

Changed cycling of P, N, Si, and DOC in Danish Lake Nordborg after aluminum treatment

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Abstract: Loading, retention, and in-lake cycling of phosphorus (P), nitrogen, silica, and dissolved organic carbon (DOC) were studied 1 year before and 3 years after P-inactivation by aluminum (Al) hydroxide in Danish Lake Nordborg in 2006. Simultaneously, external P loading was reduced by 40% via establishment of precipitation ponds in two inlets. After Al treatment, the internal P loading (sediment P release) during summer declined 90%–94%, owing to adsorption to aluminum hydroxide. Also, silicate regeneration from the sediment was reduced by 69%–76%, and sediment oxygen uptake as well as ammonium release declined markedly. Consequently, lake water total P, dissolved inorganic P, silicate, and DOC decreased by 73%, 97%, 87%, and 46%, respectively. The Secchi depth increased in the summer period during the first post-treatment year, but declined afterwards to pre-treatment levels, even though the mean lake-water total P concentration during summer was reduced from $\sim 240 \mu\text{g}\cdot\text{L}^{-1}$ before treatment to $26\text{--}65 \mu\text{g}\cdot\text{L}^{-1}$ in the first three post-treatment years. We conclude that a further reduction in external P loading is needed to obtain the full effect of the Al treatment in Lake Nordborg.

Résumé : Nous avons déterminé l'apport, la rétention et le recyclage au sein même du lac du phosphore (P), de l'azote, de la silice et du carbone organique dissous (DOC) un an avant et trois ans après l'inactivation du P par l'hydroxyde d'aluminium (Al) dans le lac Nordborg au Danemark en 2006. Au même moment, la charge externe de P a été réduite de 40 % par l'établissement d'étangs de sédimentation sur deux tributaires. Après le traitement à Al, l'apport interne de P (libération de P par les sédiments) durant l'été a décliné de 90–94 % à cause de l'adsorption à l'hydroxyde d'aluminium. De plus, la régénération du silicate à partir des sédiments a été réduite de 69–76 % et l'absorption d'oxygène par les sédiments de même que la libération d'ammonium ont diminué de façon marquée. En conséquence, le P total, le P inorganique dissous, le silicate et le DOC ont diminué dans l'eau du lac par respectivement 73 %, 97 %, 87 % et 46 %. La profondeur de Secchi s'est accrue durant la période d'été de la première année après le traitement, mais a décliné ensuite pour atteindre les valeurs d'avant le traitement, même si la concentration moyenne de P total a diminué de $\sim 240 \mu\text{g}\cdot\text{L}^{-1}$ avant le traitement à $26\text{--}65 \mu\text{g}\cdot\text{L}^{-1}$ dans les trois premières années après le traitement. Nous concluons qu'une réduction supplémentaire de l'apport externe de P est nécessaire afin d'obtenir le plein effet du traitement à l'Al dans le lac Nordborg.

[Traduit par la Rédaction]

Introduction

Aluminum (Al) treatment has been widely used as a restoration tool in eutrophic lakes to precipitate phosphorus (P) in the lake water, and to reduce internal P release (e.g., Smeltzer et al. 1999; Welch and Cooke 1999; Reitzel et al. 2005). Most studies of Al treatment effects have focused on changes in lake water P concentrations, primary production, and Secchi depth (e.g., Jacoby et al. 1994). Only a few studies have considered the changes in nutrient cycling following Al treatment, such as changes in nutrient retention, in-lake sedimen-

tation, internal release, and mobile sediment pools (Reitzel et al. 2005), and P has almost always been the nutrient of focus.

Aluminum hydroxide ($\text{Al}(\text{OH})_3$) adsorbs and precipitates both phosphate (PO_4^{3-}) and dissolved organic P-compounds (Reitzel et al. 2009); however, as it also absorbs silicate and some dissolved organic carbon (DOC) compounds, such as humic acids, it may potentially alter the cycling of additional elements (Koski-Vähälä and Hartikainen 2001; Berkowitz et al. 2005; de Vicente et al. 2008a). Berkowitz et al. (2005) reported a 74% decline in silicate within one hour in a laboratory experiment with Al addition, and further reductions

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during the following months. Consequently, Al treatment may, for example, decrease the productivity of diatoms by limiting silicate availability, which in turn may affect the whole phytoplankton composition and trophic level interactions, as diatoms are the preferred food source for many zooplankton species (e.g., Soltero and Nichols 1984). Silicate can also compete with PO_4^{3-} for sorption sites (Koski-Vähälä and Hartikainen 2001). de Vicente et al. (2008a) showed that a silicate concentration above $5.6 \text{ mg}\cdot\text{L}^{-1}$ significantly reduced the effectiveness of PO_4^{3-} adsorption to Al. Carbon (C) cycling may be altered after Al addition, owing to lowered production in the lake and, more directly, owing to precipitation of organic substances by the Al floc (Cheng et al. 2004; de Vicente et al. 2008a); however, in most studies the decline in DOC is relatively modest (Berkowitz et al. 2005; de Vicente et al. 2008a).

We have studied changes in nutrient cycling in the eutrophic Danish Lake Nordborg, which was restored in autumn 2006 by two measures. First, precipitation ponds with integrated sand filters were established at two major inlets and at a bypass of a third inlet to reduce the external P load (Egemose and Jensen 2009). Second, polyaluminum chloride was added to the lake water to reduce the internal P load. The target for the restoration was a 30% reduction of the external P load which should ensure a future total phosphorus (TP) steady-state concentration in the lake water below $100 \mu\text{g}\cdot\text{L}^{-1}$ according to general loading-retention models (Egemose and Jensen 2009), and improved light penetration following from reduced phytoplankton biomass. Based on the literature cited above, our hypothesis was that the restoration project would influence not only P cycling but also the cycling of silica and humic compounds. Accordingly, water and mass balances, sediment-water fluxes, sedimentation rates, lake water chemistry, and phytoplankton pigments were measured throughout 2006 and 2007 to document, for the first time, such changes on a whole-lake basis, with some of the parameters being measured in 2008 and 2009 as well. The objectives of this study were, therefore, (i) to document the changes in nutrient cycling after an Al treatment, and (ii) to investigate whether the targets for the restoration were fulfilled.

Materials and methods

Study site

Lake Nordborg is a polymictic, alkaline ($3.5 \text{ meq}\cdot\text{L}^{-1}$) lake situated in southern Denmark (Fig. 1). The surface area is 55 ha, the average depth is 5 m, and the maximum depth 8.5 m. The hydraulic retention time in the lake is 0.82 years. The catchment (1183 ha) is dominated by agriculture (63%) and urban areas (25%) (Egemose and Jensen 2009). During the last century, Lake Nordborg changed from a clear-water lake with well developed submerged vegetation to a highly eutrophic lake with turbid water, algal blooms, and an almost complete absence of submerged macrophytes. In the beginning of 1988 external loading was gradually reduced, but the lake suffered from high internal P loading and high in-lake P concentrations. During summer 2002, P release from the sediment equaled 1300 kg and the mean P concentration in lake water was $350 \mu\text{g}\cdot\text{L}^{-1}$ during summer, while the annual external P load was $\sim 530 \text{ kg}$ (County of Southern Jutland

2003). In 2004–2005 the external P load was estimated to 568 kg, and it was concluded that a further 30% reduction was required to avoid renewed eutrophication following lake restoration (Egemose and Jensen 2009).

To reinforce recovery, a restoration project was implemented in autumn 2006. During 3 weeks in October 2006, a dose of liquid polyaluminum chloride providing $52 \text{ g Al}\cdot\text{m}^{-2}$ was applied as a surface broadcast to the 46 ha of the lake with water depths exceeding 2 m, which was the maximum depth for macrophyte growth. October was chosen for the dosing time, as fall turnover has taken place, so optimal mixing conditions for aluminum hydroxide (floc) formation were ensured. The dose was calculated to obtain an Al/P ratio of 8, relative to the mobile P pool in the sediment (3.4 tons in the upper 10 cm; 1 metric ton = 1000 kg) according to Rydin and Welch (1999); Reitzel et al. (2005); and de Vicente et al. (2008b).

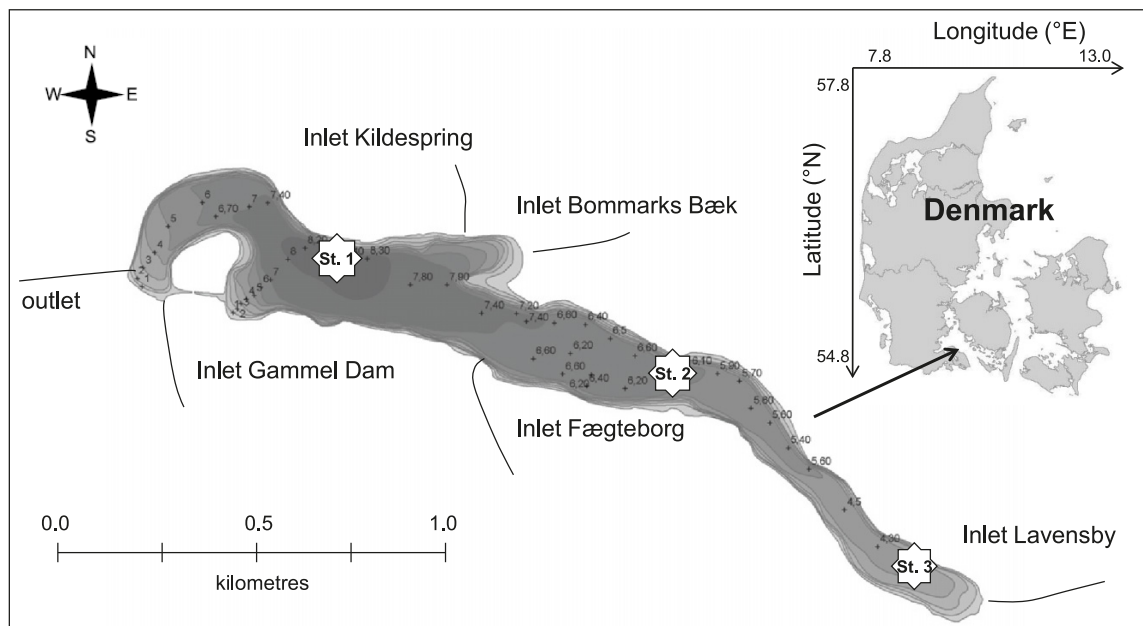
Field sampling

The lake, its inlets, and its outlet were sampled intensively one year prior to the restoration (2006) and one year after (2007). In the second and third post-treatment year (2008–2009), the lake was sampled less frequently. Details on specific sampling intensities are given below, and supplementary past data (until 1977) were obtained from the local authorities and the Danish Nationwide Aquatic Monitoring Programme.

The five major inlets (Fig. 1), representing drainage from 77% of the catchment area, were sampled monthly in 2006 and 2007. Inlet discharge was measured with an Ott Kleinflügel propeller instrument on each sampling occasion, while the outlet was measured daily by an automatic flow recorder and supplemented by monthly samples. Water samples were collected in polypropylene bottles and analyzed for TP, dissolved inorganic P (DIP), total nitrogen (TN), nitrate (NO_3^-), silicate, biogenic silica (BSi), and DOC.

Vertical profiles of oxygen (O_2), temperature, pH, and water samples were collected at the deepest station in the lake (St. 1, Fig. 1) every second week in the summer period (May–September) and monthly in the winters of 2006 and 2007. Profiles were measured by YSI probes, and Secchi depth was obtained using a 30 cm Secchi disc. Temperature and Secchi depth were also measured in 2008–2009. Water samples were collected by applying a heart valve water sampler. In 2006 and 2007 samples were collected as follows: in periods without stratification an integrated water sample was taken from the whole water column, defined as subsamples from 0.2 m, 1× the Secchi depth, and 2× the Secchi depth. When the Secchi depth was greater than 2 m, subsamples were taken every 2 m down to twice the Secchi depth. In stratified periods, two integrated water samples were taken: one from the epilimnion, and one from the hypolimnion. The epilimnion sample was taken as described above, albeit only to the upper edge of the thermocline, whereas the hypolimnion sample was pooled from subsamples taken from 2–5 depths, depending on the extension of the hypolimnion. For the determination of phytoplankton groups using marker pigments (Schlüter et al. 2006), a well-defined subsample of the integrated water sample was filtered on a GF/C filter and immediately frozen at $-80 \text{ }^\circ\text{C}$. In periods with stratification, only the epilimnion sample was used. In 2008 and 2009,

Fig. 1. Bathymetric map of Lake Nordborg including the five largest inlets and the outlet. The lake area is 54.6 ha, average depth 5 m, max. depth 8.5 m, volume 2 780 000 m³, and the catchment area is 1183 ha.



water samples were collected at depths of 1.5 m and 7.0 m and analyzed separately. In 2006 and 2007, measurements for alkalinity, DOC, BSi, color, and dissolved Al were taken monthly, whereas chlorophyll *a* (Chl *a*), TP, DIP, TN, NO₃⁻, ammonium (NH₄⁺), and silicate were measured every second week during the summer period (May–September), and monthly during winter. In 2008 and 2009, measurements for TP, DIP, TN, NO₃⁻, NH₄⁺, and silicate were taken bi-weekly in the summer period (May–September), and monthly during winter.

Duplicate sediment traps ($\phi = 8$ cm) with an aspect ratio of 5.5 were deployed 4 m below the surface from April to October 2006 and 2007 at two lake stations (St. 1 and 2, Fig. 1). The traps were emptied every second week, and the settled material was analyzed in duplicate for dry mass (DM), P, carbon and nitrogen content, BSi, and Al. In addition, the contribution of resuspended matter to the gross sedimentation rates was estimated by placing a string of replicated sediment traps at each metre from a depth of 2 m down to the bottom, at each station. Analyses of the collected DM showed that resuspended matter never reached more than 1 m above the lake bottom.

For determination of P pools and profiles of P, Fe, and Al in the sediment, three undisturbed sediment cores per station were taken with a Kajak gravity corer at three stations with a water depth of 8, 6, and 4 m, respectively (St. 1, 2, and 3; Fig. 1) in October 2006 before Al treatment and in December 2006 and November 2007 after Al treatment.

Sediment cores for pore-water P and silicate determination were taken at two stations (St. 1 and 2) 9× in 2006, 5× in 2007, and 1× in 2008.

Sediment-water fluxes

Exchange rates of O₂, DIP, NO₃⁻, NH₄⁺, and silicate between the sediment and the overlying water were measured by laboratory incubation at in situ conditions 7×, 10×, and 4× in 2006, 2007, and 2009, respectively. Measurements

were conducted monthly in the summer period in 2006–2007 and 4× in summer 2009. Each time five undisturbed sediment cores were sampled in acrylic tubes ($\phi = 5.2$ cm, $h = 40$ cm) at St. 1 and 2, as described above, and water for the experiments was sampled 0.5 m above the sediment. The cores were adjusted to provide a 15 cm water layer above the sediment. In the laboratory, the cores were placed in incubation tanks containing 14 L of lake water together with a reference core with lake water only. The overlying water in the sediment cores was mixed by a magnetic stirrer. In periods with oxic conditions at the sediment surface, aeration of the water in the incubation tank was conducted for a minimum of 12 h to ensure homogeneous oxic water conditions in all cores, and equal start conditions. Following acclimatization for 12 h, the cores were closed with a rubber lid to isolate the above-sediment water from tank water, and the cores were kept separate during all incubations. Oxygen incubations lasted for 4 h, after which the O₂ concentration was measured in all cores by a Thermo Orion 5-star meter with an O₂ probe. Afterwards, 20 mL of water was removed from each core to create an air pocket. The cores were closed again and incubated for 24 h, after which water samples were taken from each core to measure DIP, NO₃⁻, NH₄⁺, and silicate. In periods with anoxic conditions at the lake sediment surface (<1 mg O₂·L⁻¹) the O₂ flux was not measured and the nutrient flux was initiated immediately after returning to the laboratory. The cores were tightly closed and filled completely with anoxic lake water, to maintain anoxic conditions at the sediment surface, and incubated for 24 h. The flux was calculated from the difference in concentrations between the single core and the reference core, the water volume above the sediment, and the incubation time.

Chemical analysis

Lake water was filtered on Whatman GF/C filters and analyzed for DIP, NO₃⁻, DOC, color, and alkalinity. DIP was

measured by the molybdenum-blue method (Koroleff 1983). Concentrations of NO_3^- and NH_4^+ were analyzed spectrophotometrically on a flow injection system (QuickChem 8500 Series, Lachat Instruments, QuickChem method 10-107-04-1-C). Total alkalinity was measured by Gran titration (Mackereth et al. 1978). DOC was measured with infrared spectrophotometry on a TOC 5000 total organic carbon analyzer. Color was measured according to Hongve and Akesson (1996). Silicate was measured on a 0.45 μm membrane filtered sample by the method of Koroleff (1983), and BSi was measured by the method of Conley (1998) after filtration of lake water onto 0.6 μm polycarbonate filters. Samples for analysis of dissolved Al were filtered on 0.2 μm cellulose acetate filters and measured by ICP-OES (inductively-coupled plasma with optical emission spectroscopy; Optima 2100 DV, Perkin Elmer).

TP was measured as DIP after wet oxidation with persulfate, but on an unfiltered sample. TN in an unfiltered sample was measured as NO_3^- after digestion with persulfate (QuickChem method 31-107-04-3-B). Chl *a* was determined in triplicate, according to the method of Jespersen and Christoffersen (1987).

Phytoplankton pigments were extracted from the frozen filters in 5 mL 90% acetone with an ultrasonic homogenizer (2 min sonication). The extract was filtered through Whatman ANODISC 0.1 μm ($\phi = 25$ mm) and analyzed by high performance liquid chromatography (HPLC). The HPLC system was equipped with a Waters 600E solvent system, a Waters 717 autosampler, a C30 polymeric column, and a Waters 996 photodiode array detector. Pigments were separated using a modification of the method described by Kraay et al. (1992). For more details see Buchaca et al. (2005). Pigments were identified, and HPLC results calibrated with pigment standards from DHI, Hørsholm, Denmark. To calculate the contribution of Chl *a* from the various phytoplankton groups, and since phytoplankton samples were integrated from the whole water column, the pigments detected in the samples from Lake Nordborg were loaded in CHEMTAX (Mackey et al. 1996) together with average pigment:Chl *a* ratios from three different light-treated cultures (Schlüter et al. 2006).

The trapped material from the sediment traps was suspended in 1 L of lake water, and known volumes were filtered in duplicate on pre-washed and pre-dried Whatman GF/C filters for DM, loss of ignition (LOI), P, and Al, and in duplicate on 0.6 μm polycarbonate filters for BSi. Dry mass (105 °C, 24 h) and loss on ignition (450 °C, 4 h) were performed. P was measured by boiling one of the combusted filters in 1 mol·L⁻¹ HCl (1 h) followed by determination of DIP in the extract (Andersen 1976). BSi was measured as described above. CHN was measured on a CHN EA1108 Elemental Analyzer. Individual filters for Al determination were dissolved in 0.5 mL 30% (w/w) H_2O_2 and 2 mL 65% (w/w) HNO_3 via microwave digestion (250 W for 5 min, 400 W for 5 min, and 500 W for 10 min), after which Al was measured by ICP-OES.

From each station, three sediment cores for sediment P pool determination were sliced at 1 cm intervals down to minimum 20 cm depth. Afterwards, the three cores were pooled for each depth interval. Sequential chemical extraction (Psenner et al. 1984; Paludan and Jensen 1995) was per-

formed on one gram of wet sediment from the following depth intervals: 0–1; 1–2; 2–3; 3–4; 4–5; 5–6; 8–9; 11–12; 14–15; 19–20 cm and, in two cases, 24–25 cm for station 1. In this extraction scheme, loosely adsorbed P is extracted with H_2O in the first step, followed by extraction of iron-bound P by the reducing agent bicarbonate-dithionite. Subsequently, P bound to Al, humic P, and organically bound P of different forms are extracted by 0.1 mol·L⁻¹ NaOH (Jensen et al. 2005; Reitzel et al. 2006). After NaOH extraction, calcium-bound P is dissolved by cold HCl extraction and, finally, combustion of the sediment residue, and extraction in hot HCl liberate the remaining, presumably mainly organic, refractory P. Inorganic P from the first two extraction steps and extractable organic P from the first three steps are considered as the mobile P fraction under the conditions prevailing in eutrophic lakes (Jensen and Thamdrup 1993; Rydin 2000; Reitzel et al. 2005). Phosphorus was analyzed in all fractions, Fe was analyzed in the second extraction step, and Al in the third extraction step by ICP-OES. Iron from step 2 (Fe_{BD}) represents the oxidized forms that can bind P (e.g., Jensen and Thamdrup 1993), and Al recovered in the NaOH-fraction after precipitation of humic acids by acidification (Jensen et al. 2005) represents $\text{Al}(\text{OH})_3$ able to bind P by adsorption (Reitzel 2005).

The rest of the sediment was used for determination of DM, LOI, and the subsequent extraction of TP and total Fe and Al in 1 mol·L⁻¹ HCl (1 h boiling, Andersen 1976). TP was subsequently measured as DIP in the extract, whereas Fe and Al were measured by ICP-OES (see above).

In the laboratory, the cores for pore water determination were sliced, under N_2 atmosphere, into the following layers: 0–1; 1–2; 2–3; 3–4; 4–5; 7–8 cm. Immediately thereafter the fresh sediment was centrifuged (1500 rpm; 10 min) to extract the pore water, which was filtered on Whatman GFF filters for DIP and on polycarbonate filters for silicate. DIP and silicate were analyzed as specified for water samples.

Calculation of water and nutrient balances

The water balance was calculated according to eq. 1.

$$[1] \quad Q_{\text{meas}} + Q_{\text{unmeas}} + Q_{\text{prec}} + Q_{\text{gr.in}} \\ = Q_{\text{out}} + Q_{\text{eva}} + Q_{\text{gr.out}} + \Delta V$$

where Q_{meas} is the sum of water coming from the gauged inlets (77% of the catchment). The water flow was measured monthly, but to minimize the risk of over- or under-estimating the monthly and yearly water flow, the daily water flow was modeled. Depending on the type of catchment, there is a certain time lag from the beginning of a precipitation period until the water flow increases in the inlet. Therefore, the measured water flow in each inlet was correlated with the total precipitation for a number of days before sampling (1 d, 2 d, and 3 d, etc.) to find the best correlation between measured water flow and precipitation, depending on the time lag in the catchment. This was performed for the summer and winter season, respectively. The most significant correlation ($P = <0.001$ – 0.004) between measured discharge and precipitation was then used to calculate the daily discharge (Egemose, unpublished). The value for Q_{unmeas} from the ungauged catchment is calculated via comparison with a similar gauged catchment with a similar degree of, for instance, agriculture

or urban areas. Then the measured water flow, in litres per second, from the gauged catchment is used to calculate the water flow for the ungauged catchment by adjusting to a larger or smaller catchment area. The values for Q_{prec} and Q_{eva} from precipitation and evaporation were calculated on a daily basis, based on daily measurements from the Danish Meteorological Institute. Volume changes in the lake (ΔV) and inflowing ($Q_{\text{gr.in}}$) versus outflowing groundwater ($Q_{\text{gr.out}}$) is calculated by balancing eq. 1, so that for each day there could be either net inflow or outflow of groundwater. Therefore, all uncertainties in the water balance will be accumulated in the groundwater part. Groundwater contributed 10%–17% of the annual water balance; Q_{out} is the water flowing out of the lake.

The nutrient balances for P, N, Si, and DOC were conducted according to eq. 2.

$$[2] \quad P_{\text{inlet}} - P_{\text{ret}} = P_{\text{outlet}} + \Delta P_{\text{inlake}}$$

where P_{inlet} represents the sum of the contributions from the gauged inlets, the ungauged inlets calculated via comparison with a similar gauged catchment, plus contributions from precipitation and inflowing groundwater; P_{outlet} represents the outlet via the lake outlet and outflowing groundwater; and ΔP_{inlake} represents the changes of the relevant parameter in the lake water phase. Finally, phosphorus retention (P_{ret}) was calculated by balancing eq. 2.

Results

Changes in the water column

All measured changes in water column parameters after the Al treatment are shown (Fig. 2 and Table 1). Summer mean TP in the epilimnion was reduced by 89% from 2006 to 2007, and the corresponding reduction in DIP was 97%. In 2009 the reduction was still 73% and 97% for TP and DIP, respectively, compared with 2006 values. Prior to the Al treatment, P accumulated in the hypolimnion during summer, but this was eliminated after the Al treatment.

No significant changes were observed in the summer mean TN concentration, despite an increase in early summer 2006 compared with 2007. The concentration of NO_3^- increased during the first post-treatment year, but declined afterwards to pre-treatment levels. Whereas NH_4^+ decreased substantially from a mean of $0.22 \text{ mg}\cdot\text{L}^{-1}$ during summer in the epilimnion in 2006, to $0.03\text{--}0.4 \text{ mg}\cdot\text{L}^{-1}$ in post-treatment years, and accumulation in bottom water was eliminated.

The significant reduction in TP also affected the TN:TP molar ratio. The ratio was 7–18 in summer 2006, but after restoration, the summer mean ratio increased, ranging from 24 to 724 in 2007–2009.

The concentration of silicate was significantly reduced by the Al treatment, from $1.5\text{--}4.4 \text{ mg}\cdot\text{L}^{-1}$ in pre-treatment years to $0.2\text{--}0.5 \text{ mg}\cdot\text{L}^{-1}$ as summer means after treatment. In contrast, no differences were observed in the concentration of BSi. As for silicate, the DOC concentration declined from $9.4 \text{ mg}\cdot\text{L}^{-1}$ in summer 2006 to $5.1 \text{ mg}\cdot\text{L}^{-1}$ in 2007. Simultaneously, the color concentration declined from a mean of $47.0 \text{ mg Pt}\cdot\text{L}^{-1}$ during summer in 2006, to $19.1\text{--}27.9 \text{ mg Pt}\cdot\text{L}^{-1}$ in 2007–2009.

During summer, mean Secchi depth increased by almost

one metre, from 2.3 m in 2006 to 3.2 m in 2007, but declined towards the pre-treatment level in 2008 and below the pre-treatment level in 2009, compared with 2006. The concentration of Chl *a* was reduced slightly, but not significantly, from an average of $26.5 \mu\text{g}\cdot\text{L}^{-1}$ during summer in 2006, to $19.4 \mu\text{g}\cdot\text{L}^{-1}$ in 2007, but in 2009 the average during the summer increased again to $36.4 \mu\text{g}\cdot\text{L}^{-1}$. The O_2 concentration in the bottom water was higher in 2007–2009 ($5.1\text{--}6.6 \text{ mg}\cdot\text{L}^{-1}$ as the mean for summer) than in 2006 ($3.5 \text{ mg}\cdot\text{L}^{-1}$). Prior to restoration (1977 to 2002) the O_2 concentration varied from $2.7\text{--}9.4 \text{ mg}\cdot\text{L}^{-1}$. The mean summer temperature was higher in the post-treatment years ($16.2\text{--}17.4 \text{ }^\circ\text{C}$) than in 2006 ($14.3 \text{ }^\circ\text{C}$), while it varied between 11.5 and $17.3 \text{ }^\circ\text{C}$ from 1977 to 2002. No change in pH was observed after the Al treatment ($8.1\text{--}8.2$ in 2006–2008). Total alkalinity declined from a mean of $3.5 \text{ meq}\cdot\text{L}^{-1}$ during summer in the pre-treatment years, to $2.9 \text{ meq}\cdot\text{L}^{-1}$ in 2006, but returned to $3.4 \text{ meq}\cdot\text{L}^{-1}$ in 2009.

Although 24 tons of Al was applied to the lake, no significant differences in dissolved Al concentrations were observed between pre- and post-treatment years. The mean concentrations in summer of 2007 and 2009 were $44.7 \mu\text{g}\cdot\text{L}^{-1}$ and $30 \mu\text{g}\cdot\text{L}^{-1}$ compared with $41.4 \mu\text{g}\cdot\text{L}^{-1}$ in 2006.

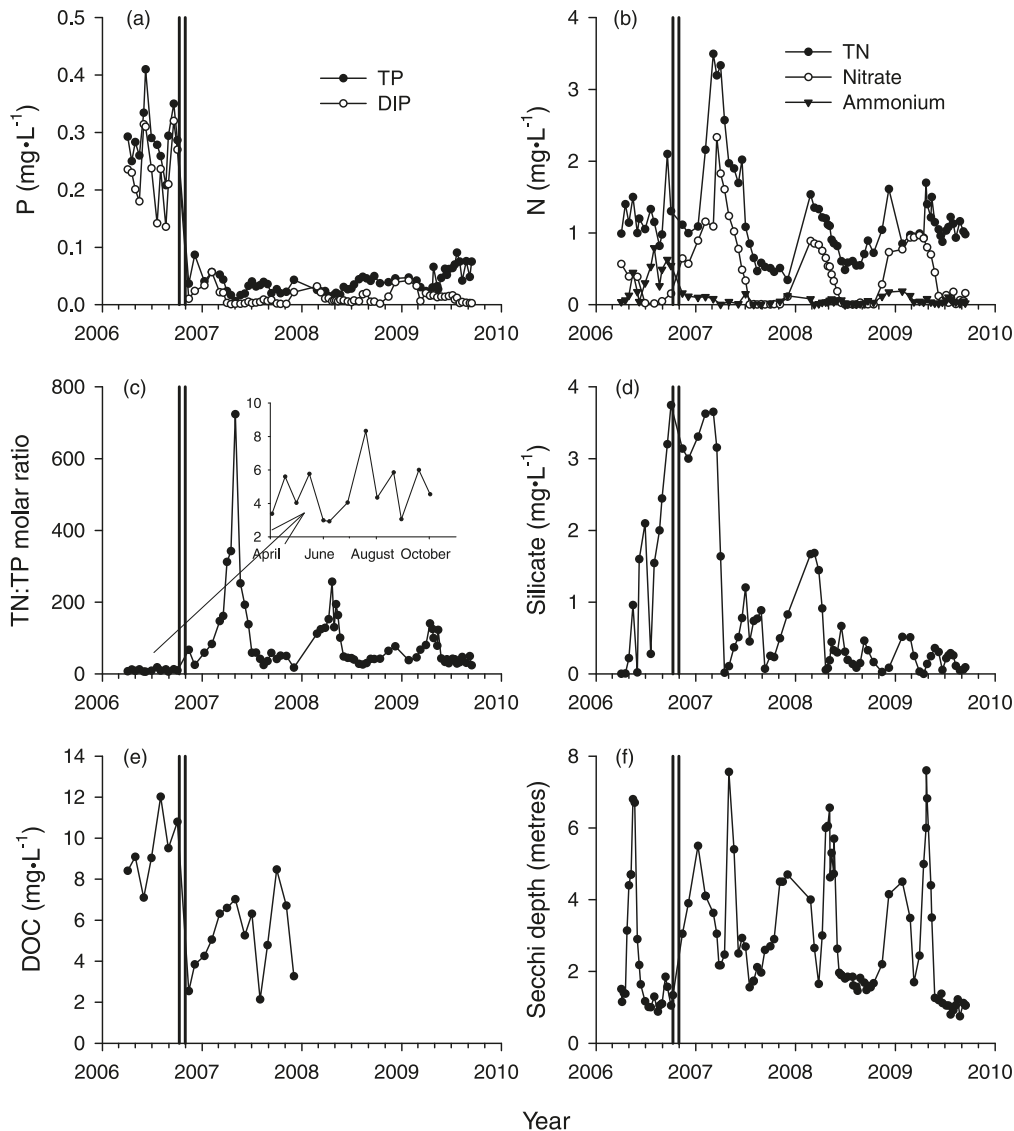
Changes in water and nutrient balances

The precipitation was 39% higher in 2007 compared with 2006, which affected the water balance (Table 2). The lake received 17% more water in 2007 and the water discharge from the lake was 22% higher in 2007. As a result, the water retention time was 1.01 years in 2006 and 0.83 year in 2007.

The external TP loading declined 40% from 2006 (581 kg) to 2007 (346 kg), and the inlet TP concentration decreased, from 0.337 to $0.117 \text{ mg}\cdot\text{L}^{-1}$ as annual average values (Table 2). In 2006, 535 kg TP was discharged from the lake compared with 126 kg in 2007, owing to a significant reduction in the TP concentration. Considering TP accumulation in the water column, TP retention in the sediment was 746 kg in 2006 compared with 265 kg in 2007 (calculated from eq. 2). The large retention in 2006 includes 682 kg (90%) in October during the Al treatment; otherwise, the retention was negative for long periods of 2006. In contrast to the change in TP loading, the external loading of DIP decreased by only 17% from 2006 (238 kg) to 2007 (198 kg), with inlet DIP concentrations of 0.134 and $0.066 \text{ mg}\cdot\text{L}^{-1}$, respectively.

The external TN loading increased 21% from 11.0 tons in 2006 to 13.2 tons in 2007 (Table 2) and TN discharge from the lake increased 63% from 2.8 to 4.5 tons, owing to an increased concentration and a higher water flow, whereas TN retention remained unchanged. The external loading of total bioavailable silicate (silicate + biogenic Si, referred to as TBSi) increased from 10.9 tons in 2006 to 12.6 tons in 2007, whereas the discharge from the lake decreased from 7.5 to 5.9 tons, because of a decreased early average TBSi concentration (Table 2). This decrease was supported by negative retention in 2006 and positive retention in 2007 (Table 2). Finally, the lake received 21.1 tons DOC in 2007 compared with 16.9 tons in 2006 (Table 2). DOC discharge from the lake increased from 16.9 to 18.5 tons from 2006 to 2007, whereas retention increased from 11.4 to 14.8 tons.

Fig. 2. Temporal development in (a) total P (filled circles) and dissolved inorganic P (open circles), (b) total N (filled circles), nitrate (open circles) and ammonium (triangles), (c) TN:TP molar ratio, (d) silicate, (e) dissolved organic carbon (DOC), and (f) Secchi depth in the water phase of Lake Nordborg before and after the AI treatment in October 2006 (treatment period indicated by the two vertical lines), given as average concentrations in the whole water column.



Phytoplankton

In spring 2006, diatoms together with euglenophytes dominated the phytoplankton community and peaked at a biomass of $43 \mu\text{g Chl } a \cdot \text{L}^{-1}$. During summer 2006, euglenophytes and chlorophytes dominated, and chlorophytes peaked twice during August and early October, contributing more than 50% of the phytoplankton biomass (Fig. 3). In spring 2007, diatoms and euglenophytes dominated again; however, their total phytoplankton biomass reached only $12 \mu\text{g Chl } a \cdot \text{L}^{-1}$. During July and August 2007, chlorophytes dominated completely followed by dominance of cryptophytes, diatoms, and euglenophytes in the following months (Fig. 3).

Changes in sedimentation rates

There was no significant difference in the sedimentation rate of DM, C, N, and AI in 2006 compared with 2007, while there was a tendency towards higher BSi sedimentation

rates in 2007 compared with 2006, but the increase was not significant (Table 3). The sedimentation rate of P was lower in 2007 than in 2006, but the decrease was significant only for St. 2, where the rate declined from a mean value of $42.8 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ in 2006 to $22.8 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ in 2007.

The sedimentation rates were evaluated at two stations, but in general there was no significant difference between the stations, except for the DM sedimentation in 2006, where the rate at St. 2 was significantly higher than at St. 1, and was unrelated to resuspension, which never reached the water height where the traps were placed (data not shown).

Changes in fluxes across the sediment–water interface

The O_2 consumption of the sediment decreased from 2006 to 2007 and 2009 (Fig. 4). On one occasion in 2006, and two in 2007 anoxic conditions occurred at the sediment surface, preventing measurement of O_2 fluxes; but otherwise,

Table 1. Mean values for summer (May–September) including standard deviations or ranges for various parameters in Lake Nordborg before (1977–2006) and after (2007–2009) external P load reduction and Al treatment in October 2006.

Parameter		1977–2002	2006	2007	2008	2009
TP (mg·L ⁻¹)	Epilimnion	0.292–1.176	0.238±0.104	0.026±0.010	0.037±0.014	0.065±0.013
	Hypolimnion	0.330–1.258	0.663±0.476	0.027±0.014	0.034±0.013	0.053±0.017
DIP (mg·L ⁻¹)	Epilimnion	0.162–0.875	0.183±0.109	0.005±0.003	0.009±0.007	0.006±0.005
	Hypolimnion	0.173–0.981	0.463±0.247	0.005±0.003	0.009±0.005	0.013±0.009
TN (mg·L ⁻¹)	Epilimnion	1.2–5.3	1.2±0.6	1.2±0.7	0.8±0.2	1.1±0.1
	Hypolimnion	1.1–5.3	1.5±0.5	1.2±0.7	0.6±0.2	1.0±0.2
NO ₃ ⁻ (mg·L ⁻¹)	Epilimnion	1.0–3.4	0.2±0.2	0.4±0.5	0.1±0.2	0.2±0.2
	Hypolimnion	1.0–3.1	0.2±0.2	0.3±0.4	0.1±0.2	0.2±0.2
NH ₄ ⁺ (mg·L ⁻¹)	Epilimnion	0.08–0.19	0.22±0.25	0.04±0.07	0.03±0.03	0.03±0.02
	Hypolimnion	0.13–0.75	1.62±1.59	0.05±0.06	0.03±0.03	0.05±0.05
TN:TP (molar)	Epilimnion	6–27	7–18	25–724	26–194	24–123
Silicate (mg·L ⁻¹)	Whole lake	2.3–4.4	1.5±1.2	0.5±0.3	0.3±0.1	0.2±0.1
BSi (mg·L ⁻¹)	Whole lake	—	0.2±0.1	0.3±0.2	—	—
DOC (mg·L ⁻¹)	Whole lake	—	9.4±1.8	5.1±1.9	—	—
Color (mg Pt·L ⁻¹)	Whole lake	—	47.0±6.8	19.6±4.8	27.9±9.2	23.6±6.0
Secchi depth (m)		0.7–2.3	2.3±1.8	3.2±1.9	2.5±1.6	1.5±0.9
Chl <i>a</i> (µg·L ⁻¹)	Epilimnion	39.4–78.0	26.5±19.2	19.4±12.4	—	36.4±19.9
Oxygen (mg·L ⁻¹)	Bottom	2.7–9.4	3.5±3.2	5.1±2.3	6.6±2.3	6.6±4.3
Temperature (°C)	Bottom	11.5–17.3	14.3±2.1	16.2±2.1	17.1±1.5	17.4±2.1
pH	Bottom	7.2–9.0	8.2±0.3	8.1±0.5	8.2±0.3	—
Total alkalinity (meq·L ⁻¹)	Whole lake	3.5	3.5±0.5	2.9±0.2	—	3.4±0.2
Dissolved Al (µg·L ⁻¹)	Whole lake	—	44.7±20.2	41.4±23.3	—	30.0±8.7

Note: 1977–2005 range covers mean summer values from a minimum of 4 years (1977, 1988, 1994, 2002) and, for some parameters, up to 6 years, except for total alkalinity where only data from 2002 are available. The parameters are given for epilimnion, hypolimnion, and the bottom of the lake, or as a volume-weighted average value for the whole water column. TP, total phosphorus; DIP, dissolved inorganic phosphorus; TN, total nitrogen; BSi, biogenic silica; DOC, dissolved organic carbon; —, indicates missing or insufficient data sets.

Table 2. Mass and water balances for Lake Nordborg in 2006 and 2007 given as the total amounts entering (inlet) and leaving (outlet) the lake expressed in kilograms per year, accumulation in the water column (Δ in lake) and retention calculated as inlet minus outlet corrected for changes in the lake (see eq. 2).

Balance	Year	Inlet (kg)	Outlet (kg)	Δ in lake (kg)	Retention (kg)	Conc. in inlets (mg·L ⁻¹)	Conc. in outlet (mg·L ⁻¹)
TP	2006	581	535	-701	746	0.337	0.242
	2007	346	126	-45	265	0.117	0.045
TN	2006	10 971	2776	342	7854	3.8	1.2
	2007	13 234	4535	1070	7630	4.7	1.7
TBSi	2006	10 900	7491	7814	-4405	6.3	3.3
	2007	12 574	5883	-9790	16 481	5.2	2.1
DOC	2006	16 919	16 913	-11.341	11 347	8.4	2.1
	2007	21 059	18 447	-12.156	14 768	8.9	2.0
		Inlet (1000 m ³)	Outlet (1000 m ³)	Retention time			
Water	2006	2800	2742	1.01			
	2007	3268	3338	0.83			

Note: The concentrations (mg·L⁻¹) in the measured inlets (draining 77% of the catchment area) and outlet are given as water flow weighted early averages. TP, total phosphorus; TN, total nitrogen; TBSi, total bioavailable silica (the sum of silicate and biogenic silica); DOC, dissolved organic carbon.

summer mean O₂ consumption rates were 2.1 g·m⁻²·d⁻¹ and 3.8 g·m⁻²·d⁻¹ in 2006 at St. 1 and St. 2, respectively. In 2007, the corresponding rates were 0.2 g·m⁻²·d⁻¹ and 1.3 g·m⁻²·d⁻¹ and, finally, 0.9 g·m⁻²·d⁻¹ and 1.3 g·m⁻²·d⁻¹ in 2009.

The release of DIP from the sediment surface declined dramatically after the Al treatment (Fig. 4). In summer 2006, the sediment released DIP with rates up to 0.085 g·m⁻²·d⁻¹, and the accumulated P release was 1807 kg during the period May–September from the 46 ha

lake area deeper than 2 m, which is assumed to contribute to the internal P load. In 2007, after the Al treatment, the internal P load was significantly reduced. The maximum release rate was 0.006 g·m⁻²·d⁻¹ in June, and on several occasions P uptake from the water was recorded. The overall estimated P release in summer 2007 was 103 kg. In 2009 the DIP flux was still low, with a maximum release rate of 0.006 g·m⁻²·d⁻¹ and an accumulated estimated release of 188 kg P during summer.

Similarly, the NH₄⁺ flux changed markedly. In 2006, NH₄⁺

Fig. 3. Temporal development in chlorophyll a (Chl a, $\mu\text{g}\cdot\text{L}^{-1}$) and the relative contribution of the different phytoplankton groups in 2006 and 2007 (chlorophytes, black; dinoflagellates, white; euglenophytes, dark gray; diatoms, light gray; cryptophytes, hatched dark gray; cyanobacteria, chequered white).

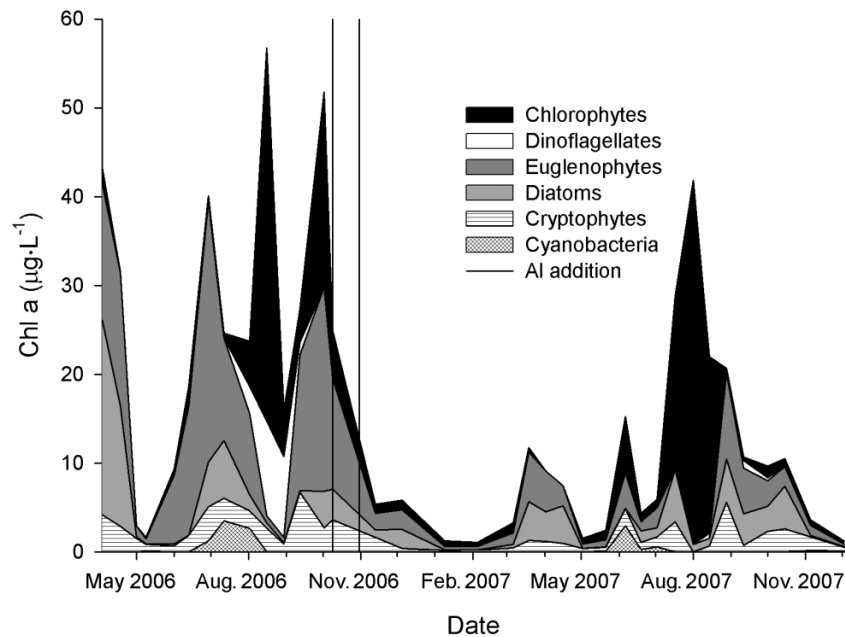


Table 3. Sedimentation rates (mean \pm SD) at two stations in Lake Nordborg in 2006 and 2007.

	Station 1		Station 2	
	2006	2007	2006	2007
DM*	5.8 \pm 3.5A	9.0 \pm 5.2	8.8 \pm 3.1B	12.3 \pm 8.5
C*	1.1 \pm 0.8	1.7 \pm 1.4	1.6 \pm 0.9	1.7 \pm 1.2
N [†]	134 \pm 82	206 \pm 241	184 \pm 86	168 \pm 110
P [†]	32.5 \pm 18.9	27.8 \pm 29.7	42.8 \pm 20.0b	22.8 \pm 12.8a
BSi [†]	258 \pm 215	444 \pm 403	326 \pm 190	533 \pm 497
Al [†]	123 \pm 58	116 \pm 61	177 \pm 105	139 \pm 66

Note: Lowercase letters indicate a significant difference between 2006 and 2007, and capital letters imply significant difference between St. 1 and St. 2 in the relevant year.

*Measured in $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$.
[†]Measured in $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$.

was released from the sediment especially in June, July, and August, with a maximum rate of $0.51 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. In 2007 and 2009 the NH_4^+ release was much lower with a maximum rate of $0.11 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ and $0.09 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, respectively. In 2006 the accumulated estimated NH_4^+ release equaled 17242 kg, but declined to 2888 kg in 2007 and 3688 kg in 2009.

The silicate release followed the same development as described for P and NH_4^+ . The maximum rate was $0.58 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ in 2006, $0.16 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ in 2007, and $0.12 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ in 2009. The accumulated estimated silicate release declined from 17818 kg in 2006, to 5532 kg in 2007, and 4341 kg in 2009.

Changes in supply ratios

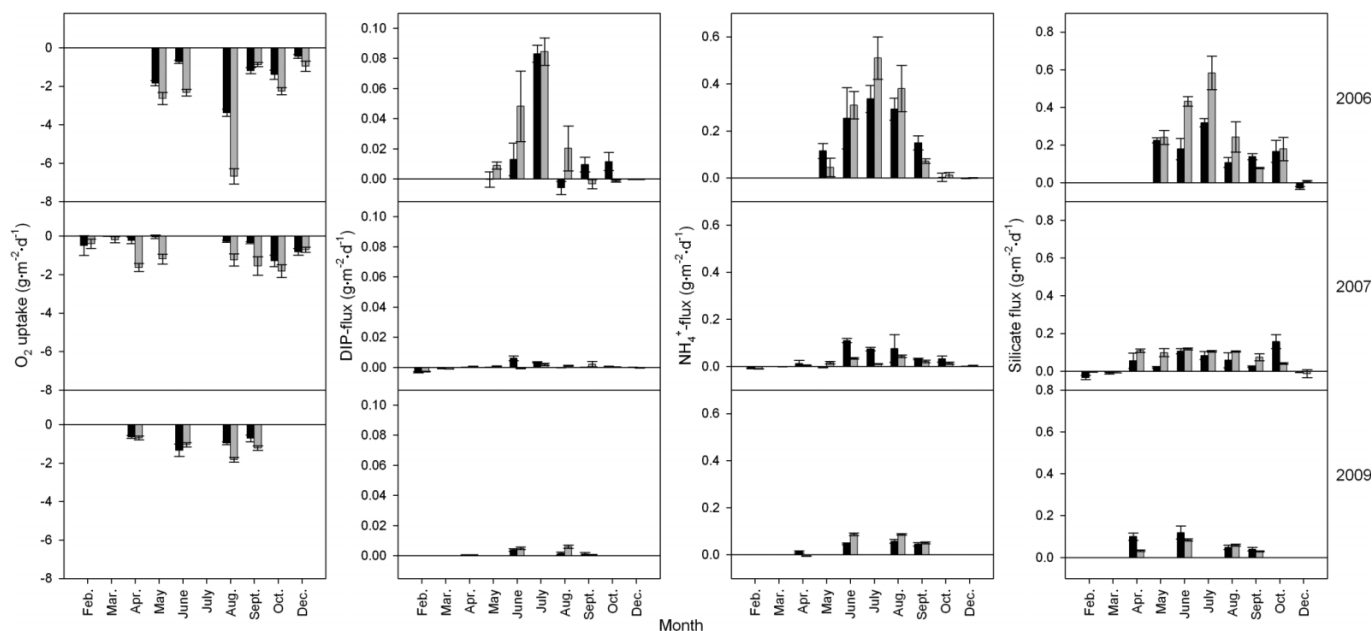
The proportion between external and internal supply changed after the Al treatment during April–September (Fig. 5), and so did the standing stock of nutrients at the beginning of the season in March. The standing stock of DIP declined by 91%, from 653 kg in 2006 to 60 kg in 2007.

The internal supply ranged from 44–1173 kg in 2006 depending on the month, but declined to 4–37 kg in 2007, whereas the external DIP contributed 13–37 kg, depending on the month, in 2006 and 2–32 kg in 2007. The contribution from internal supply decreased from 73%–99% in 2006, to 32%–76% in 2007. As for DIN, the standing stock increased from 2006 (1581 kg) to 2007 (4744 kg). The internal DIN supply was 1507–6283 kg in 2006, but declined to 231–1306 kg per month in 2007, whereas the external DIP supply remained more or less unchanged. The internal DIN supply contributed 72%–97% in 2006 compared with 49%–84% in 2007. Finally, the standing stock of silicate increased from 610 kg in 2006 to 9400 kg in 2007. The external supply of silicate did not change markedly, but the internal supply decreased notably by a factor 2–5, and the percentage of internal supply decreased from 72%–95% in 2006, to 50%–75% in 2007. The reductions in both internal and external supply affected the molar ratios of nutrient supply to the water column, since the N:P ratio increased from an average of 60 in 2006 to 148 in 2007, most pronouncedly in April. The development was similar for the molar Si/P ratio, which increased from 32 in 2006, to 104 in 2007.

Changes in pore water P and silicate

The pore water concentration of DIP and silicate measured as profiles in the upper 8 cm of the sediment decreased significantly after the Al treatment (Fig. 6). The mean DIP concentration at St. 1 and 2 in the first cm of the sediment decreased from $2.27 \text{ mg}\cdot\text{L}^{-1}$ before the treatment, to $0.03 \text{ mg}\cdot\text{L}^{-1}$, equivalent to a 99% reduction. The mean silicate concentration at the two stations decreased from $11.2 \text{ mg}\cdot\text{L}^{-1}$ to $2.6 \text{ mg}\cdot\text{L}^{-1}$ (76% reduction). In general, the concentrations of both DIP and silicate were higher at St. 1 than at St. 2, and the duration of high pore water concentrations was also longer at St. 1.

Fig. 4. Exchange rates of oxygen, dissolved inorganic phosphorus (DIP), ammonium, and silicate across the sediment surface at St. 1 (black columns) and St. 2 (gray columns) measured in the laboratory in 2006, 2007, and 2009, under in situ oxygen and temperature conditions. In July 2006 and June–July 2007, the lake went anoxic at the sediment surface, and therefore, oxygen flux was not recorded. All 2006 exchange rates are pre-treatment, except December, which is post-treatment.



Changes in the sediment P and Al pools

The sediment pools were calculated for the upper sediment layers down to a mass depth of $1 \text{ g DM}\cdot\text{cm}^{-3}$, corresponding to a sediment depth of 6–12 cm, depending on the station and the sampling date. This layer was deep enough to catch the new Al layer. Using mass depth eliminates differences in DM before and after treatment, and between stations, and allows us to calculate content per area. During the Al treatment, $52 \text{ g Al}\cdot\text{m}^{-2}$ was added to Lake Nordborg, representing a molar ratio of 8:1 relative to the mobile P pool. The background content of NaOH-extractable Al in the upper sediment was $0\text{--}5 \text{ g}\cdot\text{m}^{-2}$ depending on station (Table 4). One month after treatment, the Al_{NaOH} content at the deep station (St.1), which represents the accumulation part of the lake bottom, was double that of the added amount ($110 \text{ g}\cdot\text{m}^{-2}$). At the moderately deep St. 2, where resuspension occurs, the content was similar to the added amount ($48 \text{ g}\cdot\text{m}^{-2}$), whereas at the shallow St. 3, where resuspension also may occur, the content was $27 \text{ g}\cdot\text{m}^{-2}$, and thereby lower than the amount added. After one year, the Al content had decreased further at all three stations to 71, 17, and $10 \text{ g}\cdot\text{m}^{-2}$ at St. 1, 2, and 3, respectively.

As expected, the Al-bound P increased at all stations after treatment (Table 4). At St. 1 the content increased from $1.4 \text{ g P}\cdot\text{m}^{-2}$ before Al treatment to $3.1 \text{ g P}\cdot\text{m}^{-2}$ after one month, and to $4.6 \text{ g P}\cdot\text{m}^{-2}$ after one year. Also at St. 2 and 3, Al-bound P increased after one month, whereas after one year the content had decreased again, but remained higher than before the treatment.

Before treatment, the mobile P pool in the sediment equaled $2\text{--}7 \text{ g}\cdot\text{m}^{-2}$ depending on station. This represents 29%–39% of TP_{sed} (Table 4). The TP_{sed} content as well as the mobile P content increased one month after the treatment, and the fraction of mobile P remained unchanged (30%–

38%). However, after one year the mobile P had decreased at all stations (22%–29%).

Prior to the treatment the molar ratio between NaOH-extractable Al and Al-bound P was 0–5, but increased to 41 at St. 1, and 14 at St. 2 and St. 3, one month after Al addition, whereas after one year, the ratio had decreased to 18, 10, and 7 at St. 1, 2, and 3, respectively (Table 4). The above presented ratios represent extractable Al and Al-bound P, whereas the ratio $\text{Al}_{\text{NaOH}}:\text{P}_{\Delta\text{NaOH}+\text{mobil P}}$ represents the ratio between extractable Al and Al-bound P above background concentrations (the amount bound after the treatment) plus the remaining mobile P pool, which potentially could be bound. This ratio is, respectively, 13, 5, and 5 at St. 1, 2, and 3 after one month, but had declined to 10, 5, and 2, respectively, after one year.

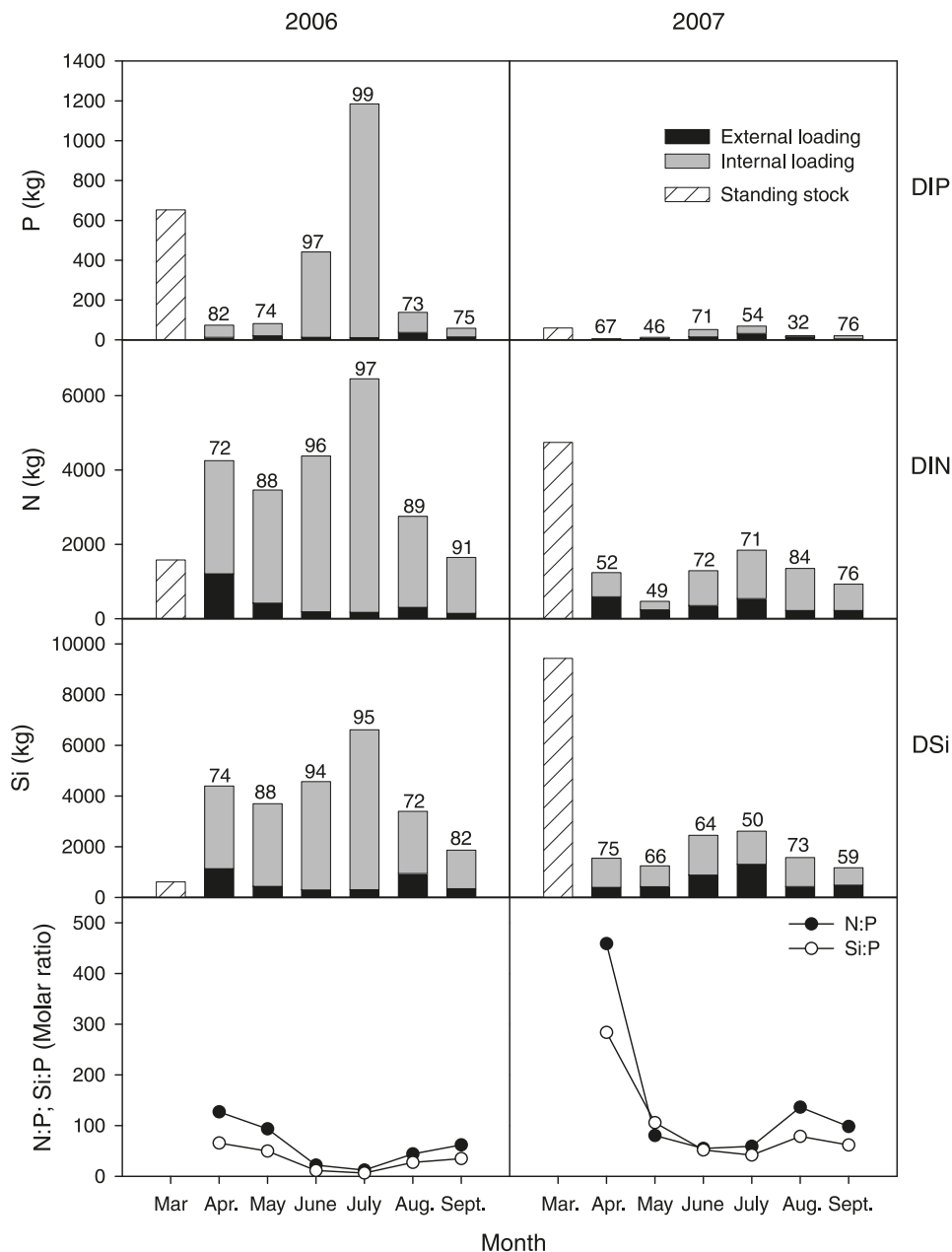
Discussion

Changes in nutrient cycling

This detailed study in Lake Nordborg before and after Al treatment clearly demonstrates that, as we hypothesized, the nutrient cycling is affected not only for P, but also directly for silicate and DOC, and indirectly for N.

The Al treatment, in combination with the reduction of external loading, led to a significant decline in lake water P, mainly owing to precipitation of DIP and P-containing particles during the application of Al, combined with a very effective decrease in internal P loading. This observation is similar to that described by Welch and Cooke (2005) and Reitzel et al. (2005) who reported reductions in internal P loading of 54%–83% in five lakes. In 2009, 3 years after the Al treatment, lake water TP was still 77% lower than before the treatment, despite a tendency to increasing mean concentrations during summer of both TP and DIP from 2007–2009.

Fig. 5. Standing stock, as mass in the water column, in March (hatched columns) as well as external (black columns) and internal (gray columns) supply from April to September of dissolved inorganic P (DIP), N (DIN) and silicate (kg) in the upper 6 figures. Values above bars are the contribution (%) from internal supply. The two lower figures show the molar ratio of N:P (filled circles) and Si:P (open circles) in the total supply to the water column.

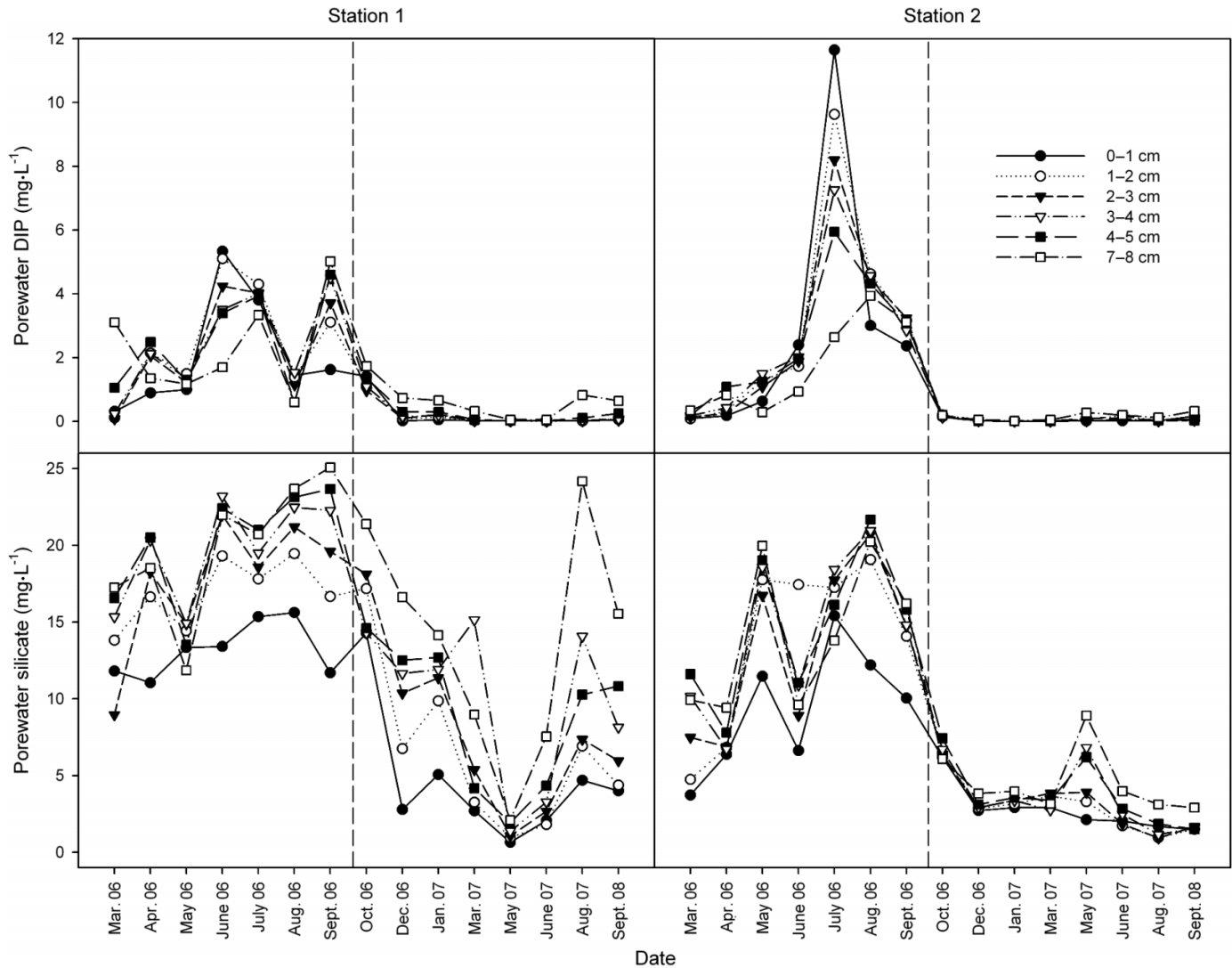


TP increased 42% from 2007–2008 and 76% from 2008–2009, which can prevent an improvement of water quality and maintain the lake in a eutrophic state. The increasing P concentration can be due to either renewed internal loading or adjustment towards a new steady state related to the external loading. Accumulation of P in the bottom water, as an indication of internal loading, has not been observed after the Al treatment, and the sediment P release was still 90% lower in 2009 compared with pre-treatment values. In other Al-treated lakes, the reduction of internal P loading has been of similar magnitude as in Lake Nordborg, but with very varying longevity and effects on lake-water clarity (from <1 year to 13 years; Cooke et al. 1993; Smeltzer et al. 1999; Stein-

man and Ogdahl 2008). The substantial reduction in pore water DIP concentrations is another evidence of the effective binding of DIP to $\text{Al}(\text{OH})_3$ and the reason why no P accumulation is observed in the bottom water. Therefore, the most likely explanation for the increase in P concentrations from 2007–2009 is a move towards a new steady state set by the new inlet P concentration. To reach a lower in-lake P concentration, the external P loading must be reduced even more than the present annual average inlet concentration of $0.12 \text{ mg}\cdot\text{L}^{-1}$ TP.

The minor decrease in the lake water silicate concentration directly associated to the Al treatment can be ascribed to co-precipitation of silicate by the Al floc, as silicic acid adsorbs

Fig. 6. Temporal and spatial (0–8 cm sediment depth) variation in the porewater concentration of dissolved inorganic phosphorus (DIP) and silicate at two stations in Lake Nordborg in 2006, 2007, and a single measurement in 2008 (two-digit years noted on x-axis). Broken line indicates Al-addition.



strongly to Al by co-precipitation and subsequent formation of hydroxyaluminosilicate (Chappell and Birchall 1988; Berkowitz et al. 2005; de Vicente et al. 2008a). The silicate concentration stabilized in 2007 at a much lower level compared with 2006. This decrease is not related to a reduction in the external silicate supply, which actually increased in 2007, but a shift from negative to positive silicate retention in the lake. This is also supported by our measurements of silicate fluxes showing that the release rate is reduced by a factor 4, and by the major reduction in pore water silicate concentration after Al treatment. The reason is most likely that silicate is bound to $\text{Al}(\text{OH})_3$ in the sediment (Koski-Vähälä and Hartikainen 2001), but it may, in part, be due to reduced mineralization of organic matter (Søndergaard et al. 2005a), as indicated by the decreased oxygen consumption. Even though silicate availability decreased after the Al treatment, no significant effect was observed on either lake water BSi concentration or on the BSi sedimentation rate, even though the diatom biomass was lower in spring and early summer 2006 compared with 2007, as discussed later.

The increase in NO_3^- concentration during the first post treatment year is not directly related to the Al treatment, but a consequence of increased TN and NO_3^- supply from the catchment in 2007, and maybe also due to a switch from N limitation to P limitation of the phytoplankton production, as suggested by the N:P ratio. In consequence, N accumulated in the water phase. The reduced sediment O_2 consumption rate (57%–91%) after the Al treatment cannot be explained by lower carbon supply, as the sedimentation rate of C remained unchanged; however, the sedimentation of labile C may have decreased due to improved mineralization in the water column. Another explanation could be that the reduced O_2 consumption rate is due to P limitation of the bacteria community (e.g., Enrich-Prast 2002) or an Al-related toxic effect on the microbial processes, resulting in reduced C-mineralization rates. The lake water concentration of NH_4^+ remained low after the Al treatment, owing to the decrease in NH_4^+ release from the sediment. This can be explained by increased O_2 concentrations in the bottom water causing higher nitrification rates of the available NH_4^+ as well as reduced

Table 4. Various pools in the top sediment layers, from the surface to a mass depth of 1 g DM·cm⁻³, corresponding to 6–12 cm sediment depth, before Al treatment and one month (1 month) and 1 year (1 year) after Al treatment at three stations.

Parameter	Unit	Station 1			Station 2			Station 3		
		Before	One month after	One year after	Before	One month after	One year after	Before	One month after	One year after
Al _{NaOH} ^a	g·m ⁻²	1	110	71	0	48	17	5	27	10
P _{NaOH}	g·m ⁻²	1.4	3.1	4.6	0.4	3.9	2.0	1.1	2.1	1.7
P _{mobile} ^b	g·m ⁻²	7.2	7.8	5.3	2.1	7.3	2.1	5.4	5.8	4.6
P _{mobile} Of TP	%	39	38	25	29	30	22	33	30	29
Al _{NaOH} :P _{NaOH}	Molar	1	41	18	0	14	10	5	14	7
Al _{NaOH} :P _{ΔNaOH+mob}	Molar	0	13	10	0	5	5	1	5	2
TP _{sed}	g·m ⁻²	18	21	20	7	23	9	15	20	17
TAI _{sed}	g·m ⁻²	146	284	216	55	164	74	117	127	141
TFE _{sed}	g·m ⁻²	160	164	145	69	174	61	122	178	164

Note: Station 1 is a deep accumulation station, while St. 2 and St. 3 are moderately deep and shallow, both with resuspension potential.

^aAdded aluminum (52 g·m⁻²) will mainly appear in the Al_{NaOH} fraction (e.g., Reitzel 2005; Reitzel et al. 2005).

^bThe mobile P pool is the sum of inorganic P in the H₂O- and BD-fraction plus organic P (NRP) in the H₂O-, BD-, and NaOH-fraction.

ammonification, as indicated by the lower sediment O₂ uptake after treatment.

Prior to restoration, Lake Nordborg was likely N-limited most of the year (County of Southern Jutland 2003), but after treatment the lake presumably shifted towards P limitation. The N:P supply ratio increased, owing to reduced internal and external P loading, although in April this was especially due to P removal in the newly-established retention ponds. Similarly, the Si:P supply ratio increased. Overall, the increased supply ratios of inorganic N:P and Si:P support the occurrence of P limitation by algae production (e.g., Soltero and Nichols 1984), and phytoplankton pigment analyses demonstrated a small reduction in cyanobacteria biomass from 2006 to 2007. The limited size of the reduction may be due to the fact that substantial long-lasting blooms of cyanobacteria, reported from previous years, were not observed in the relatively cold summer of 2006 or that light was a limiting factor as well in 2006. Diatom biomass was relatively unaffected by the reduced silicate availability, it being, however, lower in spring and early summer 2007 than in 2006 despite that the clear water period, following the diatom blooms, was unchanged after the Al application. Wetzel (2001) reported that dissolved Si concentrations < 0.23 mg·L⁻¹ may affect diatom production, indicating that the diatom production in Lake Nordborg could be periodically Si-limited; however, as the Si:P ratio increased it seems probable that P became limiting instead.

The major decrease in lake water DOC immediately after the Al addition was likely caused by co-precipitation of DOC by the Al-floc (Hall et al. 1985; Cheng et al. 2004). Even though the external DOC supply was 24% higher in 2007 owing to higher runoff, the in-lake DOC concentration decreased 46% the first year after treatment as the higher external DOC load was counterbalanced by a 30% higher retention, attributable to binding to the Al-floc. Closely related to DOC is color, which thinned and remained thin during all three post-treatment years. The explanation is probably related to a decreased release of humic substances from the lake sediment owing to their binding to the Al floc (Jiang and Graham 1998; de Vicente et al. 2008a).

Changes in sediment pools of P and Al

Even though Al was distributed evenly over 46 ha of the lake bottom at all depths above 2 m, an estimation of the Al content in the upper 10 cm of sediment one month after treatment showed very different amounts at three stations. Seemingly, horizontal redistribution of the Al floc resulted in transport of Al from lake areas exposed to resuspension towards the deeper accumulation areas (Table 4). This became even more pronounced after one year. The observation is supported by, for instance, Garrison and Knauer (1984) and Van Hullebusch et al. (2002), who reported movement of the Al floc in lakes, and by Egemose et al. (2009), who showed that freshly formed Al floc is more easily resuspended than natural sediment 2–4 months after addition. Additionally, Egemose et al. (2010) showed that bottom currents in Lake Nordborg were sufficiently strong to cause horizontal transport of freshly formed Al(OH)₃ floc.

The percentage of mobile P in the sediment decreased one year after treatment. The mechanism is transformation to Al-bound P (Lewandowski et al. 2003; Reitzel et al. 2005). The transformation was not pronounced after one month, but became significant after one year, as transformation is gradual, depending on P release from iron-bound and organic forms and the subsequent binding to the Al floc. The different amounts of Al at the three stations also resulted in different molar Al:P ratios. The ratio was much higher at the deep accumulation station (40) than at the two stations exposed to resuspension (14) after one month, indicating that excess binding capacity was left at the deep station, whereas the floc was more saturated at the two other stations. After one year the tendency remained the same, but with generally lower ratios (7–18) as the Al floc became more saturated with P. de Vicente et al. (2008b) evaluated the realized binding ratios between Al and P in a number of lakes and concluded that at a ratio of 10:1 Al(OH)₃ would be saturated with PO₄³⁻. Al in Lake Nordborg was dosed at a ratio of 8:1 relative to mobile P, and when comparing this ratio with the Al_{NaOH}:P_{ΔNaOH+mobile} ratio, it is obvious that at St. 2 and 3 the available Al does not suffice to immobilize the entire pool of mobile P, whereas at St. 1 the ratio was 10 one year

after addition. However, after 3 years the binding capacity of the Al floc remains sufficiently high to suppress sediment P release at St. 1 and 2, regardless of the low Al:P ratio at St. 2.

Changes in lake water quality

The overall goal in Lake Nordborg was to improve the lake quality by reducing the lake water P concentration. This objective, as well as the reduction in external P load, was also fulfilled 3 years after restoration, whereas an increased light penetration was only obtained during the first post-treatment year where an increased Secchi depth was observed, despite the fact that no significant effects were recorded on the Chl *a* concentration or the sedimentation rates of C and N. However, the higher transparency did not last and in 2009 the Secchi depth returned to pre-treatment levels.

The fact that the Secchi depth increased in 2007 without a concomitant decrease in Chl *a* may be partly due to the sampling procedure, where Chl *a* was measured on a sample mixed from depth up to twice the Secchi depth. Most probably, the improved light climate increased phytoplankton distribution in the water column in 2007, as the light compensation depth as summer average increased from 3.4 m in 2006 to 4.8 m in 2007. That could result in similar Chl *a* concentrations at increased Secchi depths in the mixed water samples. This phenomenon is also a likely explanation as to why no reduction was observed in C and BSi sedimentation rates from 2006 to 2007. The color reduction in all post-treatment years may also partly explain the improved Secchi depth, and may in itself lead to better conditions for phytoplankton growth. In accordance with our results, no Chl *a* reduction was observed in an Al-treated fish pond studied by Lelkova et al. (2008), despite changes in the phytoplankton structure and abundance, and no changes in the summer biomass of phytoplankton were observed in the Eau Galle Reservoir following Al treatment (Barko et al. 1990).

The fish community structure, abundance, and habitat distribution seemingly responded rapidly to the increase in Secchi depth, as investigated in August 2006 and 2007 (Lund et al. 2010). The proportion of perch (*Perca fluviatilis*) in overnight gill net catches increased, while that of roach (*Rutilus rutilus*) decreased, and the average mass of all key species rose. Accordingly, large-bodied zooplankton increased in abundance. Moreover, the habitat distribution of perch and roach changed from a high proportion in the upper pelagic and littoral zones in 2006 towards enhanced proportions in the deeper pelagic and profundal zones in 2007, which may be attributed to an enhanced risk of predation in the upper pelagic and the littoral zones, owing to higher water clarity, and perhaps also improved oxygen concentrations in the deeper profundal zone (Lund et al. 2010). Thus, on the short term, a shift occurred towards fish and zooplankton communities characterizing less eutrophic conditions (Jeppesen et al. 2005).

We conclude that the Al treatment succeeded in reducing the lake water P concentration in the short term, but due to continuously excessive external loading the achieved concentration, seems to be too high to create long-lasting improvements in water clarity. In connection with the implementation of the European Water Framework Directive, Søndergaard et al. (2005b) suggested target concentrations for lake water TP

of 25–50 $\mu\text{g}\cdot\text{L}^{-1}$ in shallow lakes and 12.5–25 $\mu\text{g}\cdot\text{L}^{-1}$ in deep lakes, for achieving good ecological status. These recommendations are based on experiences from Danish lakes. Although the average summer TP concentration in Lake Nordborg declined dramatically, it remained above 25 $\mu\text{g}\cdot\text{L}^{-1}$ in 2007 and above 50 $\mu\text{g}\cdot\text{L}^{-1}$ in 2009, and phytoplankton biomass changed only negligibly. This could suggest a shift in the algal community towards species with higher affinity for P, or to species recycling P more rapidly in the water column. The latter is supported by the lower P sedimentation rates after restoration. Also Steinman and Ogdahl (2008) found that 20–50 $\mu\text{g}\cdot\text{L}^{-1}$ TP was sufficiently high to stimulate phytoplankton production in Spring Lake, USA, where the P concentration decreased, but chlorophyll remained high after Al treatment. Thus, it can be concluded that the in-lake P concentration in Lake Nordborg should be even lower than previously anticipated (Egemose and Jensen 2009) to efficiently control phytoplankton biomass and therefore further reductions of the external P loading are needed.

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