ratio of BPP/PP and the respective SDs 514 had considerably increased from 21 (9.7 SD) % to 49 (33.9 SD) %, (Fig. 8C). 515

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517 *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 -518 October). While the grand mean of phytoplankton biomass during the period 2006 - 2010 was 519 0.80 mg C L⁻¹, it significantly dropped to 0.30 mg C L⁻¹ following the treatment (Welch-test, t 520 = 3.3, p = 0.023, df = 5.0). Likewise, SD of the readings significantly decreased from 0.47 to 521 0.15 (Welch test of seasonal standard deviations, t = 4.8, p = 0.006, df = 4.8), indicating that 522 the variance dropped because phytoplankton maxima were significantly reduced after the 523 treatment. Also, the grand mean of seasonal (April – October) Chla concentration dropped 524 from 0.018 (0.012 SD) mg L^{-1} prior to the treatment to 0.011 (0.006 SD) mg L^{-1} afterwards 525 (data not plotted). However, the results regarding the filamentous cyanobacteria were less 526 clear. Although there was an obvious trend towards lower standing stocks (0.44/0.11 mg C L⁻ 527 ¹). the average biomass recorded after the aluminium treatment did not significantly decrease 528

(t = 2.0, p = 0.11, df = 4.6). The same applies to the proportion of cyanobacteria within total 529 phytoplankton (42/28 %, t = 1.1, p = 0.31, df = 9.6, data not plotted). In contrast, the average 530 seasonal SD dropped significantly from 0.40 to 0.07 (t = 3.6, p = 0.018, df = 4.5) pointing to 531 much lower peak values. The community composition of cyanobacteria, however, did not 532 change substantially (Fig. 9C). In 11 out of 12 years, *Pseudanabaena limnetica* dominated (\geq 533 45 % of total cyanobacterial biomass), accompanied by Aphanizomenon sp. (9 - 45 %). 534 Finally, during early spring of 2015, the filamentous cyanobacteria nearly disappeared from 535 the plankton and never recovered. 536

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538 *pH*, *O*₂, *carbon buffering system, water clarity*: The average pH remained almost constant

539 (8.57/8.43, Fig. 10A) regardless of the treatment, but the SD decreased significantly

540 (0.43/0.27, t = 3.2, p = 0.018, df = 5.8), pointing to a lower photosynthetic activity by the

541 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 =

- 543 4.5, p = 0.005, df = 5.5), *i.e.* the oxygen oversaturation as a consequence of algal 544 photosynthesis was less.
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The average calcite saturation index showed a significant decline (Fig. 11A, 7.69/5.30, t = 546 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 =547 0.018, df = 5.8). However, the average calcite concentration did not reveal a significant 548 reduction, although the difference between the pre- and post-treatment period was obvious 549 (Fig. 11B). The SD, however, dropped (1.16/0.64, Welch test of standard deviation, t = 3.3, p 550 = 0.009, df = 8.8); *i.e.* the concentration maxima substantially decreased. Very little calcite 551 was detected in 2015/17 (0.14/0.48 mg L^{-1}), but in 2016 the concentration was slightly higher 552 553 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, 554 from 2015 - 2017 the average seasonal (March – October) water clarity increased to 2.1 - 2.9555 m. The maximum values recorded were 4.2/3.7/4.5 m. 556

557

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 - 3years 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*,

significantly smaller. Whereas total crustacean biomass did not change significantly, the SD 564 did (0.13/0.05, p = 0.03, df = 4.44). Small cladocerans as a group (Bosmina, Ceriodaphnia, 565 Diaphanosoma) revealed a significant decrease both regarding average annual biomass 566 $(0.019/0.010 \text{ mg C L}^{-1}, p = 0.011, df = 9.9)$ and SD (0.029/0.012, p = 0.019, df = 5.3; data not567 plotted). 568 569 Water clarity, CaCO₃ phytoplankton biomass: Finally, a multiple linear regression showed 570 that both phytoplankton and CaCO₃ had a diminishing impact on Secchi transparency (Fig. 571 13) and explained 60 % of its variance ($r^2 = 0.604$, p < 0.001, df = 2/15). However, the slopes 572 of the standardized predictor variables indicated a 1.7-fold higher influence of CaCO₃ on 573 Secchi transparency as compared to phytoplankton (slope = -0.31/-0.18). The interaction term 574 between CaCO₃ and phytoplankton was not significant (p = 0.72) and can thus be neglected. 575 576 4. Discussion 577 General trends: The collective information obtained from our study documents that except for 578 579 water clarity all anticipated restoration goals were achieved within a reasonable period. Although delayed by 4 years, even transparency clearly increased eventually. Thus, as 580 intended, Haussee's overall water quality substantially improved and is now in a range typical 581 for mesotrophic lakes (LAWA 2014). During the seven years subsequent to the Al treatment, 582 the volume-weighted, mean annual TP concentration ($< 0.025 \text{ mg L}^{-1}$) remained well below 583 the restoration target (0.034 mg L^{-1}). This is of paramount importance for the sustainability of 584 the management measure. Although the dose of 27 g Al m^{-2} was relatively low (Cooke et al., 585 2005), the drastically reduced TP values indicate that the calculated amount of aluminium 586 necessary to inactivate the phosphorus released from the sediment and introduced through 587 external loading was sufficient. All water quality parameters indicated a clearly reduced 588 metabolic activity of the whole planktonic community. Nevertheless, the future persistence of 589 improvement primarily depends on how reliably the Al dosage was calculated and, 590 consequently, how the sediment P-binding capacity develops in the long term. This applies 591 especially to a robust assessment of potentially mobile P in the upper sediment layer and to 592 the parameters implemented in the one-box model (TP_{in} , β , τ , σ), because in part the Al dose 593 was calculated based on these results. 594 595

Thermocyclops, Cyclops, $0.079/045 \text{ mg C L}^{-1}$, p = 0.05, df = 5.64). However, the SD was not

Phosphorus budget, sediment, modelling: The P content of sediments is a site-specific 596 attribute particularly impacted by the trophic status of a given lake (Gonsiorzcyk et al., 1998) 597 modified both by horizontal patches and vertical gradients (Grüneberg et al., 2015). 598 Moreover, depending on the P-binding forms, the mobile fraction (P_{mobile}) of the sediment TP 599 may considerably fluctuate (Hupfer et al., 1995). Also, Wauer (2006) and Hupfer et al., 600 (2016) pointed out that the fractionation method may substantially overestimate the pool of 601 potentially mobile P. Nevertheless, an independent test applying the gradient method (Hupfer 602 & Scharf 2002) resulted in a similar content of approximately 2 g P_{mobile} m⁻², (Gonsiorczyk, 603

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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,

609 Schauser et al. 2003, see Methods section, equations 1, 6 - 8). According to the LAWA

610 (2014) scheme of classification, the lake would thus retain a slightly eutrophic status.

unpublished data) confirming a reliable quantification.

However, Gächter & Imboden (1985, see methods section, equation 1) indicated that in

response to reduced external loading, the equilibrium concentration TP_{stat} depends on TP_{in} ,

613 the stratification factor β , the water residence time τ and the net-sedimentation coefficient σ .

614 While τ of seepage lakes is likely to be more or less constant, β may increase or decrease

depending on whether the concentration differences between the mixed layer and the deep

616 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), σ is likely to increase

618 up to a threshold which corresponds to the actual external loading and the chemical

619 constitution of the sediment (Gonsiorzcyk et al., 1998, Grüneberg et al., 2011).

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Concerning the Haussee, β both before and after the Al treatment fluctuated around 0.753 621 (0.123 SD) without any noticeable trend. In contrast, σ calculated based on annual average TP 622 concentrations and net sedimentation linearly increased from 0.166 yr⁻¹ in 2007 to 0.256 yr⁻¹ 623 in 2010 ($r^2 = 0.95$). This indicates that the '*natural*' (without any treatment) P-binding 624 capacity of the sediment was still growing and the lake had not yet reached steady-state 625 conditions. Given the present external nutrient loading ($TP_{in} = 230 \ \mu g \ L^{-1}$), the calculated 626 maximum σ at a steady-state concentration of 0.043 µg TP L⁻¹ would be 0.51 yr⁻¹ (Tab. 4, 627 supplementary material). Brett & Benjamin (2008, p. 202, Tab. 4, hypothesis 4) concluded 628

that for a specific TP_{in} the magnitude of σ is an inverse function of τ . Applied to the residence

time of Haussee (8.9 yrs.), σ would approach 0.35 yr⁻¹. The difference between these two 630 values demonstrates that σ is hard to estimate and subject to a remarkable level of uncertainty. 631 If, however, the value of 0.51 yr⁻¹ is assumed to be realistic for σ , then the extra binding 632 capacity provided by the PAC overdose could raise σ to 0.95 yr⁻¹ (as supported by the 633 constantly low TP concentrations shown in Fig. 7A/B). The initial extra capacity in σ of 0.44 634 yr⁻¹, decreasing over time, would inactivate a total of ca. 2 t of P, either coming from the 635 drainage basin or ascending from deeper sediment layers (Fig. 3, Scenario C; Tab. 4, 636 supplementary material). The extra binding capacity is likely to be exhausted 30 years after 637 the treatment. Whether this elevated binding capacity will truly remain for this many years is 638 unclear because several factors are hard to control (Hupfer & Scharf 2002). Some of the most 639 important are: 'aging' of the aluminium flock by binding organic substances or silicate 640 (Vincente et al., 2008), burial of the active Al-layer by new sediment (Lewandowski et al., 641 2003), and the intensity of diagenetic processes within the uppermost sediment layers (Huser 642 et al., 2011). Regardless of these possible impairments the continuously low TP concentration 643 644 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 645 646 used for the treatment.

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Phytoplankton biomass, community structure: Filamentous cyanobacteria have dominated 648 Haussee's phytoplankton since 1985 (Krienitz et al., 1996, IGB unpublished data). Although 649 the biomass of filamentous cyanobacteria clearly decreased after Al-treatment, their 650 continuing overall high proportion within total phytoplankton from 2011 - 2014 (18 - 61 %)651 was unexpected. However, during spring 2015 they suddenly vanished almost completely 652 from the plankton, and in 2016/17 their biomass approached zero. Cyanobacteria are known 653 654 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 655 carbon (Merz 1992). Although the impact of the N/P ratio on their growth is still a matter of 656 debate (Dolman & Wiedner 2015), there is ample evidence for the P concentration to be of 657 prime importance. Lathrop et al., (1998) showed that the likelihood of severe cyanobacterial 658 blooms diminishes when the external P loading is adequately reduced. Also, empirical studies 659 suggest that cyanobacterial dominance is less likely when the summer epilimnetic TP 660 concentration is below $0.035 - 0.055 \text{ mg L}^{-1}$ (Dolman et al., 2012). 661

After May 2011, the annual average volume-weighted TP concentration was $< 0.025 \text{ mg L}^1$. 663 Except for rare instances in early spring and autumn, the SRP supply was almost always 664 exhausted. Thus, as suggested by the drastic decline of planktonic primary production, P 665 shortage was very likely the reason for impaired growth of both phytoplankton as a whole but 666 also cvanobacteria in particular. Ptačnik et al., (2008) concluded that with growing diversity, 667 any phytoplankton community is increasingly capable of effectively utilising the whole 668 spectrum of available resources, which in turn means that the dominance of a single species or 669 group of species by monopolising resources is unlikely. From May to September 2015 the 670 phytoplankton of Haussee was characterised by a diverse community of cryptophytes (25.7 671 %), chrysophytes (21.4 %) and dinophytes (21.2 %). A similar situation was encountered in 672 2016/17 but with a higher proportion of chlorophytes (27 %). The drastic increase of TN/TP 673 from 23.7 (10.1 SD) to 58.2 (24.1 SD) in response to Al-treatment may have assisted the 674 complete alteration of the phytoplankton community structure (Teubner et al., 1999). 675 676

As a result of their elongated cell shape and accessory pigments, filamentous cyanobacteria 677 are known to be superior competitors for light (Mc Causland et al. 2001). Though differences 678 679 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, 680 cyanobacteria suffer a competitive disadvantage if more light penetrates deeper into the water 681 column. Haussee's euphotic depth increased from 4.0 m in 2011 – 2014 (May – September) to 682 683 6.3 m in 2015 - 2017, which might also have contributed to terminating the prevalence of filamentous cyanobacteria. 684

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Carbon buffering system, calcite: Following Al treatment, the grand averages (2006 -686 2010/2011 - 2017) of pelagic calcite concentration did not change significantly; although in 687 2015/17 little calcite was detected. Calcite precipitation is both a long-known and common 688 phenomenon of hard-water lakes (Koschel et al., 1983). Despite being a complex 689 biogeochemical process (Kelts & Hsü 1978), the major prerequisites are a sufficiently high 690 calcium-carbonate alkalinity, elevated pH and a low concentration of free CO_2^* (dissolved 691 CO_2 plus dissociated H₂CO₃). Koschel et al., (1997) hypothesized that the proportion of CO_2 692 uptake by photosynthesis and CO₂ release by respiration are of central relevance for the 693 position of the carbonate buffering system of lakes and thus for calcite precipitation. 694 Furthermore, Maberly (1996) demonstrated that during thermal stratification neither the 695

- 697 considerable importance for the CO_2 balance of the mixed layer.
- 698

Although photosynthesis by any phytoplankton community has the potential to decrease CO₂ 699 concentration and thus to increase pH, Koschel et al., (1987) observed that intense calcite 700 701 precipitation is frequently associated with a high abundance of cyanobacteria. It seems that at 702 least some taxa may have the rare physiological ability to not only exhaust the CO₂ supply (Shapiro 1997), but also to take-up and decompose bicarbonate and subsequently release OH⁻ 703 ions (Merz 1992). As a consequence, the pH in a narrow layer near the cell wall can be higher 704 than in the ambient water, favouring calcite precipitation by increasing the carbonate super-705 saturation (Dittrich et al., 2003). Moreover, because calcite precipitation in lakes is always 706 heterogeneously nucleated, it takes a surface to induce crystal growth (Küchler-Krischun & 707 Kleiner 1990). It has been shown that, at high cell densities, the cell surface of cyanobacteria, 708 709 and especially picocyanobacteria, provides an ideal matrix to initiate micro-crystals which then detach and continue to grow (Dittrich & Obst 2004). 710

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712 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 713 1.67 (1.96 SD) mg L⁻¹ remained low on average but was considerably variable (CV 117 %). 714 Proft & Stutter (1993) demonstrated that beyond a threshold pH of approximately 7.5, the 715 calcite saturation index (SI) progressively increases. Koschel et al., (1997) indicated that for 716 intensive calcite precipitation the CO_2^* concentration should be < 1 mg L⁻¹. Looking at the 717 respective data from 2006 to 2017, it turns out that at pH < 8.25, very little calcite (< 0.2 mg 718 $CaCO_3 L^{-1}$) was precipitated. When the pH increased beyond this threshold, results varied 719 between 0 and 4.1 mg CaCO₃ L⁻¹. The opposite applies to CO_2^* concentration, with 1.25 mg 720 L^{-1} being the upper threshold for high but variable calcite concentrations (data not plotted). 721 We, therefore, speculate that minor differences both in pH and CO_2^* , as impacted by the 722 delicate balance between planktonic photosynthesis and respiration governed by the structure 723 of the planktonic community might be the ultimate reason for whether or not calcite is 724 precipitated. 725

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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

⁷³² *'heterotrophic'*; *i.e.* the CO₂ balance might have been inclined in favour of production rather

than uptake, which may have halted the precipitation of calcite.

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In summary, we conclude that the anticipated goals of our restoration measure have been 735 accomplished. Since the present external P-loading rate is apparently tolerable relative to the 736 binding capacity of the sediment, there is reason to believe that the improved water quality 737 738 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., 739 2005, Huser et al., 2011, Gonsiorczyk et al., 2015). Nevertheless, our study also shows that 740 even if a project is well designed and implemented, unexpected effects can be encountered 741 742 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 743 744 parameters differed by several years. Gächter & Imboden (1985) and Carpenter (1999) concluded that lakes follow a different trajectory depending on whether loading is increasing 745 746 or decreasing. In some cases, it might be necessary to drastically reduce both the external Ploading and sediment release well below a lake-specific threshold in order to reach the 747 restoration goal (hysteresis behaviour). Lake Feldberger Haussee and the related project of 748 749 remediation and restoration represent a nice example for that conclusion.

750 751

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Criterion	Measured/calculated		
	parameter		
Drainage basin (ha)	712		
Lake surface (ha)	132		
Mean depth (m)	5.8		
Maximum depth	12.5		
Volume $(m^3 10^6)$	7,695		
Discharge (m ³ 10^6 yr ⁻¹)	0.861		
¹⁾ Water residence time (yrs.)	8.9 (±3.0 SD)		
Thermal stratification	May – September		
External nutrient loading (mg P m ⁻² yr ⁻¹)	151		
Storm water sewer (mg P m ⁻² yr ⁻¹)	64		
Ground water (mg P m ^{-2} yr ^{-1})	25		
Atmospheric deposition (mg P m ⁻² yr ⁻¹)	34		
Drainage basin run-off (mg P m ⁻² yr ⁻¹)	28		
²⁾ Annual average TP concentr. (mg P L^{-1})	0.087 ±0.011 SD		
³⁾ Annual average TN concentr. (mg N L ⁻¹)	1.183 ±0.321 SD		

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

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

1019 1020

Abbreviation	Unit	Explanation		
TP_{stat}	$(mg L^{-1})$	equilibrium TP concentration as related to external nutrient loading		
		(restoration target)		
TP_0	$(mg L^{-1})$	in-lake TP concentration prior to treatment		
TP_{lake}	$(mg L^{-1}, kg)$	in-lake TP concentration, or average annual TP content		
TPout	(kg yr^{-1})	annual TP export		
TP(t)	$(mg L^{-1})$	mean annual in-lake TP concentration at year (<i>t</i>) subsequent to treatment		
TP _{in}	$(mg L^{-1})$	TP inflow concentration, sum of annual external TP input divided by hydraulic loading (see Tab. 1)		
TP_{Lin}	$(g m^{-2} yr^{-1})$	areal external TP loading		
q_s	$(m yr^{-1})$	areal hydraulic loading		
σ	(yr ⁻¹)	TP net-sedimentation coefficient		
β	-	TP stratification factor		
τ	(yrs)	water residence time ¹⁾		
V	$(m^3 \ 10^6)$	lake volume		
NS	(kg yr ⁻¹)	TP net sedimentation (annual difference of external input and output by discharge)		

1022 Table 2: Abbreviations of parameters, units and explanations for P mass balance calculations using the

1023 model of Gächter & Imboden (1985) as modified by Hupfer & Scharf 2002 and Schauser et al. (2003).

1024 ¹⁾ phosphorus-relevant residence time (see methods section)

- 1027 before/after 2006 as a single constraint, and corresponding permutation test (3999 replicates) of the
- 1028 data collected from 2006 2016. Higher principal components (5 to 9) explained less than 6% to the
- 1029 overall variance and were omitted.

	PCA			
Criterion	PC1	PC2	PC3	PC4
Eigenvalue	5.551	2.646	0.727	0.435
Proportion explained	0.551	0.2658	0.073	0.043
Cumulative proportion	0.551	0.816	0.889	0.932
RDA				
Criterion	Variance		Proportion	Rank
Total	10.0000		1.0000	
Constrained	4.5276		0.4518	1
(grouping before/after 2011)				
Unconstrained	5.4824		0.5482	10
Permutation test	F=8.24			P=0.002
(3999 permutations)				

1032	Table 4 (supplementary material): Time series of in-lake TP concentration (TP_{lake}) and TP retention of
1033	the sediment (TP _{retention}) as impacted by the net sedimentation coefficient (σ) implemented for Scenario

1034 C (Fig. 3). $\sigma_{natural}$: 2004 – 2010, linear increase as regressed upon field observations from 2006 - 2010;

1035 2011 - 2016 - predicted based on this regression. The threshold value of 0.510 was calculated using 1036 equation (1) in the methods section resolved for σ and is considered the '*natural maximum*' that could

1037 be reached without any treatment (see below). $\sigma_{\text{treatment}}$: 2006 -2010, as with σ_{natural} , 2011 – 2015, a

1038 hypothetical increase to 0.950 as a result of PAC application, 2016 – 2039, linear decrease towards the

- 1039 'natural maximum' is a approached as a consequence of continuing external P input and a gradual loss
- 1040 of binding capacity of the applied PAC.

				TP _{lake}	TP _{retention}	TP _{retention}
Year	$\sigma_{natural}$	$\sigma_{treatment}$	$\sigma_{\text{difference}}$	$(mg L^{-1})$	$(kg yr^{-1})$	(kg accumulated)
2004	0.173	0.173		97.7		
2005	0.202	0.202	-0.308	95.6		
2006	0.230	0.230	-0.280	91.8		
2007	0.258	0.258	-0.252	86.8		
2008	0.287	0.287	-0.224	81.3		
2009	0.315	0.315	-0.195	75.7		
2010	0.343	0.343	-0.167	25.0	389.8	389.8
2011	0.371	0.950	0.440	24.9	84.4	474.2
2012	0.400	0.950	0.440	24.9	84.3	558.5
2013	0.428	0.950	0.440	24.9	84.3	642.8
2014	0.456	0.950	0.440	24.9	84.3	727.1
2015	0.485	0.950	0.440	24.9	84.3	811.5
2016	0.510	0.930	0.420	25.2	81.5	892.9
2017	0.510	0.910	0.400	25.7	78.9	971.9
2018	0.510	0.890	0.380	26.2	76.4	1048.3
2019	0.510	0.870	0.360	26.7	73.8	1122.1
2020	0.510	0.850	0.340	27.2	71.2	1193.3
2021	0.510	0.830	0.320	27.8	68.4	1261.7
2022	0.510	0.810	0.300	28.4	65.5	1327.2
2023	0.510	0.790	0.280	29.0	62.5	1389.7
2024	0.510	0.770	0.260	29.7	59.3	1449.0
2025	0.510	0.750	0.240	30.3	56.0	1505.0
2026	0.510	0.730	0.220	31.1	52.5	1557.6
2027	0.510	0.710	0.200	31.8	48.9	1606.5
2028	0.510	0.690	0.180	32.6	45.1	1651.6
2029	0.510	0.670	0.160	33.4	41.1	1692.7
2030	0.510	0.650	0.140	34.3	36.9	1729.6
2031	0.510	0.630	0.120	35.2	32.5	1762.0
2032	0.510	0.610	0.100	36.1	27.8	1789.8
2033	0.510	0.590	0.080	37.1	22.8	1812.7
2034	0.510	0.580	0.070	37.9	20.4	1833.1
2035	0.510	0.570	0.060	38.6	17.8	1850.9
2036	0.510	0.560	0.050	39.2	15.1	1866.0
2037	0.510	0.550	0.040	39.9	12.3	1878.2
2038	0.510	0.540	0.030	40.5	9.3	1887.5
2039	0.510	0.510	0.000	41.7	0.0	1887.5
2040	0.510	0.510	0.000	42.4	0.0	1887.5

1041

1042 $\sigma = \left(\frac{TP_{in}}{TP_{stat}} - \beta\right) \frac{1}{\tau} = \left(\frac{230}{43} - 0.779\right) \frac{1}{8.9} = 0.51 \ a^{-1}; \text{ TP}_{in}, \text{ TP}_{stat}, \sigma, \beta, \tau - \text{ as outlined in the results}$ 1043 section and Table 2.





Fig. 1: Feldberger Haussee, location and bathymetric map (courtesy of Mecklenburg-1047

Vorpommern Ministry of Agriculture and Environment, Schwerin, Germany). White marks 1048

indicate the places where sediment cores (x) and water samples (\bullet) were taken. 1049





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 1058 1985, see methods section, Table 2). The situation in 2006 is considered the starting point; 1059 $TP_{in} - 0.230 \text{ mg L}^{-1}$, $\tau - 8.9 \text{ yrs.}$, $\beta - 0.776$; Scenario A – no treatment, σ linearly increasing 1060 from 0.173 to 0.510 yr⁻¹ within 12 years (see Tab. 3, supplementary material), Scenario B – 1061 phosphorus precipitation from the water only, σ linearly increasing from 0.173 to 0.510 yr⁻¹ 1062 within 12 years, Scenario C – phosphorus precipitation from the water with additional 1063 sediment P inactivation, σ linearly increasing from 0.173 - 0.510 yr⁻¹ within 7 years and a 1064 step-like increase to 0.95 yr⁻¹ during year 8 as a result of precipitation agent overdosing. 1065 During the subsequent 25 years, σ is allowed to slowly drop to 0.510 yr⁻¹. Scenario D – to 1066 sustain an annual average TP concentration of 0.025 mg L⁻¹ solely by decreasing the external 1067 loading with a linear increase of σ from 0.173 to 0.510 yr⁻¹ within 12 years, TP_{in} would need 1068 to remain below 0.133 mg L^{-1} , which corresponds to a 58 % reduction of the present input. 1069 Reasons for the selection of various σ are detailed in the discussion section. For comparison, 1070 the annual average volume-weighted TP_{lake} concentrations are presented. 1071



1072





1075 Fig. 4: Concentration and content of aluminium before during and after the treatment;

1076 dissolved Al (top), seston size fractions (central) and selected groups of zoobenthos (bottom);

1077 whiskers indicate standard deviation.



1080 Fig. 5: Sediment content of metal oxide bound phosphorus and SRP concentration in pore





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).





1092 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 1096 the ratio of BPP/PP (C). Both PP and BPP were measured from May – October (n = 6). No 1097 estimates are available before 2010; □ average, • minimum/maximum, - median, box 25/75 1098 % quartile, whiskers 1/99 % percentile. 1099

2011 2012 2013 2014 2015 2016 2017

2006 2007 2008 2009 2010







- 1103 Fig. 9: Boxplots of biomass (March October, n = 7 13) of total phytoplankton (A),
- 1104 filamentous cyanobacteria (B) and the structure of the cyanobacterial community (C) in the
- 1105 mixed layer. The genus *Dolichospermum* was formerly known as *Anabaena*. The empty space
- 1106 in 2016 means no filamentous cyanobacteria were detected; \Box average, \bullet
- 1107 minimum/maximum, median, box 25/75 % quartile, whiskers 1/99 % percentile.



1111 18); □ average, • minimum/maximum, - median, box 25/75 % quartile, whiskers 1/99 %
1112 percentile.



1116 Fig. 11: Boxplots of calcium saturation index (A; March - October, mixed layer, n = 7 - 15),



- 1118 water clarity (C; Secchi transparency, March October, n = 9 17); \Box average, •
- 1119 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.



1127

1128 Fig. 13: Multiple linear regression with annual means of the vegetation period (May –

September) of Secchi transparency (SD) as a function of calcite concentration (CaCO₃) and phytoplankton biomass (PB). Regression equation with standardized explanation variables: $SD = 2.87 - 0.88 CaCO_3 - 0.58$ Phytoplankton; $r^2 = 0.60$ (F = 11.47 with 2 and 15 d.f., p

1132 <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.