Lake Restoration by Dosing Aluminum Relative to Mobile Phosphorus in the Sediment

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In the shallow, hypertrophic Lake Sonderby, Denmark, potentially mobile phosphorus (Pmobile) was determined by a sequential extraction technique as the sum of porewater P, iron-bound P, and nonreactive P (i.e., polyphosphates and organic P). A good agreement was observed between loss rates of Pmobile in the top 10 cm of the sediment from winter to summer, P release rates measured in undisturbed sediment cores, and rates of P accumulation in the lake water from winter to summer (22, 32, and 30 mg of P m² day⁻¹, respectively). This suggests that the operationally defined Pmobile was the sediment P fraction responsible for the internal loading in the lake. In autumn 2001, 11 mg of aluminum (Al) L⁻¹, equivalent to 31 g of Al m⁻², was added to the lake water. This dosage represented a 4:1 molar ratio between Al and Pmobile. The Al treatment significantly decreased lake water P, and P precipitated from the lake water was recovered as Al-bound P in the sediment after the treatment. Internal P loading was reduced by 93% in the two posttreatment years, relative to 2001. Accordingly, average summer concentrations of total P in lake water declined from 1.28 (SE = 0.17) and 1.3 (SE = 0.14) mg L⁻¹ in the two pretreatment years to 0.09 (SE = 0.01) and 0.13 (SE = 0.01) mg L⁻¹ in the posttreatment years. pH levels remained unchanged relative to pretreatment levels, while the total alkalinity was reduced from 3.2 (SE = 0.04) to 2.7 (SE = 0.03) mequiv L⁻¹.

Introduction

Despite reduced external phosphorus (P) loadings, many lakes have failed to recover from eutrophication due to P release from the sediment during summer (internal P loading). This chemical resilience can maintain lakes in a eutrophic state for up to 30 years (1) and is especially pronounced in lakes with a long residence time (2). It is therefore of major interest to develop restoration methods to overcome the resilience and to speed up the recovery process of eutrofied lakes. Numerous restoration methods have been employed with various successes to improve the water quality in lakes (1, 3, 4). Addition of aluminum (Al) has been used in many lakes, mainly in the United States (5).

Like iron hydroxides, Al hydroxides [Al(OH)₃] are natural P adsorbents in lake sediments, but in contrast to iron-bound P (Fe=P), aluminum-bound P (Al=P) is not dissolved in reducing sediments and may therefore provide a long-lasting sink for bioreactive P. This makes Al addition an attractive method for immobilizing the potentially mobile P pool in the sediment. Aluminum has generally been applied to lakes as alum [Al₂(SO₄)₃·18 H₂O] dissolved in acids (3). When Al is added to lake water, a rapid three-step alkalinity-consuming hydrolysis of Al³⁺ to Al(OH)₃ (Al floc) occurs. Since Al³⁺ can be toxic to fish at low pH values (6), the lake water alkalinity determines the maximum amount of Al that can be added to the lake without lowering pH too much. In particular, the maximum dosage of applied Al is often determined as the maximum amount of Al that can be added until the lake water pH decreases to a value of 6 (3). This dose determination ensures maximum formation of the P-binding Al(OH)₃ with low to no occurrence of the potentially toxic Al³⁺. However, the alkalinity-based dosing of Al does not consider the amount of the mobile P pool in the sediment and lake water. Hence, this approach is subject to potential over- or underdosages of Al, since the mobile P pool is unrelated to the alkalinity of the lake water. Laboratory sediment studies have shown that the mobile P pool that contributes to the internal P loading is composed primarily of Fe=P (7) and nonreactive P (nRP) forms as defined by sequential P extraction techniques (8, this study). In support of this, Hupfer et al. (9) showed that inorganic polyphosphates could constitute up to 46% of the nRP extracted from some German lake sediments. As polyphosphates (9) and pyrophosphates (10) degrade rapidly in sediments, these inorganic P compounds should be taken into account when the mobile P pool in sediments is estimated.

Ryden and Welch (11) proposed dosing of Al to lakes based on the concentrations of porewater P and Fe=P in the sediment. This approach addresses the problem more directly than does the alkalinity-based dosage provided that the amount of P inactivated by Al can be predicted for a given Al dose. In this study, we suggest that nRP should be included in the operationally defined mobile P pool (Pmobile), and that a molar ratio between Al and Pmobile of 4:1 is sufficient to ensure a low concentration of phosphate in solution. The suggested ratio is in contrast to Ryden and Welch (11), who recommended a 85:1 ratio. While they based their estimate on observations of Al=P in Wisconsin lakes, our suggestion is based on studies involving pure phases of Al(OH)₃ and dissolved inorganic phosphate (DIP) (12), results from wastewater treatment (13), and on laboratory studies and enclosure experiments (14) where Al was added in a molar ratio of 4:1 relative to Pmobile in the sediment. In the present paper we test the effectiveness of the method in a full-scale lake restoration project in the hypertrophic Lake Sonderby, Denmark. The 4:1 dosage used in Lake Sonderby was about 4 times lower than the alkalinity-based dosage would have been if alum was used. The Al addition was carried out in autumn 2001, and data on sediment P distribution, sediment P efflux, and lake water P from two pretreatment years and two posttreatment years are presented. Furthermore, an estimate of how the aluminum treatment might have changed the mass balance for P is provided.

Materials and Methods

Study Site. Lake Sonderby is a small (8 ha, mean depth = 2.8 m, maximum depth = 5.7 m), hard water (surface alkalinity ~3 mequiv L⁻¹) and hypertrophic lake situated in the southern central part of Denmark (55° 11′ 46″ N, 9° 21′ 90″).
E) (Figure 1). The catchment area is 122 ha, with farmland contributing 85%, wetland 6%, and roads and urban areas 9%. Inlets are through subsurface drainpipes, and outlet occurs through seepage (90%) and by pumping at high water levels in winter (10%). Water balance is calculated from the runoff height measured in similar nearby, gauged watersheds representing 68% of the watershed as well as on experience from similar gauged watersheds. As a result of the sewage diversion, the annual average lake water TP concentration declined from 3 to 1.5 mg L⁻¹ in 1997 but was still high in 2001.

The lake continued to be dominated by massive blooms of cyanobacteria, which resulted in average summer (1 May to 30 September) Secchi depths between 0.5 and 1.3 m in the postdiversion period. Because of low summer Secchi transparency, submerged macrophytes were almost nonexistent. Thus, only one specimen of Potamogeton crispus was observed in 1991 and none in the following years.

Sediment Analysis. Sediment was sampled at two stations (station 1 at ~5 m depth, station 2 at ~2 m depth; Figure 1) with a Kajak gravity corer (inner diameter = 7.2 cm, height = 40 cm) in February and August 2001 to represent pretreatment conditions, and at station 1 in February 2003 to represent posttreatment conditions. In December 2004, longer cores (60 cm) from the two stations were sampled for sediment dating. Except for these cores, which were analyzed individually, replicates of three sediment cores were sectioned at intervals of 1 cm down to 5 cm and at 2-cm intervals from 5 to 15 cm depth, and the three slices from each depth interval were pooled before analysis. The sediment was extracted according to Paludan and Jensen (15) with a series of extractants (water, bicarbonate-dithionite, 0.1 mol L⁻¹ NaOH, and 0.5 mol L⁻¹ HCl), resulting in the following P fractions: water-soluble P (P_water), redox-sensitive P (P_red), NaOH-extractable P (P_NaOH), humic-bound P (P_humic), HCl-soluble P (P_HCl), and the remaining P not extracted (P_not). Inorganic P in solution (DIP) was determined as molybdenum-reactive P (16), and TP in the extracts was measured after wet oxidation by potassium permanganate (16). From the difference in TP and DIP in the P_water, P_red, and P_NaOH extracts, the nrP was calculated. The sum of nrP in the three extracts is believed to represent labile P compounds (8, 17). P_mobile is the upper 10 cm of the sediment was determined as the sum of P_water, P_red, and nrP since these fractions constitute the P that can be released during anoxic periods and by degradation of organic matter.

Total sediment P was determined on parallel sediment samples by ashing (520 °C, 8 h) followed by 1 mol L⁻¹ hot HCl extraction and measurement of DIP in the extract. DIP was measured as molybdenum blue complexes on extracts from all steps (16).

Aluminum was measured in all the extracts, but data are only shown for the NaOH extracts (AlNaOH) as this was the only extract with an increase in Al after the Al treatment. Also, results from a study of pure phases (18) show that Al(OH)₃ is recovered specifically in the NaOH step of the extraction procedure. AlNaOH was measured by flame atomic absorbance spectrometry at 309 nm with a N₂O flame.

The sediment was also analyzed for dry weight (DW) (105 °C, 24 h) and loss on ignition (520 °C, 8 h). Addition of Al to the sediment led to an increase in sediment DW (19). To avoid misinterpretations due to DW changes, all comparisons of pre- and posttreatment sediment data are expressed per volume as micrograms per cubic centimeter.

Sediment cores used for dating were sliced at 1-cm intervals down to 35 cm (station 1) and 25 cm (station 2), freeze-dried, and analyzed for unsupported ²¹⁰Pb and ¹³⁷Cs by nondestructive γ ray detection. Concentrations of unsupported ²¹⁰Pb were related to mass depth and analyzed by the constant initial concentration (CIC) method (20).

P Release Measurements. In February 2001 and 2002, five sediment cores (inner diameter = 5.2 cm, height = 30 cm) were sampled at station 1 for measurement of sediment P release rates. The cores were placed in darkness in incubation chambers containing oxic lake water at 16 °C for 26 days. Sediment height was adjusted to give 15 cm of overlying water in all cores, and a magnetic stirrer was placed 5 cm above the sediment surface to ensure mixing of core water with water in the incubation chamber in the periods between measurements of DIP effluxes. Effluxes of DIP over the sediment—water interface were measured as changes in DIP concentrations over 24 h in the 15 cm water column, which was isolated from the incubation chamber by a rubber lid during measurements. Water removed by sampling was replaced with lake water. Efflux measurements were carried out five times during the experiment. Accumulated P release rates for 26 days were calculated for each core by interpolation between measurements. Results are presented as the daily release rate for the five replicate cores. Comparison between control cores and the Al-treated cores was performed by a t-test.

In-Lake Monitoring. Due to thermal stratification during the summer period, mixed water samples from 0.2 m, 1× Secchi depth, and 2× Secchi depth at station 1 were pooled and analyzed for total nitrogen (TN), TP, DIP, and chlorophyll a (Chl a). Samples were collected at least once a month, but in summer 2002 sampling was more frequent. Surface water samples were analyzed for total alkalinity (TA) and pH. All samples were analyzed according to the Danish Nation-wide Monitoring Program (21).
On the basis of evaluation of the TP concentrations in the water, the net internal P loading (including loss of P by sedimentation) was determined as the difference between the maximum accumulation of TP in the lake water and the background P level just before the onset of internal P loading. Since the external P is mainly brought to the lake in the winter, the possible contribution of external P loading to the summer increase in lake water TP was neglected. In support of this, our results showed that lake water TP increased by more than 300 kg of P during the summer period while annual external P loading was only 50 kg.

**Application of Aluminum.**  
$P_{\text{mobile}}$ for the whole lake was calculated from the amounts of $P_{\text{mobile}}$ present in the top 10 cm of sediment, sampled in winter, from water depths below 1.5 m. Stations 1 and 2 each represented 3 ha of the lake bottom, and $P_{\text{mobile}}$ was calculated as 720 kg.

To reach a 4:1 molar ratio between Al and P, 26 m$^3$ of buffered polycationic polyaluminum chloride solution (PAXXI-60, Kemira Miljù A/S) were applied to the lake during two periods: 25–26 October and 8–9 November 2001. The Al solution was pumped to an application boat where the Al solution was applied directly to the propel water of the outboard engine on the boat, behind which a mixing aggregate was mounted. This ensured a rapid floc formation and an efficient horizontal distribution of the resulting Al floc. After application, the Al floc covered most of the lake (~85–90%) except for the near shore area, corresponding to a dose of 31 g of Al m$^{-2}$.

**Results**  

Depth distribution of the seven various sediment P pools at stations 1 and 2 was measured in February 2001 (Figure 2). At both stations $P_{\text{BD}}$ and $nrP$ constituted a relatively large proportion of TP in the upper centimeters of the sediment. These P pools decreased rapidly with increasing sediment depth, and $P_{\text{mobile}}$ had a half-lifetime of 10.3 years ($r^2 = 0.90$, $n = 8$, $p = 0.003$) and 10.7 years ($r^2 = 0.98$, $n = 8$, $p = 0.0001$) at stations 1 and 2, respectively. In comparison, $P_{\text{HCO}_3}$, $P_{\text{NH}_4}$, and $P_{\text{NaOH}}$ remained much more constant with increasing sediment depth. At station 1 these P pools remained constant in the upper 15 cm, and thus no half-lifetime could be estimated. At station 2, these immobile P pools had a half-lifetime of 104 years ($r^2 = 0.90$, $n = 8$, $p = 0.003$).

In the deepest sediment layers analyzed (30–35 cm at station 1 and 20–25 cm at station 2), where the sediment was approximately 50 years old, TP concentration was constant at 1.35 mg of P g$^{-1}$ dry matter at both stations, with $P_{\text{mobile}}$ contributing only 0.25 mg of P g$^{-1}$.

Sediment accumulation rates calculated from $^{210}$Pb dating were $500 \pm 200$ g DW year$^{-1}$ at station 1 and $300 \pm 40$ g year$^{-1}$ at station 2. In comparison with the $^{210}$Pb chronology, $^{137}$Cs increased in concentration from year 1986 to 1990 at both stations. This is likely due to deposition of $^{137}$Cs from the Chernobyl accident in 1986. Thus, the two methods agreed fairly well in the resulting accumulation rates. The burial flux of P was calculated from the constant concentration in the 50-year-old sediment with the two stations each representing 3 ha of the lake bottom. The resulting burial flux was 32.1 kg of P year$^{-1}$.

Sediment concentrations of $P_{\text{mobile}}$ from February 2, 2001 and August 24, 2001 at station 2 showed that the winter concentration of $P_{\text{mobile}}$ was almost twice as high as the summer concentration in the upper 4 cm of the sediment, whereas this difference gradually decreased below 4 cm sediment depth (Figure 3). Station 1 was not sampled in August.

**Changes in Lake Water Chemistry due to Al Addition.**  
The addition of Al resulted in a dramatic reduction in lake water TP and DIP, from 1.5 mg L$^{-1}$ to 0.04 and 0.003 mg of...
The characteristic summer peaks in TP and DIP in the pretreatment years were not observed in 2002 and 2003. High average summer TP and DIP concentrations prevailed before the Al treatment (Table 1). After the treatment the average summer TP concentrations were reduced significantly from 1.28 mg L\(^{-1}\) (SE = 0.17) in 2000 and 1.13 mg L\(^{-1}\) (SE = 0.14) in 2001 to 0.09 mg L\(^{-1}\) (SE = 0.01) in 2002 and 0.13 mg L\(^{-1}\) (SE = 0.14) in 2003. The average summer DIP concentration was reduced significantly from 1.16 mg L\(^{-1}\) (SE = 0.16) in 2000 and 1.11 mg L\(^{-1}\) (SE = 0.12) in 2001 to 0.04 mg L\(^{-1}\) (SE = 0.01) in 2002 and 0.05 mg L\(^{-1}\) (SE = 0.01) in 2003.

After the Al treatment, the laboratory and in-lake measurements of P release rates were lowered by \(90\%\) (Table 2). The two methods for estimating P release (observed rate of P accumulation in the lake water and direct measurement of P release from intact sediment cores) showed good agreement both prior to and after the Al treatment.

Generally the TN:TP molar ratio was below 10 in the pretreatment years 2000 and 2001 with summer averages of 3 (SE = 0.47) and 4 (SE = 0.92), respectively (Table 1). Al

### TABLE 1. Average Summer (May–September) Values of TP, DIP, Chl \(a\), Secchi Depth, pH, Alkalinity, and TN:TP in the Lake Water

<table>
<thead>
<tr>
<th>Year</th>
<th>TP (mg L(^{-1}))</th>
<th>DIP (mg L(^{-1}))</th>
<th>Chl (a) ((\mu)g L(^{-1}))</th>
<th>Secchi depth (m)</th>
<th>pH</th>
<th>Alkalinity (mequiv L(^{-1}))</th>
<th>TN:TP (molar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>1.28 (0.17) a</td>
<td>1.16 (0.16) a</td>
<td>51 (5) a</td>
<td>1.04 (0.06) a</td>
<td>8.35 (0.09) a</td>
<td>3.33 (0.13) a</td>
<td>3.12 (0.47) a</td>
</tr>
<tr>
<td>2001</td>
<td>1.30 (0.14) a</td>
<td>1.11 (0.12) a</td>
<td>98 (35) a,b</td>
<td>1.17 (0.11) a</td>
<td>8.46 (0.09) a</td>
<td>3.20 (0.04) a</td>
<td>3.88 (0.92) a</td>
</tr>
<tr>
<td>2002</td>
<td>0.09 (0.01) b</td>
<td>0.04 (0.01) b</td>
<td>31 (6) b</td>
<td>2.38 (0.54) a</td>
<td>8.22 (0.09) a</td>
<td>2.72 (0.03) b</td>
<td>22.6 (2.6) b</td>
</tr>
<tr>
<td>2003</td>
<td>0.13 (0.01) b</td>
<td>0.05 (0.01) b</td>
<td>44 (14) a,b</td>
<td>1.88 (0.40) a</td>
<td>8.39 (0.09) a</td>
<td>2.74 (0.02) b</td>
<td>22.2 (2.6) b</td>
</tr>
</tbody>
</table>

* Weighted average values are calculated for each month. Different letters indicate values that are significantly different \((p < 0.05)\) in a t-test with Bonferroni adjusted probabilities. SE is given in parentheses.

### TABLE 2. Amounts of \(P_{\text{mobile}}\) in the Sediment and TP in the Lake Water during Winter and Summer for Two Years before and Two Years after Al Addition

<table>
<thead>
<tr>
<th>Year</th>
<th>(P_{\text{mobile}}) in sediment</th>
<th>TP in lake water</th>
<th>Accumulation</th>
<th>Sediment P efflux</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>winter (kg)</td>
<td>summer (kg)</td>
<td>(kg)</td>
<td>(mg m(^{-2}) d(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>2001 (b)</td>
<td>2001 (c)</td>
<td>2001 (d)</td>
<td>2001 (e)</td>
</tr>
<tr>
<td></td>
<td>1037</td>
<td>686</td>
<td>351</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>67</td>
<td>401</td>
<td>334</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>109</td>
<td>357</td>
<td>248</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>49</td>
<td>406</td>
<td>357</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>35</td>
<td>24</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>35</td>
<td>26</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>32 (11.5)</td>
<td></td>
<td></td>
<td>5 (1.6)</td>
</tr>
</tbody>
</table>

* Accumulation of TP in the lake water is compared with changes in \(P_{\text{mobile}}\) for year 2001 and with measured sediment P release rates for years 2001 and 2002 (before and after Al addition). Calculations of accumulation and P release rates are based on the following assumptions: lake area is 78 000 m\(^2\) and lake volume is 223 000 m\(^3\). Notice that the two TP accumulations in the lake water in 2001 are based on different calculations.

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**P L\(^{-1}\)**, respectively (Figure 4). The characteristic summer peaks in TP and DIP in the pretreatment years were not observed in 2002 and 2003. High average summer TP and DIP concentrations prevailed before the Al treatment (Table 1). After the treatment the average summer TP concentrations were reduced significantly from 1.28 mg L\(^{-1}\) (standard error of the mean \(SE = 0.17\) in 2000 and 1.13 mg L\(^{-1}\) \(SE = 0.14\) in 2001 to 0.09 mg L\(^{-1}\) \(SE = 0.01\) and 0.13 mg L\(^{-1}\) \(SE = 0.01\) in 2002 and 2003, respectively. The average summer DIP concentration was reduced significantly from 1.16 mg L\(^{-1}\) \(SE = 0.16\) in 2000 and 1.11 mg L\(^{-1}\) \(SE = 0.12\) in 2001 to 0.04 mg L\(^{-1}\) \(SE = 0.01\) in 2002 and 0.05 mg L\(^{-1}\) \(SE = 0.01\) in 2003.

After the Al treatment, the laboratory and in-lake measurements of P release rates were lowered by \(\sim 90\%\) (Table 2). The two methods for estimating P release (observed rate of P accumulation in the lake water and direct measurement of P release from intact sediment cores) showed good agreement both prior to and after the Al treatment.

Generally the TN:TP molar ratio was below 10 in the pretreatment years 2000 and 2001 with summer averages of 3 \(SE = 0.47\) and 4 \(SE = 0.92\), respectively (Table 1). Al
addition resulted in a significant increase in the summer average TN:TP molar ratios to 23 (SE = 2.6) in 2002 and 22 (SE = 2.6) in 2003.

Compared to pretreatment years, the average summer Chl a concentrations decreased from 51 μg L⁻¹ (SE = 5) and 98 μg L⁻¹ (SE = 35) in 2000 and 2001, respectively, to 31 μg L⁻¹ (SE = 6) and 44 μg L⁻¹ (SE = 14) in 2002 and 2003, respectively (Table 1). Due to large month-to-month variations during the summer, only the years 2000 and 2002 have significantly different values (Table 1).

During the summer periods of 2002 and 2003, the Secchi depth increased compared to pretreatment years with the following summer averages: 1.04 m (SE = 0.06) in 2000, 1.17 m (SE = 0.11) in 2001, 2.38 m (SE = 0.54) in 2002, and 1.88 m (SE = 0.40) in 2003 (Table 1). As for Chl a, the values are not significantly different due to large month-to-month variations (May and June had monthly average values of 3–4 m after the treatment but only 1–1.4 m before treatment).

The pH decreased from 8 to 7.5 immediately after Al addition but returned to pretreatment levels within 6 days. The summer averages remained almost the same before and after Al treatment (Table 1). Total alkalinity was reduced significantly by ~0.5 mequiv L⁻¹ after Al addition. This reduction was maintained throughout the monitoring period (Table 1).

Changes in Sediment Chemistry due to Al Addition.

Increased amounts of PNaOH and TP (Figure 5) were found in the upper 5 cm of the sediment at station 1 in the posttreatment year 2003 relative to the pretreatment level in 2001. PNaOH increased from ~13 to 90 μg cm⁻³ in the upper 3 cm and from 13 to 140 μg cm⁻³ in 3–5 cm sediment depth after Al addition. Below 6 cm depth, PNaOH showed pretreatment concentrations. Total P increased in a similar way as PNaOH, with a peak at 5 cm depth (336 μg cm⁻³). The PBD showed a small increase from 40 to 50 μg cm⁻³ in the upper 4 cm of the sediment. At 5 cm an increase from 34 to 60 μg cm⁻³ was observed in 2003. Below 6 cm, the PBD in 2003 showed pretreatment concentrations (Figure 5).

Significant correlations were found between increases in TP and increases in PNaOH, PBD, and (PNaOH + PBD). The correlations revealed the following equations: \( P_{\text{NaOH}} = 0.73TP + 10.5 \) \((r^2 = 0.84, n = 6, p = 0.006)\), \( P_{\text{BD}} = 0.16TP + 5.00 \) \((r^2 = 0.73, n = 6, p = 0.02)\), and \( (P_{\text{NaOH}} + P_{\text{BD}}) = 0.88TP + 5.45 \) \((r^2 = 0.93, n = 6, p = 0.001)\). Thus, PNaOH was responsible for most of the observed increase in TP from 2001 to 2003.

In 2001 the concentration of AlNaOH in the upper cm of the sediment was 100 μg cm⁻³, but below 2 cm depth AlNaOH decreased to 0 (Figure 5). In 2003 the AlNaOH concentrations in the upper 5 cm of the sediment was 400 μg cm⁻³ in the upper centimeters of the sediment and increased to 900 μg cm⁻³ at 5 cm depth. Below 5 cm the AlNaOH remained constant at ~250 μg cm⁻³.

A correlation of the increases in PNaOH and AlNaOH revealed the following equation: \( P_{\text{NaOH}} = 0.13Al_{\text{NaOH}} - 2.5 \) \((r^2 = 0.85, n = 6, p = 0.006)\), which is equivalent to a molar Al:P binding ratio of 7.7.

The laboratory DIP release measured in intact sediment cores collected from the profundal zone in 2001 and 2002 showed a reduction from 32 to 5 mg m⁻² day⁻¹ after Al addition \((n = 5, p = 0.07)\) (Table 2).

Mass Balance for P. The mass balance for P is estimated for pretreatment and posttreatment years (Table 3) but is subject to large uncertainties. The external P loading after 1983 is probably fairly accurate, while the burial flux as calculated from the constant P concentration in 50-year-old sediment may represent a too-high estimate for the burial flux after sewage diversion. Sedimentation rates, however, seemed rather constant for the entire period. The net loss of PBD for the period 1983–2001 \((14.5 \text{ kg year}^{-1})\) is calculated from the decrease in maximum lake water TP concentration observed at summer for the period 1983–2001. \(^*\) The estimate for P lost with outflowing water is calculated by assuming a balanced budget for the years 1983–2001 and by assuming an average concentration of 0.025 mg of P L⁻¹ for the years 2002 and 2003. This value is the winter average PO₄³⁻ concentration in the two posttreatment years.

<table>
<thead>
<tr>
<th>TABLE 3. Mass Balances for P before and after the Aluminum Treatment in 2001*</th>
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</thead>
<tbody>
<tr>
<td>external P loading</td>
</tr>
<tr>
<td>burial in sediment</td>
</tr>
<tr>
<td>net loss of Pmobile (^*)</td>
</tr>
<tr>
<td>estimated loss by seepage and outflow (^*)</td>
</tr>
<tr>
<td>balance</td>
</tr>
</tbody>
</table>

\(^*\) All values are in kilograms of P per year. \(^*\) The number for net loss of mobile P is calculated from the decrease in maximum lake water TP concentrations observed at summer for the period 1983–2001. \(^*\) The estimate for P lost with outflowing water is calculated by assuming a balanced budget for the years 1983–2001 and by assuming an average concentration of 0.025 mg of P L⁻¹ for the years 2002 and 2003. This value is the winter average PO₄³⁻ concentration in the two posttreatment years.
balance the P budget for 1983–2001, this requires a gross outflow of P of 32.4 kg year\(^{-1}\). This implies that the water lost by seepage and pumping should have a P concentration of 0.16 mg L\(^{-1}\), which is well below observed winter DIP concentrations for most of the period. For the years after aluminum addition, the loss of P with seepage water is estimated at a maximum of 5.6 kg year\(^{-1}\), corresponding to a P concentration of 0.025 mg L\(^{-1}\), which is the new winter DIP concentration. With these assumptions the mass balance shows a small surplus of P in the inlet of 2.3 kg (Table 3), indicating that the P concentration in the lake water will increase until equilibrium with the external P load and loss processes is reached.

**Discussion**

By dosing Al relative to \(P_{\text{mobile}}\), in the sediment, the lake water P concentration was reduced dramatically, without any negative effects on pH. Thus, a 93\% reduction in the internal P loading relative to 2001 was achieved in the two posttreatment years. The effectiveness of the Al treatment was further supported by the laboratory P release measurements, where an 84\% reduction in the P release was observed relative to pretreatment conditions. Statistically, this reduction was not significant due to a relatively high variation in the experiment from 2001. The reduced P concentration in the lake led to increased molar TN:TP, and high Secchi depths in posttreatment years resulted in the reestablishment of submerged macrophytes. Correspondingly, there was a tendency for decreased Chl \(a\) concentrations in posttreatment years. The lack of a stronger response in Chl \(a\) could be due to N limitation in pretreatment years keeping Chl \(a\) at a moderate level. Compared to 2001, the average summer TP concentrations in 2002 and 2003 were reduced by 92\% and 89\%, respectively, leading to TP concentrations between 0.05 and 0.16 mg L\(^{-1}\).

**Mass Balance for P.**

The annual mass balance for the posttreatment years suggests that loss processes nearly balanced the external P loading. The small surplus of 2.3 kg year\(^{-1}\) will, however, result in an annual increase of 0.01 mg of P L\(^{-1}\) year\(^{-1}\) until a new equilibrium is reached with increased losses with seepage and pumping. The mass balance for the pretreatment years with a net loss of 14.5 kg of P year\(^{-1}\) indicates that it would have taken at least 50 years to reach the same P level in the lake as was obtained by the aluminum addition and the 20\% reduction in external loading.

The release of 351 kg of P from \(P_{\text{mobile}}\) in the sediment from winter to summer in the pretreatment year 2001 corresponded to the increase in the lake water TP during the same period. Assuming low external P loading during the summer and that station 2 represents the whole lake, the link between \(P_{\text{mobile}}\) and the lake water TP provides a strong argument supporting our assumption, that \(P_{\text{mobile}}\) is indeed represented by the three fractions (\(P_{\text{Water}}, P_{\text{BD}}, \) and \(P_{\text{nr}}\)). This finding is also supported by Rydin (8), Hansen et al. (19), and Reitzel et al. (14). Furthermore, the low and similar half-lifetimes of \(P_{\text{mobile}}\) (10 years) at the two stations compared to the immobile P pools (half-lifetimes above 100 years) further support our hypothesis. Additional evidence for the assumption that the lake water TP during summer was controlled by internal P loading is the good agreement between pretreatment P release rates based on laboratory experiments and in-lake measurements of TP changes. The very good agreement between the released \(P_{\text{mobile}}\) and the internal P loading in Lake Sønderby suggests that it is generally possible to define the sediment P pools that are responsible for the internal P loading by use of the sequential extraction scheme applied for this study.

**Binding Sites for Sediment P after Al Addition.**

The immobilization of lake water and sediment P with Al was clearly reflected in the upper 5 cm of the sediment profiles as increases in \(P_{\text{NaOH}}\), TP, added to a lesser extent \(P_{\text{BD}}\), when sediment samples from 1991 and 2003 were compared. 88\% of the increase in TP was explained by the combined increases in \(P_{\text{BD}}\) and \(P_{\text{NaOH}}\). A similar correlation between TP and \(P_{\text{NaOH}}\) showed that 73\% of the increase in TP was explained by the increase in \(P_{\text{NaOH}}\). We conclude from this that the majority of the P precipitated by Al was recovered in \(P_{\text{NaOH}}\). This finding is in agreement with, for example, Rydin and Welch (11), Hansen et al. (19), and a study of P bound to pure phases of Al(OH)\(_3\) (18). The small increase in \(P_{\text{BD}}\) in the upper 5 cm of the sediment is probably a result of extraction of loosely sorbed Al=P by the BD solution. Reitzel (18) extracted ~5% of the Al=P by the BD solution.

Quantitatively, the Al-induced increase in TP in the upper 5 cm of the sediment equaled 6.6 g of P m\(^{-2}\). This increase was caused by (1) P initially removed from the water column by precipitation with Al, (2) P from sedimentation in the posttreatment period, and (3) P released within and below the Al layer. Since ~4.6 g of TP m\(^{-2}\) was precipitated from the water phase at the Al addition, the remaining 2 g of TP m\(^{-2}\) represent P from the sediment and P brought to the Al layer by sedimentation. Due to the small increase in lake water TP in 2002, the resulting sedimentation should be low, and we therefore assume that most of the 2 g of TP m\(^{-2}\) originated from P migrating from deeper layers of the sediment due to postdepositional mobility, in agreement with Carignan and Flett (22). As a consequence, the migrating P represented ~1/3 of the total increase in Al=P after ~18 months. Thus, we hypothesize that the Al floc not only captures phosphate from lake water and pore water at the moment of addition but also provides a barrier against phosphate diffusing from deeper sediment layers as long as there is excess binding capacity for P.

Since Al hydroxides are expected to be extracted by NaOH (15, 18), an increase in \(P_{\text{NaOH}}\) was expected after the Al treatment. In fact, the highly significant correlation between increases in \(P_{\text{NaOH}}\) and increases in \(P_{\text{NaOH}}\) showed that the increased P binding capacity in the sediment was actually due to the Al treatment. This finding is in agreement with Rydin and Welch (11) and Lewandowski et al. (23). The Al:P molar binding ratio in the NaOH extract was 7.7. Other comparable Al:P molar ratios from Al-treated lakes range from 2.2 (23) to 12.6 (24). As the Al:P molar ratio is affected by the amount of Al added, P forms in the sediment, and probably also by diagenic processes, these ratios are difficult to compare. In Lake Süsser See, 100 g of Al m\(^{-2}\) was added to sediment with ~2 mg of TP (g DW\(^{-1}\)) (23). Depending on the amount of \(P_{\text{mobile}}\) at the time of dosing, this dose should theoretically result in a higher Al:P molar binding ratio compared to the Al:P molar ratio in Lake Sønderby, where 31 g of Al m\(^{-2}\) was dosed to sediment with ~3 mg of TP (g DW\(^{-1}\)). Because the Al treatment in the study by Lewandowski et al. (23) took place in 1977–1992, the Al floc has been subject to diagenetic processes for a longer period than the floc in Lake Sønderby. Therefore, the lower Al:P ratio in Lake Süsser See could imply that the Al:P molar binding ratio decreases with time as long as the Al layer has excess P binding capacity. Then a high Al:P molar binding ratio might indicate either excess binding capacity for P, and thus give an indication of the longevity of the Al treatment, or an Al layer that is less efficient in P immobilization.

In this study we provided strong evidence for the assumption that the internal P loading in Lake Sønderby was caused by three operationally defined P pools in the sediment. This finding enabled us to perform a specific dosing of Al relative to \(P_{\text{mobile}}\). In the sediment with only 1/3, the Al dose recommended by Cooke et al. (3). Still, positive effects on important water quality parameters were observed in the first two posttreatment years. Further development of the
concept “potentially mobile P” to other sediment types will provide important information regarding the source for internal P loading, and thereby this concept may become an important tool in lake management.

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Literature Cited

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