Biochemical Oxidation of Polluted Lake Sediment with Nitrate - A New Lake Restoration Method

Report

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A method for restoration of lakes which have been polluted by sewage is described. The method is based on the *in situ* oxidation of sediments by means of suitable oxidation agents. The chemicals, iron chloride, slaked lime and calcium nitrate, were injected into the sediments, improving the binding capacity for phosphorus and reducing the amounts of easily degradable organic matter. The nutrient recycling to the water body, as well as the biological oxygen demand (BOD) at the sediment surface, were thus reduced. In Lake Lillesjön, Sweden, a drastic reduction of the nutrient levels and an improvement of the oxygen conditions in the water near the bottom during summer 1975 were achieved. The method is less expensive, and more rapid than sediment dredging methods. Restricted areas of sediments with high oxygen demand can be treated, and the recycling of phosphorus from these polluted sediments thus avoided.

Many lakes, especially those situated in the vicinity of densely populated areas, have been used as receivers for water degraded by different sources of pollution. Depending on size, hydrological and morphometrical conditions, the lakes have sooner or later been damaged. These lakes often become an environmental nuisance because of fermentation processes during anoxic periods, H_2S development and fish deaths.

Lake restoration has in recent times become a subject of considerable interest (1, 2). Several measures to restore lakes have been proposed. The dredging of the uppermost nutrient-rich sediments has proved satisfactory under certain conditions. In Lake Trummen, improvements in the water quality were obtained by suction dredging (3). In special cases the removal of hypolimnetic waters by means of Olszewski tubes improved the conditions in lakes (4, 5). In other cases, aeration of the water temporarily suppressed anaerobic fermentation and, through iron-phosphorus interactions, decreased the trophic status. This has been accomplished in Wahnbachtalsperre, Germany (6), Swiss lakes (7), Järlasjön, Sweden (8) and in Lake Grebinersee, Germany (9). In the United States, Fast (10) has done a thorough study of this method. A prerequisite for all these means of restoration is of course a previous diversion of all sewage, or the installation of efficient water-treatment plants which reduce the nutrients rigorously.

The restoration method described here is based on the *in situ* oxidation of the nutrient-rich organogenic sediments by nitrate as an oxidant. Easily degradable organic matter is oxidized through denitrification processes. The reaction products in these processes, maintained by microbial denitrifiers, are CO_2 and molecular N_2 released to the atmosphere. No other gases (*eg* NO_x) have been detected in these studies. Laboratory studies, field studies and a tentative restoration of a lake have been performed. In the lake the added nitrate was denitrified after seven weeks and very low levels of nitrate were obtained in the water as well as in the interstitial water. Laboratory studies on sediment cores revealed that addition of nitrate to reduced sediments would result in:

1. *Rapid oxidation of the upper layer of the sediments.* At a temperature of 20°C, five to eight cm of the sediment surface was oxidized within one week. As a result, the sulfides disappeared, the color due to oxidized iron turned brown, and the phosphorus concentration in the water above the sediment decreased to normal levels found under oxidized conditions.
2. *Decrease in oxygen demand.* The oxygen demand of the nitrate-treated sediment decreased markedly. This was not only observed during the time nitrate was present but also after the nitrate had disappeared. If suitable amounts of nitrate are applied, a consistent permanent effect may be achieved by this treatment.
3. *General retardation of the exchange reactions of phosphorus and iron.*
4. *Almost immediate denitrification.* The added nitrate disappeared and a vigorous gas development occurred, which was mainly molecular nitrogen. At the same time methane fermentation was disrupted and H_2S was no longer produced.

DESCRIPTION OF LAKE LILLESJÖN

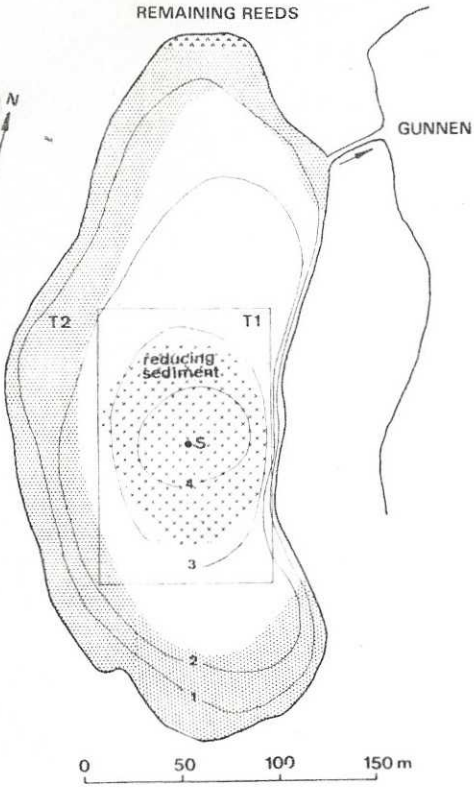
Lake Lillesjön is situated in the south Swedish uplands close to the town of Värnamo in the county of Jönköping (Figure 1, Box 1). A small community has used the lake as a receiver for sewage for several years. In 1971 sewage was diverted from the lake to a treatment plant (11). Because of the size and the protected site of the lake, the ecosystem was severely damaged. Dead fish were often seen and the lake was high in nutrients. Early in the spring it was covered by *Lemna minor* (Box 2). After the occurrence of *Lemna*, a heterotrophic community consisting of bacteria and in the upper water layers zooplankton such as *Daphnia* (Box 2) consumed almost all the available oxygen in the total water column. On several occasions oxygen concentrations of 0.5 mg O_2/l at a depth of 0.2 meters were found. In the late summer, vigorous gas development took place in the sediments.

Thermal stratification appeared early after the break-up of the ice and lasted until late autumn, accompanied by H_2S development in the hypolimnion.

The sediment in Lake Lillesjön was very loose, and no distinct interface between sediment and water could be established. The content of organic matter in this sediment was very high (56 percent of the dry matter content). Because of the long and periodic anoxic conditions, the sediment had become depleted in iron and manganese. While sediments of nearby lakes showed values of 30–50 mg Fe/g dry matter, the sediments in Lake Lillesjön had a content of 9–23 mg Fe/g dry matter. Even the phosphorus content when related to the dry matter was rather low (1.4–3 mg P/g dry matter). Very high values of phosphorus were, however, found in the interstitial water.

Laboratory exchange experiments showed that, under anaerobic conditions, the concentration at equilibrium in water above the sediment was about 10 mg P/l. The rate of exchange was at that time impossible to determine because of the sediment properties, mainly the fermentation activity, and the vigorous gas production. *In situ* measurements showed that a short time after stratified conditions had been established, the phosphorus concentrations in the hypolimnion increased to levels of

Figure 1. Map of Lake Lillesjön with depth data.
S = Sampling point at maximum depth 4.2 m.
T1 = Area of sediment treatment.
T2 = Area of vegetation treatment.



more than 3 mg P/l. The phosphorus concentrations in the epilimnion varied between 0.1 and 2 mg P/l. The nigrogen content in the interstitial water was extremely high (about 60 mg NH_4-N/l in the upper sediment layers). In the hypolimnion, 20 mg NH_4-N/l was recorded.

RESTORATION PROCEDURES IN LAKE LILLESJÖN

The treatment of the lake was divided into two different procedures: the treatment of the sediment and the treatment of the vegetation.

Box 1.
Morphometrical and hydrological data for Lake Lillesjön

Coordinates: 57°10'N, 13°56'E
Height above sea level: 166 m
Area: 4.2 hectares
Maximum depth: 4.2 m
Mean depth: 2 m
Precipitation area: 1 km^2
Average run-off to the lake:
≈ 10 l × sec^{-1} seepage
Theoretical water retention:
3–4 months
Geological characteristic of area:
1. Moraine from archaean rocks
2. Peat areas
Vegetation of the surroundings:
Spruce forest

Treatment of the sediment. The sediment was treated after the restricted deep zone had been stratified for about two months at the end of April 1975. The treated area comprised 1.2 hectares (Figure 1). Box 3 gives all important information concerning the chemical treatment of the lake.

As the first additive, solutions of iron were chosen. The natural iron already deposited in the sediments was in a reduced state as ironsulfide, hardly exerting any phosphorus-binding properties. A solution of trivalent iron-chloride with an iron content of 175 g Fe/l (Ferriflock, EKA Bohus) was mixed in a container and diluted tenfold with lake water. This solution was applied to the sediments by means of a special device (see Figure 2). When the mixture was applied, it diffused down to the sediments and was covered by the resedimenting particles. When the acid iron-chloride solution was introduced, the pH in the sediment was decreased by protolysis of the iron solution, and the sulfides became un-

Box 2.
Common names of plants and animals

Lemna minor = duck weed

Daphnia = water flea

Calla palustris = water arum

Nuphar = yellow water lily

Nymphaea = white water lily

Chara, **Nitella** = stoneworts

Box 3.
Restoration data for Lake Lillesjön

1. Sediment, treatment
Treated area: *ca* 1.2 ha
1 st additive:
13 tonnes $FeCl_3$ (Ferrifloc) = 146 g Fe × m^{-2}
Reactions in sediment:

$$Fe^{+++} + 3H_2O \rightarrow Fe(OH)_3\downarrow + 3H^+$$

$$FeS + 2H^+ \rightarrow H_2S\uparrow + Fe^{++}$$

$$2Fe^{++} + 1/2O_2 + 2H^+ \rightarrow 2Fe^{+++} + H_2O$$

The mechanisms of phosphorus precipitation depend on complex heterogenous reactions. Phosphorus is usually co-precipitated with $Fe(OH)_3$. Adding nitrate causes organic matter to be oxidized. This reduces oxygen demand in the sediments, thus inhibiting the recycling of phosphorus.

Treatment time: 6 days
Sediment pH after treatment: 3

2nd additive:
5 tonnes $Ca(OH)_2$ = 180 g Ca × m^{-2}
Reactions in sediment: Neutralizing of pH
Treatment time: 1 week
Sediment pH after treatment: 7.5

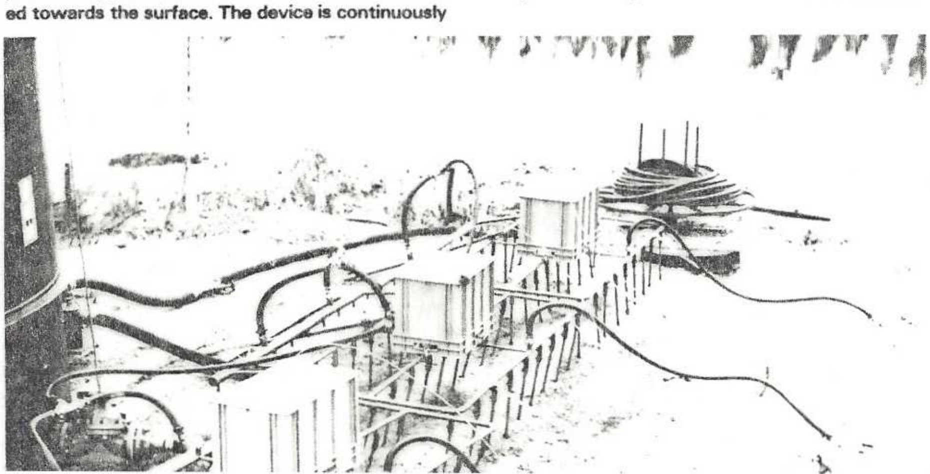
3rd additive:
12 tonnes $Ca(NO_3)_2$ = 141 g N × m^{-2}
Reactions in sediment:

$$2NO_3^- + 3CH_2O \rightarrow N_2\uparrow + 3CO_2\uparrow + 3H_2O$$

Treatment time: 1 week

2. Macrophyte treatment
Treated area: *ca* 1.8 ha
Removed biomass wet: *ca* 83 tonnes
1st step: removal of emergent vegetation
2nd step: root-extraction
Treatment time: 8 days

Figure 2. The distribution of the chemicals was done with a special prototype device developed by Atlas Copco's Central Laboratories, with which the Institute of Limnology at the University of Lund has close cooperation in several lake restoration projects. This device, shown in the photograph, blows compressed air into the sediment through a large number of small nozzles at the ends of the vertical pins. The upper layers of the sediment are thus lifted towards the surface. The device is continuously drawn forward and at the rear the chemicals are distributed through special tubes. The chemicals are thereby thoroughly mixed with the resettling sediments to a considerable depth. All auxiliary functions (maneuvering of the device, mixing and pumping of chemicals, *etc*) are performed with air from the compressor. The device, which is about 6 meters wide, is drawn over the treated area repeatedly, distributing one of the chemicals each time.



stable. As a result H_2S was evolved (Box 3) and the efficiency of the nitrate treatment could be increased. A total of 13 tonnes (1 tonne = 1000 kg) of iron solution was applied to the sediment (Box 3).

In acidic environments, denitrification processes proved to be extremely slow. For this reason, to further precipitate all iron from solution, lime in the form of $Ca(OH)_2$ was applied in the same way as the iron solution (Box 3). The lime was mixed in the container with a tenfold amount of water by weight and the slurry was applied after the sediment had been stirred up and vented. By this treatment the pH of the sediment was adjusted to between 7 and 7.5, which was found to be optimal for the denitrification processes.

After the lime treatment the oxidizing agent was applied in the form of $Ca(NO_3)_2$, an agricultural product used for fertilizing. Twelve tonnes of this material was mixed with lake water and applied in the same manner as described above. The total amount of nitrate applied was 141 g NO_3-N/m^2 of the treated area. The treatments were conducted within one week each (Box 3).

During the first two weeks after the treatment an increase in transparency from 2.3 m up to the maximum depth of lake, 4.2 m, occurred. After this period a vigorous gas production took place, which stirred up the sediment. The temperature during this period was 15° to 17°C at the bottom and up to 25°C at the lake surface. The transparency decreased to 2.8 meters because of the increased amount of particulate sediment material in the hypolimnion. The phosphorus concentration dropped to about 40 μg P/l, and *Lemna* disappeared. The algal community, at first mainly consisting of colonial green algae, developed into a chrysophyceae-dominated community. Oxygen was abundant during the whole denitrification period. During a period of seven weeks practically all nitrate disappeared from the water column as well as from the interstitial water. In the epilimnion the nitrate concentration never exceeded 5 mg NO_3-N/l, at the same time in the interstitial water the initial concentration over a depth of 20 cm was 460 mg NO_3-N/l. The rate of denitrification was calculated to be 3.2 g N $\times$ m^{-2} $\times$ day^{-1}, which in oxygen equivalents means 14.1 g O_2 $\times$ m^{-2} $\times$ day^{-1} (Figure 3). The average amount of gas released per day was calculated to be approximately 5 l N_2 $\times$ m^{-2} $\times$ day^{-1}.

After the treatment had taken effect, biochemical oxygen demand measurements of the sediments were taken. The oxygen demand of the sediment after the treatment showed a reduction of about 50 percent (Figure 4). The analyzed lake concentrations of nitrate and total phosphorus before, during and after the treatment are given in Figure 5. The sediment cores taken after the restoration showed reduced amounts of nutrients in the interstitial water. The oxygen uptake, measured in cores sampled after the treatment, is now comparable to lakes of similar oligotrophic and mesotrophic character (12).

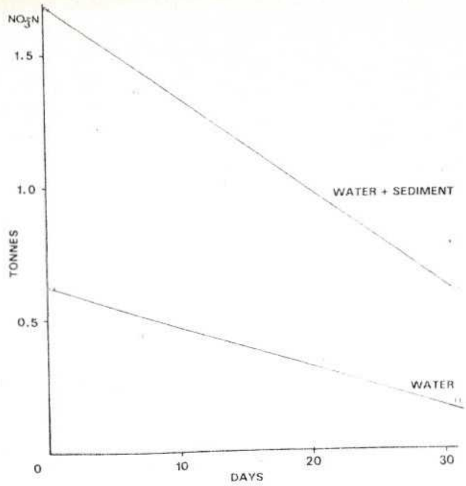


Figure 3. Nitrate reduction in water and sediment from Lake Lillesjön during summer 1975. The y-axis denotes the total amount of N added to the lake. Profile studies in both water and sediment of NO_3-N and NO_2-N made it possible to follow the disappearance of the added N in the water and sediment with time.

Laboratory experiments indicated that the oxygen content of the lake would last for an ice period of at least five months. The usual length of the ice period in this area is about 3–4 months.

Treatment of the vegetation. Because of the heavy pollution of Lake Lillesjön, dense reed beds had expanded greatly in the lake. In some places *plaurs* were formed and a former bathing place with a gravel shore was overgrown by a dense lawn of *Calla palustris* (Box 2) and other weeds. A rich *Nuphar* and *Nymphaea* (Box 2) community occurred down to a depth of almost 2.5 meters. Of the total area of the lake, about 30 percent was covered with macrophytes. The organic matter produced by the macrophytes, together with the periodical development of *Lemna*, caused a high organic internal recycling. This resulted in a lack of oxygen in the lake, and caused an additional recycling of nutrients from the sediments.

In August 1975 the vegetation over an area of 1.8 hectares was removed and only a small part of the reeds was left in the northern part of the lake to serve as a nesting place for water fowl. Eighty-three tonnes of macrophyte biomass were removed with a pontoon-equipped mowing machine, especially constructed for the removal of weeds and other macrophytes. Thereafter the root felt was extracted, cut and removed by a rotocultivator. These measures induced a temporary increase in phosphorus, ammonia and silica concentrations in the water and a reduction in oxygen concentrations. However, the measures were undertaken during one week and then the previous conditions were rapidly restored. Sediment samples taken after the removal of the vegetation indicated that the sediment was hardly affected.

DISCUSSION

It is intended that the restoration will not only temporarily restore the lake, but also produce a permanent effect. It was anticipated that these measures would produce a self-maintaining oxygen balance decreasing internal nutrient loading. This lowered loading would be due to better sorbing capacity of the sediments and a reduced organic load from macrophytes. The improved light climate in the lake could allow colonization of the bottom by *Chara* (Box 2) or *Nitella* (Box 2), which have already been observed in the deeper parts of the lake. The oxygen production of the phytobenthos would contribute to a stabilization of the sediments during the stratified periods. Zoobenthos could then occupy the former anoxic sediments and contribute to a stabilization of the newly oxidized sediment layers. In the laboratory it was shown that the restored sediment can support chironomids, tubificids and other animals.

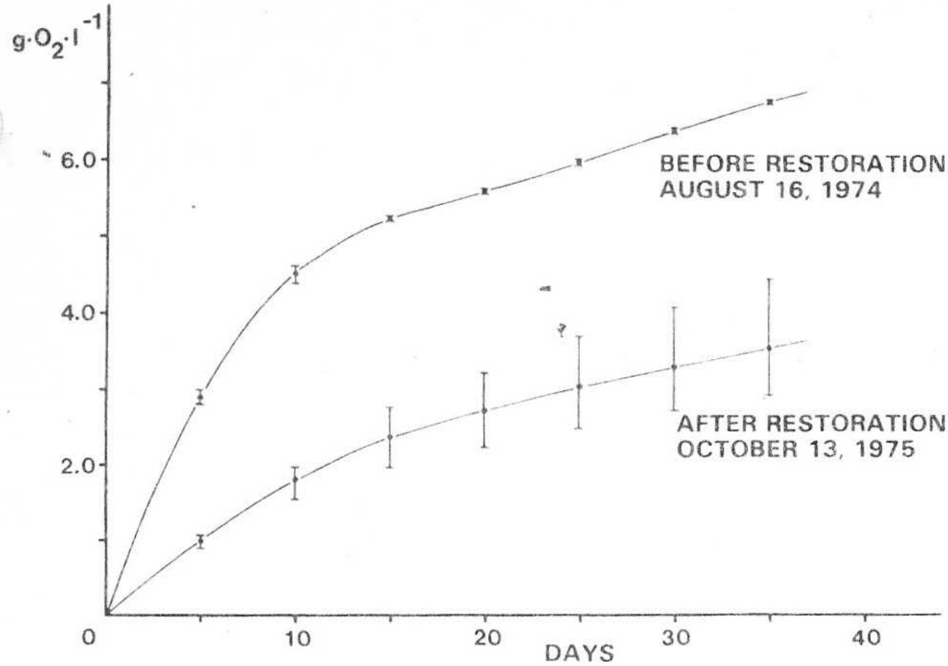
As mentioned above, iron and lime were applied to the sediment of the lake in order to increase the phosphorus-binding capacity of the sediment and to provide optimal conditions for denitrification processes. It is conceivable that these chemicals need not to be used in all cases. Laboratory experiments have shown that denitrification rates vary according to differences in sediment structure and properties. Thorough investigations have to be conducted in advance to assess these sediment parameters. Also the optimal dosage, the necessary area to be treated and the effects of the treatment on the lake ecosystem have to be evaluated. It is possible to determine in the laboratory the best mixing ratio for the chemicals and the behavior of the chemicals in the sediment which would be of importance for the required depth of treatment. The density of the mixed chemicals, together with the sediment properties, would determine the depth of diffusion to the sediment.

It is clear that the use of chemicals in lake treatment requires special precautions, and without thorough investigations serious damage can be done. Whether it is used on land or in lakes, nitrate is an agricultural fertilizer. Applied in too high a dosage, or at the wrong time, it can have disasterous effects on water bodies. Only if the processes are controlled can the nitrate's properties be beneficial when applied to lake sediments.

THE COSTS OF THE SEDIMENT TREATMENT

Since the restoration of Lake Lillesjön was an experimental test of a new technology, relevant costs are somewhat difficult to state. In Table 1, however, an estimate has been made. The vegetation treatment is a marketed technique and the costs for that and for the chemicals for the sediment treatment amounted to about 150 000 Sw

Figure 4. Comparison of BOD curves of Lake Lillesjön sediments before and after the sediment treatment. The maximum and minimum values in the different series are given. The data from sediment before the treatment refer to three experiments. The data for the curve after restoration refer to six experiments.



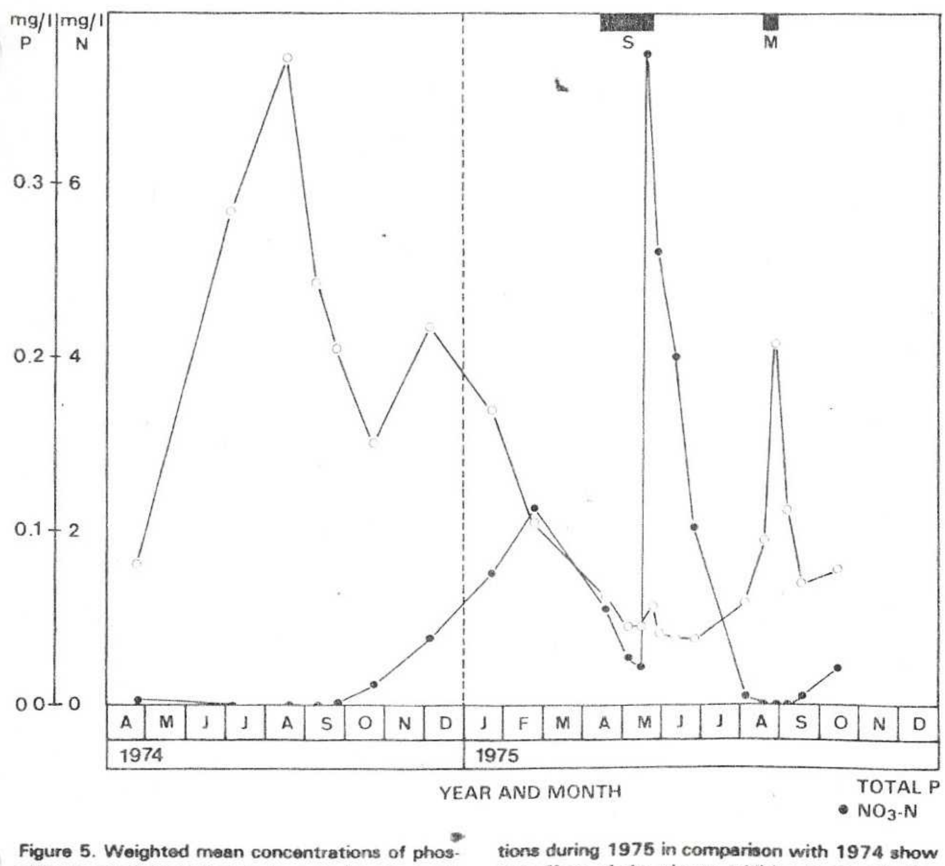


Figure 5. Weighted mean concentrations of phosphorus and nitrate before during and after the treatments. The water profile measurements (5 samples on each occasion) with respect to phosphorus and nitrate were weighted with the corresponding water volumes, added together and thereafter divided by the total volume of the lake. The rapidly decreasing nitrate peak indicates the high level of denitrification activites. The low phosphorus concentrations during 1975 in comparison with 1974 show the effect of the nitrate addition in combination with the other chemicals on internal phosphorus recycling. The temporary peak in phosphorus concentrations during August 1975 was caused by the root felt extraction over an area of 1.8 ha during the vegetation treatment.
S = Sediment treatment
M = Macrophyte treatment

Kr. To this one must add costs for planning and investigations (mainly done by the Institute of Limnology) and costs for the device that distributed the chemicals into the sediment (done by Atlas Copco). The latter may be used in other lakes as well, thus reducing the investment cost per lake. As a rough estimate the costs for Lake Lillesjön amounted to a total of about 250 000 Sw Kr, which must be considered competitive in comparison with sediment dredging.

The chemical method would probably be suitable for partial treatments of lakes. In the case of Lillesjön the anoxic areas which influenced the whole lake were restricted to the deeper zones only. Together with other restoration methods, the use of chemicals seems to be a valuable tool in repairing damaged aquatic ecosystems.

Table 1. Costs of sediment treatment in Lake Lillesjön.

Items	Costs Sw Kr*
Installation costs (not dependent on treated area)	70 000
Chemicals/ha	15 000
Rental of equipment	20 000
Labor	35 000
Preliminary investigations and restoration device (Atlas Copco)	110 000
Total	250 000

Figures given for 1975.
* US $1 = *ca* 4.40 Sw Kr

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