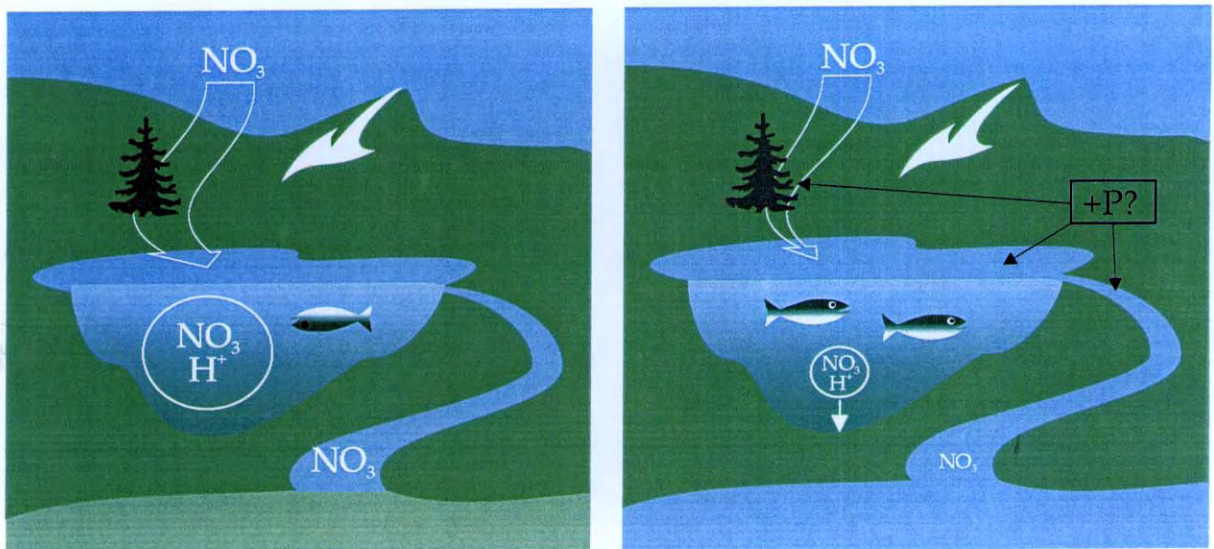


Importance of phosphorus for terrestrial and aquatic retention of nitrogen and acidity reduction

A literature study



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Abstract <p>Many catchments in high N-deposition areas have low N retention. It has been hypothesised that under such conditions P addition may increase N retention in both terrestrial and aquatic ecosystems. Fertiliser trials in N-saturated terrestrial ecosystems show that P addition can cause increased plant uptake of N. Few studies, however, have focused on N leaching to surface waters. Theoretical considerations and limited empirical data suggest that P addition to acidic, oligotrophic lakes will stimulate NO₃⁻ assimilation and thereby increase alkalinity and N retention within the lake. Near-shore coastal waters may benefit from reduced riverine N loading during summer in terms of reduced algal biomass and reduced probability of development of toxic dinoflagellate blooms. P treatment may be suitable to neutralise moderately acidified lakes and streams (pH>5.2). P addition will also increase biodiversity, stimulate aquatic production and improve the resource base for fish production. In more acidic lakes and streams, a combination of liming and moderate P addition may be an optimal management tool. We conclude that a large-scale experiment is necessary to test if P addition (both terrestrial and aquatic) might provide a mitigation technique for areas experiencing high NO₃⁻ levels in surface waters.</p> <p>Possible technological solutions on how to use P to increase pH and stimulate biological production in acidified areas have been evaluated. Instead of adding P as PO₄³⁻ salts, P-containing wastewaters can be utilised at relatively low cost, after removing particulate matter, BOD, and N, but not P.</p>
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**Importance of phosphorus for terrestrial and
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- a literature study

Preface

In order to study the complex processes concerning nitrogen retention in terrestrial and aquatic ecosystems, a pre-project "Importance of phosphorus for terrestrial and aquatic retention of nitrogen and acidity reduction" was established in 1997. The main objective of this project has been to (1) prepare a project plan, (2) forward applications, (3) chose study sites, carry out simple field investigations, and (4) to make a literature study. This report, which is a synthesis of the literature study, contains three main chapters:

Nitrate retention in terrestrial ecosystems by phosphorus addition. (*R. F. Wright*)

Nitrate retention and base generation in acid lakes by phosphate addition. (*Ø. Kaste, A.Lyche Solheim, T.E. Brandrud E.A. Lindstrøm, and A. Skiple*)

Technical solutions in an ecological perspective. (*Rune Bakke and Roald Kommedal*)

The pre-project is financially supported by Hydro ASA and Norwegian Institute for Water Research. Contact person at Hydro ASA has been Espen E. Hoell.

Grimstad, February 1998

Øyvind Kaste

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General introduction

Since 1980, the concentration of sulphate (SO_4^{2-}) in precipitation over southern Norway has decreased by about 40-60%, whereas nitrogen (N) has remained unchanged. In south- and southwestern Norway many catchments show low N retention. This is especially evident in non-forested and mountainous areas, which often have thin soils and sparse vegetation cover. Leakage of nitrate (NO_3^-) from soils can cause freshwater acidification and marine eutrophication.

Calculations made for the Bjerkreim catchment in SW Norway show that NO_3^- contributes up to 40% to the freshwater acidification today. After fulfilment of the second sulphur (S) protocol in 2010, the relative importance of N in freshwater acidification will increase. In anticipation of reduced N deposition there is a need for temporary measures to reduce the negative effects of NO_3^- in freshwater and in marine ecosystems.

One hypothesis is that the terrestrial ecosystems gradually are becoming limited by nutrients other than N. Experiments performed in Wales, UK, suggest that phosphorus (P) under some conditions can be a limiting nutrient in forest ecosystems. In most aquatic ecosystems P is the limiting nutrient, such that P addition leads to increased uptake of N.

As a first step in investigating the potential for increased N retention in terrestrial and aquatic ecosystems through the addition of P, a literature study was performed in 1997. This report is a synthesis of the literature study and contains three main chapters:

Nitrate retention in terrestrial ecosystems by phosphorus addition. (R. F. Wright)

Nitrate retention and base generation in acid lakes by phosphate addition. (Ø. Kaste, A. Lyche Solheim, T.E. Brandrud, E.A. Lindstrøm, and A. Skiple)

Technical solutions in an ecological perspective. (Rune Bakke and Roald Kommedal)

The chapters are independent and have their own introductions and summary/conclusions.

Extended summary

As a first step in investigating the potential for increased N retention and pH in acidified terrestrial and aquatic ecosystems through the addition of P, a literature study was performed in 1997. This report is a synthesis of the literature study and contains three main chapters:

- Nitrate retention in terrestrial ecosystems by phosphorus addition.
- Nitrate retention and base generation in acid lakes by phosphate addition.
- Technical solutions in an ecological perspective, evaluating the possible use of wastewater as a P-source, after removal of nitrogen and organic matter.

1. Nitrate retention in terrestrial ecosystems by phosphorus addition.

In areas of southern Norway in which surface waters contain elevated concentrations of NO_3^- , plant growth is probably limited by another nutrient such as P or K. Fertiliser trials in a wide range of ecosystem types show that in N-saturated systems, P addition can cause increased plant growth and thus increased uptake of N. Few studies, however, have focused on N leaching to soil and surface waters. The P addition experiment of Stevens *et al.* (1993) showed clear reductions in NO_3^- in leachate. No such experiment has been conducted on heathlands typical for the N-saturated areas of Norway. Although P addition to this type of ecosystem might cause increased plant growth, the theoretical long-term potential for N retention is unknown. More research is required to answer this question. One approach might be to conduct a large-scale, long-term experiment with P addition in an area experiencing high NO_3^- levels in surface waters. Although such an experiment would require commitment of sufficient funds for at least 5 years, it would provide direct information as to whether P addition can be used as a mitigation technique for freshwater acidification.

2. Nitrate retention and base generation in acid lakes and streams by phosphate addition.

N retention

The most important mechanisms contributing to N retention in lakes are assimilation, sedimentation, and denitrification. As a rough theoretical estimate, P additions can give a 40% reduction in NO_3^- outputs from Lake Nedre Lundetjenn during the growing season and a 15% reduction on a yearly basis. Since the relative contribution from riverine sources to available nutrient concentrations in the coastal areas is highest during summer (Hessen *et al.* 1997b), the 40% reduction in NO_3^- loading estimated for the growing season may both contribute to reduced algal biomass in near-shore coastal areas during summer periods with N-limited algal growth, as well as to a lower N/P ratio, which will reduce the probability for development of toxic dinoflagellate blooms (Skjoldal 1993).

Deacidification

Theoretical considerations and limited empirical data suggest that the base production following P treatment will be enough to increase the pH from 5.0 to 5.5 during the growing season in a non-buffered system. During the dormant season the pH-increase will be less (e.g. from 5.0 to 5.1). The P addition method will work best in moderately acidified lakes with initial pH-values above ~5.2. In more acidic lakes it may be difficult to raise pH above 5.5 without use of additional neutralising agents. However, such a pH-increase during the growing season may still be sufficient to allow survival and recolonization of many acid-sensitive species in the lake, who are able to avoid the acidic

surface water during the dormant season. The stream biota may not be expected to recover as much as the lake biota, due to the low pH in the streams during the dormant season and early spring.

P addition will significantly increase NO_3^- retention in acid lakes during the growing season, whereas traditional neutralising methods such as liming will have little or no effect on NO_3^- retention. P addition will also increase biodiversity, stimulate aquatic production and improve the resource base for fish production, whereas liming has little or no effect on aquatic production *per se* (although biodiversity will increase after liming). To obtain both increased NO_3^- retention and sufficient pH-increase to restore aquatic life in highly acidified lakes and streams, a combination of liming and moderate P addition may thus be the optimal management tool.

Bacteria

Due to increased supply of organic carbon from increased phytoplankton production, the pelagic bacterial biomass is expected to increase slightly with moderate P addition, following the general pattern with increasing biomass with increasing tot-P concentration. The bacterial activity in the sediments may also increase after P addition due to enhanced supply of autochthonous organic carbon. This may increase the mineralization of organic matter in the sediments, and reduce the oxygen level on the sediment surface. Dissimilatory NO_3^- reduction will then be enhanced.

Phytoplankton

According to an empirical model for shallow Norwegian lakes (Berge 1987), P addition up to a tot-P concentration of 15 $\mu\text{g/l}$ in lake Nedre Lundetjenn will yield a phytoplankton biomass of roughly 6-8 $\mu\text{g chl a/l}$. There is, however, considerable variation in the chlorophyll response in different lakes at similar P concentrations, due to inter-lake differences in food web structure, and other factors. Lakes with an efficient grazer food chain will have less algal biomass than lakes with a very low grazing pressure. Initially, a large part of the phytoplankton production in Lake Nedre Lundetjenn will probably not be grazed, due to lack of large efficient grazers, and will thus sink to the sediments, and thereby increase N retention.

The probability for cyanobacterial dominance should be low after P addition to acidic lakes, since this group of phytoplankton rarely dominates at pH-levels < 7.0, with the exception of the non-toxic *Cyanobacteria*-species *Merismopedia tenuissima* (Brettum 1989). Phytoplankton groups normally dominating in acidic lakes are dinoflagellates (i.e. *Peridinium inconspicuum*), mixotrophic chrysophytes and some chlorophytes (i.e. *Mougeotia spp.*) (Brettum 1989). Since P addition probably will not raise pH above 6.0, it is likely that these groups will continue their dominance also after P addition, maybe with reappearance of some cryptophytes like *Rhodomonas spp.* (Brettum pers. comm.)

Zooplankton

Both biomass and species diversity in the zooplankton community is expected to increase with moderate P addition and pH increase, but the magnitude of the increase is difficult to predict. The soft-water-adapted cladoceran *Holopedium gibberum* may be expected to increase its biomass significantly, along with *Bosmina longispina* and *Cyclops scutifer*. The calanoid copepods may also be expected to increase in biomass. These changes will most likely cause a moderate increase in the grazing rate, as opposed to the large increase in grazing rate that would occur if large *Daphnia*-species reappear. The increased zooplankton biomass will also contribute to increased N retention through natural mortality and sinking, especially if calanoid copepods continue to dominate. Calanoid copepods have a high specific N content (> 10% of dryweight) (Andersen and Hessen 1990, Hessen and Lyche 1991).

Periphyton

P addition will contribute to increased standing crop and production of periphyton and thereby increase the N retention in the lake. The effect of P addition on periphyton production and standing crop will probably be at least as pronounced as on phytoplankton. Increased periphyton production will increase the benthic fauna, mainly by providing a better food supply for the herbivore invertebrates, but also by increasing pH through increased primary production and NO_3^- assimilation.

Macrovegetation

Moderate P addition will probably lead to little macrovegetation response in most acidified lakes in Norway since most of these lakes are characterised by soft and clear water, and normally have a C-limited plant growth. An increase in pH from (below) 5.0 to 5.5 will give possibilities for the re-establishment of soft-water, acid-sensitive species (mainly *Myriophyllum alterniflorum* and some *Potamogeton spp.*). The effects will probably be comparable to those of moderate liming, which can lead to an increase of 20-30% of the macrophyte diversity.

3. Technical solutions in an ecological perspective, evaluating the possible use of wastewater as a P-source, after removal of N and organic matter

P additions can alleviate acidification problems in watersheds exposed to high N loads. Available global P reserves are, however, limited and must be utilised accordingly, implying that P fertilisation strategies must be developed within strict ecological frameworks. P containing waste streams are typically not in abundance along watercourses suffering from acid rain. Logistics and technological solutions must bear this in mind, striving towards a minimum of energy expenditures for transport. There are, however, some P containing waste streams in areas suffering from acid rain, which should be utilised locally. Local utilisation of available P in waste streams in exposed areas is the most ecologically sound measures available.

A holistic approach in which scientific tools as well as nutrient cycle technology is utilised to maximise the effects of added P, must therefore be developed. It is so far concluded that wastewater have significant amounts of P which can be utilised at relatively low costs. Changing policies regarding P removal from sewage, making wastewater treatment demands recipient dependent, removing particulate matter, BOD (biochemical oxygen demand) and N, but not P (in relevant locations), is presently the most efficient and easily implemented measure both from an ecological and economical perspective. New strategies to recover P from various waste streams must be implemented as ecologically sound sources of P. It also appears that existing advanced ecological treatment plants, implemented in relevant locations, may serve as model systems to study the influence of P on pH, N removal, and plant (food) production potential.

Nitrate retention in terrestrial ecosystems by phosphorus addition

Richard F. Wright

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1. Introduction

Nitrogen (N) is commonly the growth-limiting nutrient in temperate and boreal terrestrial ecosystems (Tamm 1991, Aerts *et al.* 1992, Chapin *et al.* 1986, Vitousek and Howarth 1991). To conserve limited supplies of nitrogen terrestrial ecosystems commonly have very tight N cycles, with only a small fraction of the annual amount of N cycled lost to runoff. Chronic deposition of N from the atmosphere in the form of wet and dry deposition may alter this situation, and lead to N saturation, manifest as increased leaching of N to surface waters (Aber *et al.* 1989). In regions sensitive to acidification the result is acidification of soils due to the loss of accompanying base cations, and acidification of surface waters due to the accompanying acid cations H^+ and inorganic Al.

In Norway N saturation to date is a problem mainly in non-forested heathlands, such as the counties of Vest-Agder and Rogaland in southwestern Norway (Henriksen *et al.* 1997, Kaste *et al.* 1997). Here median retention of incoming N is only 80% (in contrast to >95% in eastern Norway), median NO_3 concentrations in lakes is $5 \mu eq l^{-1}$ while SO_4 is $24 \mu eq l^{-1}$, and nitrate accounts for 10-40% of the sum of non-marine mobile anions (Skjelkvåle *et al.* 1997).

The role of nitrate in freshwater acidification is likely to increase in the future. International agreements on SO_2 emissions in Europe (Oslo protocol of 1994) will lead to further reductions in sulphate deposition and concentrations in surface waters. Nitrogen emissions and deposition, however, are likely to continue unabated, unless ongoing international negotiations are successful in obtaining agreements for reductions in emissions in Europe. And continued N deposition can only increase the extent and degree of N saturation in southern Norway. Achieving reductions in acidification to below the critical load will thus depend on reductions in N deposition (Henriksen *et al.* 1997).

In the meantime, just as liming provides a means by which water acidification can be mitigated, there may be measures by which nitrate retention by terrestrial ecosystems can be increased such that leaching of nitrate to freshwaters is diminished. The fact that the terrestrial ecosystems loose a significant fraction of the incoming N indicates that another factor may be limiting to growth. Possible factors are other nutrients such as phosphorus (P) or potassium (K).

Phosphorus addition to N-saturated ecosystems may cause increased N retention and thus act to diminish nitrate losses to runoff and decrease freshwater acidification. A field-scale experiment with P addition to a N-saturated Sitka spruce forest in Wales, UK, conducted in 1990 indicated that such a measure may be successful in retaining N (Stevens *et al.* 1993). Here I review the literature on N and P limitation in terrestrial ecosystems with the focus on the potential of P additions to increase terrestrial retention of N.

2. Growth-limiting nutrients in forests, heathlands and wetlands

The concept of nutrient limitation comes from agriculture and refers to the limitation of productivity of individual crop species due to insufficient supply of an essential nutrient in the soil. Ingestad (1973) extended this concept and determined the mineral nutrient requirements for optimal growth of several species characteristic of northern boreal ecosystems. His approach was to grow single plants in the laboratory in hydroculture in which the roots were supplied with solutions containing various concentrations of macro- and micronutrients. For birch and 2 species of *Vaccinium* (blueberry) the optimal ratio of N:P was about 100:7 (Ingestad 1973). Such information can be used to assess the possible P limitation in areas receiving excess N deposition.

The laboratory approach has been taken a step further by Harrison and Helliwell (1979), who developed a root bioassay procedure to determine nutrient limitation. This technique has been used in the field to assess nutrient limitation of tree and shrub species in areas subject to varying degrees of N deposition (Jones *et al.* 1991, Harrison *et al.* 1995), and to interpret results from forest fertilisation experiments (Jones *et al.* 1994). The possible limitation of P in forests receiving N deposition is suggested.

The concept of nutrient limitation applies to individual species. For plant communities the situation is more complex, because of the natural heterogeneity of both soils and plants in the natural landscape (Chapin *et al.* 1986).

Several studies in wetlands indicate that P can be growth limiting when N supply is sufficient. An early study conducted in wet heathlands in the UK show conditions of N and P limitation depending on soil chemical conditions (Loach 1966). Similar conclusions were made following nutrient addition trials at an acid mire in the UK (Hayati and Proctor 1991). Aerts and Berendse (1988) showed that at wet heathlands in the Netherlands fertilisation with P caused increased growth of one species (*Molina caerulea*) and a decrease of a second species (*Erica tetralix*). N deposition in the Netherlands is high, and the response was found only when P was added. In a related study conducted in *Sphagnum*-dominated bogs in Sweden Aerts *et al.* (1992) found that in northern Sweden growth responded to both P and N additions, while in southern Sweden only P addition gave growth response. This was interpreted as indicating that in southern Sweden the N deposition had caused the plants to be P-limited.

Koerselman and Meuleman (1996) suggest that the N:P ratio in vegetation may provide a diagnostic index of nutrient limitation in wetland ecosystems. They found that N:P ratio > 16 indicates P limitation at the community level while N:P ratio < 14 indicates N limitation.

3. Field experiments with P addition to increase N retention

While there have been numerous field trials with fertilisation by N, P and K aimed at increasing growth, there has been only 1 field trial with P addition designed specifically to investigate the effect on nitrogen retention. This experiment was conducted in June 1990 on a mature Sitka spruce stand at Beddgelert, Wales, UK (Stevens *et al.* 1993). This area receives 20 kg N ha⁻¹ yr⁻¹ and the forest is N-saturated, in that soil solution contains high levels of nitrate and leaching losses are about 15 kg N ha⁻¹ yr⁻¹. A mixture of P and K was added at 2 levels (60 kg P ha⁻¹ and 100 kg K ha⁻¹; 120 kg P ha⁻¹ and 200 kg K ha⁻¹), and the effects on soil solution and foliage chemistry measured during 1 ½ years. Application of P + K at the higher level resulted in significantly lower concentration of nitrate in soil solution. Nitrate concentrations in soil solution from the Bs horizon were between 1.5 and 3.5 mg N l⁻¹ (100 - 250 µmol l⁻¹) in the control plot and only 0.1 to 1.6 mg N l⁻¹ (7-115 µmol l⁻¹) in the higher treatment plot. The lower treatment had no effect. Concentrations exhibited a seasonal pattern with

lowest levels during the growing seasons. Foliar analysis showed that additional N was present in the trees in the higher treatment. This experiment indicates clearly that P (and K) addition to N-saturated systems can result in significant reduction in nitrate leaching to surface waters.

4. Discussion

These studies give indications that in N-saturated ecosystems (as indicated by increased leaching of nitrate below the rooting zone; Aber *et al.* 1989) some other nutrient is growth-limiting. In northern ecosystems possible candidates are P and K. Fertiliser trials in forests, heathlands and wetlands all indicate that although N is normally the growth-limiting nutrient, in areas receiving high N deposition or when N is applied as fertiliser, additional growth increases are induced by P and/or K additions.

Theoretically increased growth should result in increased demand for N and thus lower amounts of N available for leaching. The experiment in Wales in Sitka spruce is the only field-scale experiment in which this effect has been demonstrated.

The regions of Norway in which nitrate concentrations in surface waters are high, receive N deposition at about 10-20 kg N ha⁻¹ yr⁻¹. P deposition is less certain, but probably is in the range 0,1-0,2 kg P ha⁻¹ yr⁻¹. Using the N:P ratios in vegetation given by Ingestad (1973) and Koerselman and Meuleman (1996), if all the P is taken up by vegetation, this would entail uptake of about 1 - 3 kg N ha⁻¹ yr⁻¹.

Vegetation, however, is probably not the final sink for either P or N in these ecosystems. Biomass and nutrients are cycled in the ecosystem through litterfall and root death to the soil. Except for woody parts of plants, the vegetation is merely a transient pool for nutrients. If N is to be retained in the ecosystem, the sink must be soil.

Soils in cool, temperate ecosystems are typically organic-rich and contain by far the largest part of the carbon (C), nitrogen and phosphorus stored in the ecosystem. Nitrogen pools are often equivalent to 100-1000 years of N deposition, and are the result of slow accumulation of organic matter during the entire post-glacial period. A small portion of the annual input of litter and roots to the soil does not decompose, and this portion adds to the organic matter pool in the soil.

Chronic N deposition leads to an enrichment of the N content in the soil organic matter. Data from European forests across a gradient in N deposition indicate that the C/N ratio in forest floor is closely related to both N deposition and the leaching of N from forests. Sites with low C/N ratios (N-rich sites) lose a substantial fraction of the incoming N (Gundersen 1995). The mechanism of N retention appears to be immobilisation by soil bacteria.

Soil must be the ultimate sink for N in the event that N is retained following P addition. Increased growth of vegetation can result in only a moderate increase in standing biomass, for most of the increase in growth will go to foliage and roots which will soon be recycled to the soil as litterfall or dead roots. The retention of N following P addition is therefore dependent on soil microbial processes. If the extra litter is not decomposed, then the rate of accumulation of soil organic matter (and N) will increase and the soil can thus serve as a sink for the N. There is no information from the studies above as to the effect of P addition on soil organic matter decomposition.

An additional uncertainty is in the seasonal demand for N by plant uptake. During the growing season plants will take up both P and N, and thus P addition should cause an increased demand for N. But during the winter plant uptake will be lower and thus the demand for N will also be reduced. This seasonal pattern of nitrate in soil solution was observed by Stevens *et al.* (1993) in the experiment in Wales. Thus although P addition can increase uptake of N, the effect will be smallest during the

dormant season. P addition is thus unlikely to affect concentrations of nitrate in the winter and snowmelt in small streams and lakes with short water retention times.

5. Conclusion

In areas of southern Norway in which surface waters contain elevated concentrations of nitrate, plant growth is probably limited by another nutrient such as P or K. Fertiliser trials in a wide range of ecosystem types show that in N-saturated systems, P addition can cause increased plant growth and thus increased uptake of N. Few studies, however, have focused on N leaching to soil and surface waters. The P addition experiment of Stevens *et al.* (1993) showed clear reductions in nitrate in leachate. No such experiment has been conducted on heathlands typical for the N-saturated areas of Norway. Although P addition to this type of ecosystem might cause increase plant growth, the theoretical long-term potential for N retention is unknown. More research is required to answer this question. One approach might be to conduct a large-scale long-term experiment with P addition in an area experiencing high nitrate levels in surface waters. Although such an experiment would require commitment of sufficient funds for at least 5 years, it would provide direct information as to whether P addition can be used as a mitigation technique for freshwater acidification.

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Nitrate retention and base generation in acid lakes by phosphate addition.

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1. Introduction

Sulphur (S) and nitrogen (N) from long-range transported air pollution have caused acidification and fish damage in many Norwegian lakes since 1950, especially in the southern and southwestern parts of the country. The area with fish damage and exceedances of critical loads is 80000 - 85000 km², about 25% of the total land area (Henriksen *et al.* 1996). In general, biodiversity of all taxonomic groups declines as lakes acidify, and there is a switch to acid-tolerant taxa (Schindler 1994). Many of the responses of species to acidification may be indirect, caused by disappearance of sensitive species of predators or prey, or by changes in habitats.

The annual mean concentrations of sulphate and strong acid in precipitation have been decreasing since the end of the 1970's, and since 1980 the content of sulphate has decreased by about 40-60% in southern Norway (Tørseth and Manø 1997). The decrease in S-deposition has led to decreased sulphate (SO₄²⁻) concentrations, higher pH- and ANC-values, and a decrease in the concentrations of inorganic aluminium in Norwegian lakes and rivers (Skjelkvåle *et al.* 1997). No significant time trends in nitrate (NO₃⁻) concentrations in lakes and rivers can be detected, but the levels are generally higher in areas with high N deposition (Skjelkvåle 1996). N leaching from N-saturated terrestrial ecosystems presently receiving high N deposition may continue long after possible international agreements on reduction of N emissions. The relative importance of NO₃⁻ in freshwater acidification is thus likely to increase in the future.

In southern- and southwestern Norway many catchments have low N retention (Skjelkvåle 1996, Kaste *et al.* 1997). This is especially evident in non-forested and mountainous areas, which often have thin soils and sparse vegetation cover. NO₃⁻ contributes to acidification in the same way as SO₄²⁻ from acid deposition; by removing base cations from the soil and, in the case of low base saturation, by mobilising Al and H⁺ (Reuss and Johnson 1986). As an illustration, NO₃⁻ contributes up to 40% to the present acidification of the Bjerkreim river in southwestern Norway (Henriksen *et al.* 1997). Leakage of NO₃⁻ can also lead to eutrophication, especially in estuaries and near-shore coastal waters during summer periods of N limitation. When the nutrient balance in coastal waters is shifted towards a high N:P ratio, phosphorus (P) may become the limiting nutrient also in marine systems. Empirical data show an increased probability for dominance of toxic dinoflagellates in coastal waters when P is the limiting nutrient, and silica is depleted (Skjoldal 1993).

P concentrations in Norwegian lakes are generally very low, and the majority of Norwegian lakes are probably P-limited. In a regional survey in 1995 of lakes with low or moderate P-supply from local sources, about 50% of the 1500 lakes had P concentrations ● 3 µg P L⁻¹ (Skjelkvåle *et al.* 1997). Low P concentrations lead to low productivity in the lakes and also low N retention capacity. Controlled P additions to lakes may increase the NO₃⁻ retention, as has been shown in a small lake in the UK by Davison *et al.* (1995). Increased NO₃⁻ uptake also led to an increase in lake pH thus reducing acidification significantly.

When discussing P addition to lakes, it is important to distinguish between eutrophic lakes (recipients) where P retention is the goal, and acidified lakes where NO_3^- reduction is the goal. In acidified, oligotrophic lakes a slight increase in primary production will probably give solely positive effects on N retention, acid neutralizing capacity, fish stocks, and biological diversity. Nearly all the added P and a greater portion of N present in the water masses will be taken up by the primary producers, sedimented and thereby retained within the lake. This will reduce loading of N to estuarine and near-shore coastal waters and thereby relieve eutrophication problems.

N retention in freshwater systems is highly variable depending on hydraulic retention time, N loading, trophic state and other factors. In southern Sweden average N retention during the period 1985-1994 has been estimated to be 45% of the nutrient load from different sources (Arheimer *et al.* 1997). In southern Norway N retention in 1993 was estimated to only 5% (Bratli 1997). Although this estimate only accounts for lake retention in the main watercourses, N retention in Norwegian lakes seems to be lower than in Swedish lakes. This may be due to high precipitation amounts, short water retention times in lakes, high atmospheric N deposition, and relatively low aquatic production due to strong P limitation.

The objective of this chapter is to (i) review the different factors/parameters that may influence the retention of N in freshwater systems, including a brief overview of the existing calculation methods, (ii) discuss natural mechanisms for in-lake NO_3^- retention and acid/base generation, (iii) evaluate the effect of P addition on NO_3^- retention and deacidification in acidified, oligotrophic lakes, when presupposing that no unacceptable eutrophication must occur, and (iv) discuss possible chemical and biological changes by gentle P additions to an acid, softwater lake.

2. N retention in lakes

2.1 Mechanisms

N retention in lakes can be defined as $(1 - (\text{N}_{\text{output}} / \text{N}_{\text{input}})) * 100\%$. The most important mechanisms contributing to N retention in lakes are assimilation, sedimentation, and denitrification (Faafeng 1989).

Assimilation

During the production season planktonic algae, periphyton and higher plants remove N from the water masses by assimilation. In lakes, most of the N assimilation is carried out by pelagic plankton (Ahlgren *et al.* 1994). Assimilation in lakes is important as a N retention mechanism if the assimilated N is buried in the sediments, accumulated in perennial plants, or removed by harvesting vegetation/fish. Annual macrophytes can be a nutrient link, by pumping N and P from the sediments to the water column (Berge *et al.* 1986).

Sedimentation

In lakes, dead organic matter either will be mineralised within the water column by bacteria and zooplankton, or it will sink to the lake bottom. The sedimented organic material can undergo mineralization and re-enter the lake's N cycle or be buried in the sediments. The latter mechanism is the only way by which N can be removed in the lake system for a long period of time.

Denitrification

The most complete, and from a long-term perspective probably most important N retention mechanism, is the microbial process of denitrification (Jansson *et al.* 1994). Here NO_3^- is transformed via nitrous oxide (N_2O) to atmospheric N_2 . Denitrifiers are heterotrophic facultative aerobic bacteria, i.e. they reduce organic compounds to obtain energy and they can use either O_2 or NO_3^- and probably

also Fe^{3+} as electron acceptors. In lakes, the reduction of NO_3^- is carried out in sediments and in hypolimnetic waters with low O_2 -concentration ($< 2 \text{ mg O}_2/\text{l}$) and an organic C-source available. NO_3^- can be supplied to the sediments either from the water above the sediment surface, or by production of NO_3^- by bacterial oxidation (nitrification) in the sediment surface.

2.2 Parameters influencing N retention

Renewal time in lakes

In a study of several lakes in Ontario, Canada, retention of inorganic N was estimated to be 24-82% (Dillon and Molot 1990). There was a positive correlation between N retention and water renewal time. In a study of two Swedish eutrophic lakes Ahlgren *et al.* (1994) found N retention values between 15-50%, also with a strong positive correlation with the lakes renewal times. N was lost from the lakes via two major pathways; denitrification (5-25%) and sediment retention with subsequent burial.

Temperature

A series of turnover-processes of N have specific temperature optima i.e. nitrification and N fixation. Low temperature will in general give little microbiological activity. The denitrification rate depends on the concentration of N as well as the temperature (Howard-Williams 1985, Seitzinger 1988). The temperature is also decisive for uptake in terrestrial and aquatic vegetation and for mineralization. N retention will thus be positively correlated to temperature.

Seasonal variation

Relative N retention are shown to be considerably higher in the vegetation period compared to the rest of the year, due to assimilation in phytoplankton, periphyton and aquatic vegetation. Since the water-flow in the summer period in general is low, however, the absolute quantity of N retention in lakes will be lower in the summer than the rest of the year (Kaste *et al.* 1995).

In rivers the N content is decreasing during the growing season both due to plant uptake within the river bed and in the terrestrial catchment. In autumn and winter this temporarily bound N will be released and transported downstream. In this way it enters the sea in the low productive season.

Trophic state

The retention of N is higher in eutrophic water bodies than in oligotrophic water bodies (Berge *et al.* 1997). Several investigations indicate up to 50-60% of N retention in very eutrophic lakes (Tirén 1983, Faafeng 1989, Fleischer *et al.* 1989). In a sample of 7 large and small Norwegian lakes with different trophic levels, N retention was estimated to be 9-66% (Faafeng 1989). The highest retention values were observed in eutrophic lakes. These findings were also supported by a study of 7 Norwegian lakes made by Berge *et al.* (1997). They found N retention values around 20-30% in eutrophic lakes (tot-P: $13\text{-}35 \mu\text{g P L}^{-1}$) and $< 5\%$ in deep oligotrophic lakes (tot-P: $2\text{-}6 \mu\text{g P L}^{-1}$).

Denitrification may contribute to a large portion of the retention of nutrients in eutrophic lakes (Ahl 1973, Ahlgren 1973, Andersen 1974, Larsen 1975, Jensen *et al.* 1990, Petterson and Boström 1990). Denitrification may also occur in mesotrophic and oligotrophic lakes (Tirén 1983). When much organic matter has been accumulated, the extent of denitrification will increase.

Acidity

Low pH-values may prevent denitrification in lake sediments, and therefore reduce N retention in acidic lakes.

N fixation

In lakes with N-fixing *Cyanobacteria*, the actual N load will be higher than the external N inflow indicates, due to N fixation of atmospheric N₂. Fixation of N will normally contribute to less than 1% of the external N load in oligotrophic and mesotrophic lakes. However, in eutrophic systems the N fixation may contribute considerably, 6-82% in a series of Swedish lakes (Petterson and Boström 1990).

2.3 Models estimating N retention

Lakes

There are relatively few studies concerning N retention in lakes, and yet there is not developed well accepted models of general applicability for this purpose. One of the few attempts of modelling N retention was performed by Fleischer *et al.* (1989) in the catchment of the Laholm Bay, southwestern Sweden. They found that N retention was mainly a function of N loading. N retention was highest in eutrophic swamps and lakes, and close to zero in well channelized rivers. This is also shown for Norwegian lakes (Faafeng 1989).

Based on empirical data from some large, low productive lakes in south-east Norway, the retention of tot-N seems to vary between 0 and 25% of the input, with a mean value of approximately 10%. For the same set of lakes the retention of tot-P was on average 50%. As a preliminary approximation of N retention in oligotrophic, well oxygenated lakes it seems reasonable to assume that most nitrogen loss is due to sedimentation via biological uptake, given by the following expression (Holtan 1991):

$$(1) \quad R_N = \frac{0.2}{1 + \sqrt{1/T_w}} + k$$

R_N = Retention coefficient of tot-N

T_w = Theoretical water residence time

k = Retention coefficient

$k=0,0$ for oligotrophic lakes (tot-P <7 µg/l, chlorophyll *a* <2 µg/l)

$k=0,1$ for mesotrophic lakes (tot-P 7-15 µg/l, chlorophyll *a* 2-4 µg/l)

$k=0,2$ for eutrophic lakes (tot-P >15 µg/l, chlorophyll *a* >4 µg/l)

In eutrophic lakes, with anaerobic deep waters and sediments, there is a N loss via denitrification, in addition to the sedimentation loss. This may vary considerably from lake to lake and is no simple function of any easily quantifiable parameter. In these lakes N retention may be 30% or more. Tirén (1983) estimates that the N retention in hypertrophic lakes is up to 50-60%. Similar results are found by Faafeng (1989) and Fleischer *et al.* (1989). Holtan (1991) added denitrification losses of 20% in eutrophic and 10% in mesotrophic lakes to the sedimentation loss. These estimates of N retention are rough approximations.

A study in a shallow, hypertrophic lake in Denmark indicated that the N loss by denitrification was closely related to the inlet and the in-lake concentration of tot-N. The loss percentage of N was not affected by a major reduction in N loading, which suggests that internal N loading is not an important delay factor for lakes recovery as often demonstrated for P (Jensen *et al.* 1992).

Another Danish study that included 16 shallow, mainly eutrophic lakes found that annual percentage retention ranged from 11 to 72%. The hydraulic retention time and the mean depth accounted for 75% of the variation in annual mean N retention. A model was developed for predicting monthly N

retention on the basis of external N loading, the lake water pool of N, hydraulic loading and the lake water temperature (Windolf *et al.* 1996).

$$(2) \quad N_{pool_t} = N_{lake_t} * Z_t * 1000$$

$$(3) \quad N_{ret-m(t+1-t)} = 0,455 * 1,087^{(Temp-mean(t+1-t)-20)} * (N_{pool_t} + N_{load(t+1-t)}) / d$$

N_{pool-t}	= the tot-N pool of the lake (mg N/m ²)
N_{lake-t}	= in-lake tot-N concentration (mg N/l) in a given month
Z_t	= mean depth (m) in a given month
$N_{ret-m(t+1-t)}$	= monthly N retention
$Temp-mean(t+1-t)$	= lake mean temperature
$N_{load(t+1-t)}$	= external N loading
d	= the number of days in the month (month t to t+1)

Rivers

In polluted, slow flowing rivers and brooks with low oxygen content, there are favourable conditions for denitrification, and a net yearly N loss is shown to take place in significant amounts:

- up to 10% (Hill 1979, Thyssen *et al.* 1986)
- 16% (Hill 1983)
- 25-30% (Jansson *et al.* 1986)

Several studies have shown that in highly productive wetlands, such as swamps and marshes, denitrification can be an even more efficient N remover. Loss values up to 60-95% are given in the literature (Nichols 1983, Fleischer *et al.* 1989). In low productive, well oxygenated rivers the retention of N on an annual basis may be disregarded.

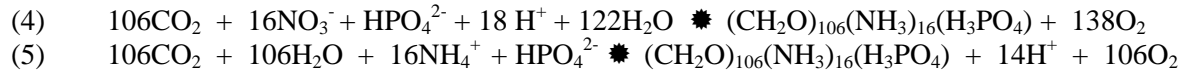
3. In-lake mechanisms of acid and base generation

There are many reactions which can consume or release hydrogen ions and in this manner affect the alkalinity of a water body. Among the processes that produce alkalinity are: Denitrification, NO₃⁻ assimilation, dissimilatory SO₄²⁻ reduction coupled with Fe reduction and precipitation of FeS, assimilatory SO₄²⁻ reduction coupled with net sedimentation of organic material, calcite dissolution, weathering of aluminosilicate minerals, and cation exchange. Among the processes that consume alkalinity are: Strong acid additions, NH₄⁺ (ammonium) assimilation, nitrification and oxidation of reduced S-compounds (Cook *et al.* 1986). The amount of base produced through assimilative and dissimilative processes depends on many factors which include: water renewal time, sedimentation rate, and gas fluxes to the atmosphere. Dissimilative processes become gradually more important as the deeper sediment layers become more anoxic.

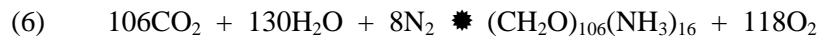
3.1 Assimilative processes

N can be assimilated (taken up by plants) as NO₃⁻ or NH₄⁺ (eq. 4 and 5). In freshwater ecosystems, uptake and metabolic use of N by plants and microbes are major forms of N removal, at least during the production season (Davison 1987). When one equivalent of NO₃⁻ is assimilated by algae or plants, approximately one equivalent of acid is consumed according to equation 4. The increase in pH must

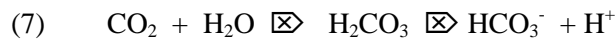
not be confused with the temporary shift in the CO₂ balance which occurs by primary production. If, however, the N is assimilated as NH₄⁺, a corresponding amount of acid is produced (eq. 5). Aquatic plants generally prefer NH₄⁺ over NO₃⁻, because NH₄⁺ uptake is energetically favourable (Davison 1987). NO₃⁻ must first be reduced before it can be used in protein-synthesis. If the organic material produced by photosynthesis is permanently buried in the sediments and then lost from the lake water, reactions 4 and 5 would represent the net gain or loss of acid to the water.



Some cyanobacteria and aerobic and anaerobic bacteria are capable of fixing atmospheric N (eq. 6). N fixation implies no production or consumption of H⁺.



Removal of CO₂ by photosynthesis will increase the water pH by pushing the equation 7 from right to left. In the pH-range 6-8, relatively small changes in CO₂ concentrations due to photosynthesis can cause a considerable shift in lake pH (eq. 8). In acid lakes (pH < 5,5) however, only small changes in pH will occur due to very low HCO₃⁻ concentrations (Jansson *et al.* 1981a).



pK₁: Equilibrium constant (25°C)
 asterisk (*) Including CO₂

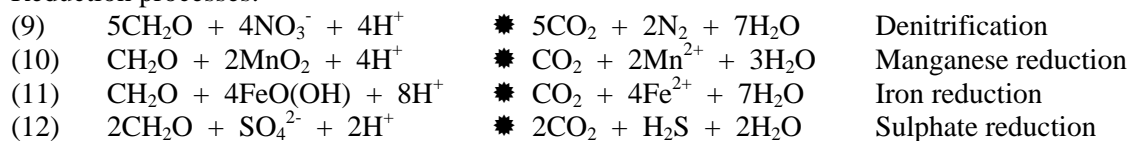
The relatively small amount of S in organic material (the molar C : S ratio is 100-150:1) results in relatively little base being generated by the burial of assimilated S. Assimilation of Fe, Mn, and Zn can be neglected in acid-base considerations (Davison 1987).

3.2 Dissimilative processes

Decomposition (mineralization) of organic matter follows the reverse of eq. 5. The conversion of organic N to NH₄⁺ consumes approximately 1 mole of H⁺ per mole of N produced. If the produced NH₄⁺ is nitrified (oxidised) to NO₃⁻ (eq. 13), it will be the same as reversing both eq. 5 and 4. Mineralization is an important process, as it recycles N that would otherwise be tied up in sediments.

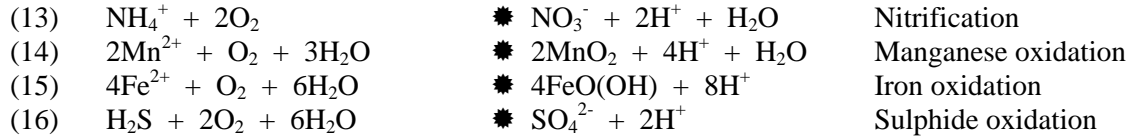
The oxidative decomposition of the CH₂O component of organic material does not generate or consume protons. When O₂ supply becomes exhausted, as in the hypolimnion of productive lakes or in sediments of oligotrophic lakes where O₂ flux is limited by diffusion, decomposition continues anoxically using other inorganic components (NO₃⁻, Fe³⁺, SO₄²⁻) as electron acceptors (Davison 1987). The resultant dissimilative redox transformations (denitrification, Mn⁴⁺ reduction, Fe³⁺ reduction, SO₄²⁻ reduction) can affect the acid-base balance (eq. 9-12).

Reduction processes:



Processes 10, 11, and 12 can effectively be reversed if the reduced products are exposed to molecular oxygen (eq. 14-16). The net effect is equivalent to CH₂O being oxidised by oxygen. The reverse process of denitrification is N fixation, organic decomposition and nitrification (Eq. 13).

Oxidation processes:



For each of these reactions, Davison (1987) calculated the acid neutralizing capacity (ANC) generated per mole of CH₂O, inorganic substrate and oxygen consumed (**Table 1**). To obtain a permanent alkalinity change in the lake, the reduced components must be exported via the outflow, released to the atmosphere, or buried in the sediments. The efficiency with which anoxic decomposition generates base can vary as much as a factor of 10, depending on the electron acceptor and the reduced product. Most redox-processes which occur in lakes are part of complete cycles, and so there is no permanent generation of acid or base. If, however, the reduced form is removed from the lake water, there is a real increase in alkalinity. The factor which determines the acid-base generation within the lake is the chemical form of the element in the inflow and outflow. Among the redox processes, the Mn-cycle is believed to have little effect on the total acid-base balance of the lake, because various conflictive Mn-components (different oxidation levels) often operate at the same time (Davison 1987).

Table 1. Redox processes affecting the acid-base balance of lakes (after Davison 1987).

Processes	☿ANC(org)	☿ANC(inorg)	☿ANC(O ₂)	Mechanism for permanent change:
9) Denitrification	+0.8	+1		Release of N ₂ to atmosphere
10) Manganese redn.	+4	+2		Export of Mn ²⁺ via outflow
11) Iron redn.	+8	+2		Burial as FeS
12) Sulphate redn.	+1	+2		Burial as FeS
13) Nitrification		-1	-2	
14) Manganese oxidn.		-4	-2	
15) Iron oxidn.		-8	-2	
16) Sulphide oxidn.		-1	-2	

☿ANC(org) ANC generated per mole of CH₂O consumed
 ☿ANC(inorg) ANC generated per mole of inorganic substrate consumed
 ☿ANC(O₂) ANC generated per mole of oxygen consumed

Denitrification (eq. 9) is the biological reduction of NO₃⁻ to produce gaseous forms of N (N₂, NO, or N₂O) which are released to the atmosphere. This is an alkalising process that consumes 1 mole H⁺ for every mole of N denitrified. Denitrification is important in aquatic ecosystems, especially in shallow lakes where sediment processes are important. NO₃⁻ is potentially available from the water column, but it is more often produced from organic matter within the sediments.

Nitrification (performed by bacteria and fungi) is a strongly acidifying process releasing two moles of H⁺ for each mole of NH₄⁺ nitrified (eq. 13). The acidifying potential of nitrification is dependent on whether the produced NO₃⁻ is assimilated again or leached. Nitrification is affected by factors as temperature, pH, C/N ratio, and supply of essential nutrients (e.g.). If the cycle is completed back to the starting materials, the acid-base balance is unaffected.

3.3 Alkalinity budgets

Hydrogen ions added to a lake will undergo one of the four chemical fates: (i) remain in the water, causing pH to decrease, (ii) react with alkaline species present in the water, (iii) exchange with other cations in the sediments, or (iv) be taken up by the biota in the water or sediments together with anions such as SO_4^{2-} or NO_3^- (Cook *et al.* 1986). Alkalinity summarises the fate of H^+ in freshwater and can be expressed by equation (17):

$$(17) \quad \text{Alk} = \text{HCO}_3^- + \text{CO}_3^{2-} + \text{OH}^- + \text{A}^- - \sum \text{Al}^{n+} - \text{H}^+ \quad (\text{eq L}^{-1})$$

where A- represents organic anions that are protolytic in the pH 4-7 range. Concentrations of CO_3^{2-} and OH^- can be neglected in this pH-range.

Acid additions to a lake may cause the alkalinity of the water to decrease (fates i, ii, and eq. 17). The capacity of a lake to neutralise acid in this way can be determined by an alkalinity titration. The reaction of H^+ with sediments or the uptake of H^+ by the biota can be determined from an alternative definition of alkalinity. Combining eq. 17 with the condition of electroneutrality for typical surface freshwaters having a $\text{pH} < 7$,

$$(18) \quad \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+ + \text{H}^+ + \sum \text{Al}^{n+} = \text{HCO}_3^- + \text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^- + \text{A}^-$$

yields

$$(19) \quad \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{Cl}^- = \text{HCO}_3^- + \text{A}^- - \sum \text{Al}^{n+} - \text{H}^+$$

The left side of eq. 19 is the definition of ANC (acid neutralising capacity), the right side corresponds to the traditional definition of alkalinity (eq. 17). Concentrations of NH_4^+ , Mn^{2+} , and Fe^{3+} , and other ions not mentioned in eq. 18 and 19 are usually negligible in Norwegian surface freshwaters.

Annual alkalinity production (P_a) in a lake can be calculated as:

$$(20) \quad P_a = \Delta M_a + O_a - I_a$$

where ΔM_a is the annual change in mass of alkalinity in the water column, O_a is the annual loss of alkalinity by outflow, and I_a is the annual alkalinity input (Cook *et al.* 1986, Schindler *et al.* 1986). Alkalinity production can be estimated by frequent sampling and alkalinity titration, or be predicted by modelling (Kelly *et al.* 1987).

In the experimentally acidified lake 223, 66-81% of the added H_2SO_4 was neutralised by alkalinity production in the lake (Cook *et al.* 1986). Alkalinity inputs from the watershed of lake 223 was very small, averaging about 5% of that produced in the lake. Nearly 85% of the in-lake alkalinity production was accounted for by bacterial SO_4^{2-} reduction, coupled with Fe^{3+} reduction and FeS formation. In this study, 60% of the alkalinity production took place in the littoral sediments, while hypolimnic processes accounted for 25%. Exchange of H^+ for Ca^{2+} and Mg^{2+} in the sediments accounted for 19% of the alkalinity generated.

3.4 Buffer-systems

Strong acids added or produced within a lake are to various degrees buffered and/or neutralised by in-lake geochemical processes. The degree depends on the alkalinity or the acid neutralizing capacity (ANC) of the lake water (eq. 17). In Norwegian lakes, the inorganic carbon buffer system (HCO_3^-), organic anions (A^-), and inorganic aluminium ($\sum \text{Al}^{n+}$) are the most important buffering agents (Lydersen 1997).

At pH-values of $> 5.5-6$ the inorganic carbon buffering system predominates. Aluminium buffering is most important for solution pH in water systems with negative ANC-values (pH values often below 5.0). Strong acids can also be buffered or neutralised by weak organic acids. An essential part of the organic acids in solution have pKa values closely related to the pH of the actual water, and thereby possess a significant pH-buffering role (Lydersen 1997). Organic humus material may also act as an acidic cation exchanger in surface water as in soils.

The buffering capacity of individual lakes can be simulated by water chemistry data and modelling, e.g. the Alchemi-model of Schecher and Driscoll (1987, 1988).

4. Effects of P addition on NO_3^- retention and deacidification in lakes

4.1 Mechanisms

Experimental P addition to lakes has been carried out in a number of areas, and especially in Canada. The purpose of these experiments has been to: (1) study nutrient dynamics in lakes and the biological responses (Schindler *et al.* 1973, Scheider and Dillon 1976, Dillon *et al.* 1979), (2) increase biological productivity, especially of fish stocks (Stockner and Shortreed 1988), and (3) increase NO_3^- retention and neutralise acid lakes (Davison 1987, Davison *et al.* 1995). In Norway, some P addition experiments have been performed to increase fish production in lakes (Langeland 1982, Johannessen *et al.* 1984, Skar 1986). This is also the purpose of a new research project "Limnocult", which was recently started in northern Norway (Skotvold *et al.* 1996). Here we mainly focus on the third purpose; to increase NO_3^- retention and to neutralise acid lakes by P additions.

A prerequisite for P additions to be effective in increasing NO_3^- -retention and reduce acidity is that P is the limiting nutrient for primary production. In south- and south-western Norway NO_3^- concentrations in lakes are often high due to high N deposition from long range transported air pollution (Skjelkvåle *et al.* 1997, Henriksen *et al.* 1997). In addition, P concentrations in acid sensitive lakes in this area are usually very low. This leads to high N/P molar ratios (often > 100) and strong P limitation of primary production (Faafeng and Hessen 1993). Morris and Lewis (1988) found that lakes with molar $\text{DIN}^1/\text{tot-P}$ ratios above 9 were always P-limited, whereas lakes with $\text{DIN}/\text{tot-P}$ ratios less than 9 could be limited by either N or P, and lakes with $\text{DIN}/\text{tot-P}$ values less than 2 were always limited by N. Most of the Norwegian acidified lakes have $\text{DIN}/\text{tot-P}$ ratios $\gg 9$, and should thus be clearly P-limited.

Both empirical data as well as theoretical models of N retention suggest that annual N retention may increase from $< 5\%$ in oligotrophic lakes to $> 30\%$ in eutrophic lakes (see sect. 2.2 and 2.3). Moderate P additions to oligotrophic lakes may thus be expected to increase the annual N retention with 10-15%. During summer the relative N retention will be much higher due to NO_3^- -assimilation in algae and aquatic plants.

When adding PO_4^{3-} to lakes with a high N/P ratio, alkalinity will be produced through NO_3^- assimilation. The assimilation of one mole of NO_3^- consumes roughly one mole of H^+ (see eq. 4), if C, N, and P is taken up by freshwater algae roughly according to the Redfield ratio of 106 : 16 : 1 (molar concentrations) or 40 : 7 : 1 (by weight). Burial of the produced organic material in the sediments ensures that there is a net gain of alkalinity in the lake water. If the produced organic material is decomposed, organic N will be mineralised to NH_4^+ (roughly one mole H^+ consumed), which either can be i) assimilated (one mole of H^+ produced), ii) nitrified (two moles of H^+ produced), or iii) lost

¹ DIN. Dissolved inorganic nitrogen (NO_3^- and NH_4^+)

via the lake outflow (no production or consumption of H^+). According to this, assimilation of one mole of NO_3^- can generate 0-2 moles of alkalinity depending on the processes involved.

Alkalinity can also be produced through the oxidative decomposition of the CH_2O component of the organic material. If oxygen is the electron acceptor during the decomposition, there is no net generation of alkalinity, but if other inorganic oxidants such as NO_3^- , SO_4^{2-} , or Fe^{3+} are used as electron acceptors, their dissimilative reduction generates alkalinity (eq. 9-12). If the reduced components are subsequently exported via the outflow, released to the atmosphere, or buried in the sediments, the alkalinity change will be permanent.

If the primary producers assimilate N and P according to the Redfield molar ratio (16:1), addition of one mole P in a P-limited freshwater system will consume 18 moles of H^+ by NO_3^- assimilation (eq. 4). This assumes that primary production remains P-limited throughout the experiment. If all the produced organic material undergoes dissimilative reduction, theoretically 94 moles of base can be generated from each mole of P added. In practice, 10-30 moles of base should be achievable (Davison 1990). Studies performed by Davison (1990) suggest that 32% of the assimilated organic matter underwent aerobic respiration, 25% was flushed out of the lake, 25% was buried in the sediments, 13% was consumed through reduction of NO_3^- to N_2 and 5% went to FeS production and burial. According to these estimates 21 moles of base was produced for each mole P added to the lake. P recycling within the lake will increase the efficiency of the added P, and theoretically provide sufficient positive feedback to approach a self-sustaining increase in productivity and pH (Davison *et al.* 1995). In practice however, some P will be buried in the sediments and some will be lost via the lake outflow.

Swedish P and N addition experiments in an acidified lake with low NO_3^- and NH_4^+ concentrations show that pH was roughly 0.5 pH-units higher in epilimnetic enclosures added P and N as NO_3^- than when the enclosures were added P and N as NH_4^+ (Blomqvist *et al.* 1989 and Blomqvist *et al.* unpubl. data). In this experiment pH was 5.0 with additions of P and N as NH_4^+ and 5.5 with additions of P and N as NO_3^- in the first experiment performed in June, whereas in a similar experiment in August, pH was 5.3 when P and NH_4^+ was added and 5.8 when P and NO_3^- was added. This is in accordance with eq. 4 and 5 above, and shows that the source of N used in primary production is of substantial importance in determining pH in the system after P addition.

The P addition technique will work best for lakes with a water renewal time in excess of a year, allowing sufficient time for NO_3^- assimilation and sedimentation. In lakes with shorter water renewal times, P must be added repeatedly, and it may be more difficult to maintain a stable water quality. The winter period will represent a problem in all lakes which are ice-covered. Due to the inverse temperature stratification, cold, acidic, and NO_3^- - rich water from the inlet brooks will rapidly flush through the lake.

4.2 Critical levels for P concentrations in lakes

To avoid any unacceptable eutrophication effects from P additions, it is important to keep the P concentrations in the lakes within certain limits. In most lakes P is the key element determining the rate of primary production and the size of algal biomass (Sakamoto 1966, Dillon and Rigler 1974). Models relating P concentrations at spring overturn to P loading, sedimentation rate, and water renewal time were refined during the 1970s and 1980s (Vollenweider 1976). In Norway, empirical P loading models of the Vollenweider type are developed for deep oligotrophic lakes (Rognerud *et al.* 1979) and shallow lakes with mean depth 1.5-15 m (Berge 1987). Using the FOSRES-model by Berge (1987) acceptable P concentration (critical limit) can be calculated by equation 21.

$$(21) \quad [P]_{\bullet} = -8.68 \cdot \ln z + 30.13$$

where $[P]_{\bullet}$ is the average P concentration in the water masses and z is the mean depth. The relationship between input concentration and lake concentration of P can be expressed as:

$$(22) \quad [P]_i = 2.293 [P]_{\bullet} T_w^{0.16}$$

where $[P]_i$ is the average input concentration and T_w is the water renewal time. Hence, when the initial P concentration of the lake and the runoff discharge is known, one can calculate the amount of P required to increase the lake P concentration to defined levels.

5. Example from a Norwegian acidified lake

5.1 Site description

For this study we have selected Lake Nedre Lundetjenn near Grimstad in southernmost Norway. The lake volume is about 1 mill. m³, if we assume a mean depth of 10 m (maximum depth is 25 m), and the water renewal time is about 0.35 years (mean annual discharge, ~ 3 mill. m³ yr⁻¹). Hydrologically, the lake is representative of small lakes in south- and southwestern Norway. During the summer of 1997 concentrations of H⁺, NO₃⁻, and tot-P in Lake Nedre Lundetjenn were approximately 10, 14, and 0.13 μmol L⁻¹, respectively (pH 5.0, 200 μg NO₃-N/L, 4 μg tot-P/L), which is a suitable water quality for studying the effect of P addition on NO₃-retention and pH.

In southernmost Norway about 2/3 of the annual runoff takes place during the period 1 November- 30 April (reference; Lake Røynealandsvatn 1993-1996; Hindar *et al.* 1996). In southwestern Norway, winter runoff can be even higher (3/4 of annual runoff in the Øygard catchment in Bjerkreim during the period 1993-1995; Kaste *et al.* 1997). In the same Øygard catchment, about 80% of the annual H⁺ and NO₃⁻ transport occurred during the period 1 November- 30 April.

5.2 Possible effects of P addition on N retention

By using eq. 21 the critical P concentration in Lake Nedre Lundetjenn can be estimated to 10 μg P L⁻¹. In a small scale experiment it is probably advisable to increase P concentrations a bit more than the critical value, for instance up to 15 μg P L⁻¹ (corresponding to 11 μg/l increase in P concentration). The most likely fate of N retention and deacidification after P addition is as follows:

Growing season

An increase of the tot-P concentration by 11 μg P L⁻¹ (0.35 μmol P L⁻¹), will increase NO₃⁻ assimilation in the standing water masses to about 80 μg N L⁻¹ (5.6 μmol/L), if all the nutrients are assimilated according to the Redfield ratio, and if NH₄⁺ is depleted in the epilimnion. If one assumes a constant NO₃⁻ input of 200 μg N/L during the growing season (1 May - 31 October), this assimilation corresponds to a 40% reduction of NO₃⁻ outputs during this period, provided that the P concentration level of 15 μg P L⁻¹ is maintained by frequent P additions. The treatment will decrease the DIN/tot-P ratio in the lake water from about 50 to 8, thus still maintaining a predominantly P-limited system, according to Morris and Lewis (1988).

Dormant season

During this period (~ 1 November- 30 April) primary production will be negligible, and effects of P additions are expected to be insignificant.

Whole year

Assuming a constant NO₃⁻ input of 200 μg N/L during the year, the P additions can give a 15% reduction in NO₃⁻ outputs from the lake (40% during summer, 0% during winter, assuming that 2/3 of

the annual runoff takes place during the winter period). This is probably a maximum estimate, in that streamwater NO_3^- concentrations usually are highest during the dormant season.

Potential as an abatement measure

Lake Lundetjenn represents a small catchment ($\sim 3 \text{ km}^2$) within the Nidelva river system, which drains a land area of about 4000 km^2 . Hence, treatment of such small lakes will have negligible effects on the overall water quality of the main river. River Nidelva each year carries 22 tons of P and 1100 tons of N to the sea. Of this, 13 tons of P and 980 tons of N originates from forests, bogs and mountainous areas. A 20% reduction of the N fluxes in River Nidelva (220 tons of N) would require yearly additions of 30 tons of P. To obtain this, P may be added to the large lakes Nisservatn, Fyresvatn, and Nesvatn in the upper parts of the catchment.

Little is known about the potential for NO_3^- retention by P additions to flowing water. P addition reduced NO_3^- concentrations in a small brook in SW Norway (Hessen *et al.* 1997a), and unpublished data from the Bjerkreim River in SW Norway indicate that P inputs from local sources increase N retention in the river system.

P addition will significantly increase NO_3^- -retention in acid lakes during the growing season, whereas traditional neutralising methods as liming will have little or no effect on NO_3^- -retention. P addition will also increase biodiversity, stimulate aquatic production and improve the resource base for fish production (see section 6), whereas liming has little or no effect on aquatic production per se (although biodiversity will increase after liming).

Although the above estimations suggest that a moderate P addition to acidic lakes may yield only 15% less NO_3^- loading from riverine sources to coastal waters on a yearly basis, the environmental benefit in marine areas may still be significant due to the estimated 40% reduction of N loading from riverine sources in the growing season. Since the relative contribution from riverine sources to available nutrient concentrations in the coastal areas is highest during summer (Hessen *et al.* 1997b), this reduction may both contribute to reduced algal biomass in estuaries and near-shore coastal areas during the summer months, as well as to a lower N/P ratio, which will reduce the probability for development of toxic dinoflagellate blooms (Skjoldal 1993).

5.3 Possible effects of P addition on acidity

Growing season

If one assumes that each mole of P added to the lake during the growing season generates 20 moles of base (Davison *et al.* 1995), the base production will be enough to increase the pH from 5.0 to 5.5 in a non-buffered system (initial $[\text{H}^+] = 10 \mu\text{mol L}^{-1}$ (pH 5.0), P addition: $0.35 \mu\text{mol L}^{-1}$, hypothesised base production: $0.35 \mu\text{mol L}^{-1} \times 20 = 7 \mu\text{mol L}^{-1}$, resulting $[\text{H}^+] = 10 - 7 = 3 \mu\text{mol L}^{-1}$; pH ~ 5.5). In an acidified system containing aluminium species and organic acids, the pH-increase will probably be less.

Dormant season

During this period (~ 1 November- 30 April) primary production will be negligible, and effects of P additions are expected to be insignificant. In addition, flushing and dilution by inflowing water will reduce the alkalinity. However, some base can be produced through dissimilative reduction of organic matter at the lake bottom. At present, little is known about the extent of this activity during the winter months. Davison *et al.* (1995) suggest that around 5 moles of base for each mole of P added should be achievable through dissimilative reduction of organic matter during the production season. If one assumes that each mole of P added to the lake during the growing season will generate 4 moles of base during the dormant season, the base production can only increase the pH from 5.0 to about 5.1 in a

non-buffered system (initial $[H^+] = 10 \mu\text{mol L}^{-1}$ (pH 5.0), P addition: $0.35 \mu\text{mol L}^{-1}$, hypothesised base production: $0.35 \mu\text{mol L}^{-1} \times 4 = 1.4 \mu\text{mol L}^{-1}$, resulting $[H^+] = 10 - 1.4 = 8.6 \mu\text{mol L}^{-1}$; pH ~ 5.1).

Whole year

The relatively poor alkalinity generated during the production season will be difficult to conserve throughout the winter in lakes with short water renewal times (< 0.5 years). However, little is yet known about the extent of alkalinity production through dissimilative reduction of organic material during the winter season.

Potential as an abatement measure

The P addition method will work best in moderately acidified lakes with initial pH-values above ~ 5.2 . In more acid lakes it may be difficult to raise pH above 5.5 without use of additional neutralising agents. However, such a pH-increase during the growing season may still be sufficient to allow survival and recolonization of many acid-sensitive species in the lake, who are able to avoid the acidic surface water during the dormant season. The stream biota may not be expected to recover as much as the lake biota, due to the low pH in the streams during the dormant season and early spring.

To obtain both increased NO_3 -retention and sufficient pH-increase to restore aquatic life in highly acidified lakes and streams, a combination of liming and moderate P addition may thus be the optimal management tool.

6. Possible biotic changes induced by gentle P addition to acid lakes

6.1 The plankton community

Bacteria

Changes along the P gradient:

Bacterial biomass increases along the P gradient, although less than the increase in phytoplankton (Cole *et al.* 1993). The increase is roughly an order of magnitude, and goes from $10 \pm 5 \mu\text{g C/l}$ in oligotrophic lakes to $100 \pm 50 \mu\text{g C/l}$ in eutrophic lakes (Hessen 1985). Empirical data show that the relative proportion of bacterial biomass in the total algal + bacterial communities decreases with the productivity of lake systems (Vadstein 1994), from a mean value of $> 30\%$ in oligotrophic lakes to $< 10\%$ in eutrophic lakes. Their proportion of tot-P is considerably higher due to the high specific P-content of bacterial cells.

Little is known about the diversity of microbes along the P gradient, but limited recent data indicate that bacterial diversity is highest at intermediate frequencies of P supply (Beck and Rothaupt, unpubl. data).

Changes along the acidity gradient:

There seems to be no clear change in bacterial biomass or metabolism with increasing acidity in clearwater lakes (Traaen 1978, Bell and Tranvik 1993), but bacterial biomass is often very high in acidic humic lakes, due to enhanced substrate supply from humic compounds (Hessen 1985). In some lakes in Canada, however, the bacterial abundance and metabolic activity were lower in acidified clearwater lakes than in non-acidic lakes: Bacterial degradation of organic matter in these acid-stressed environments was 30% less than in comparable non-stressed environments (Rao *et al.* 1989).

In acidic lakes the bacteria will hardly be utilised as a food resource for mesozooplankton, since the mesozooplankton community is dominated by calanoid copepods that are not able to eat bacteria. The bacteria may be utilised indirectly through the microbial loop, with the copepods feeding on

bacterivorous ciliates and flagellates. Through this indirect pathway of utilisation however, most of the energy, carbon and nutrients in the bacterial pool will be lost in respiration or recycled and not transferred to higher trophic levels in the food web.

Expected response to moderate P addition and pH increase

Due to increased supply of organic carbon from increased phytoplankton production, the pelagic bacterial biomass is expected to increase slightly with moderate P addition, following the general pattern with increasing biomass with increasing tot-P concentration (see above). The grazing rate on bacteria from the zooplankton may increase if bacterial feeders like *Diaphanosoma* and *Daphnia* reappear in the zooplankton community. This will increase the transfer of nutrients, energy and carbon from the bacterial pool to higher trophic levels, and reduce the loss due to respiration and viral lysis.

The bacterial activity in the sediments may also increase after P addition due to enhanced supply of autochthonous organic carbon. This may increase the mineralization of organic matter in the sediments, and reduce the oxygen level on the sediment surface. Dissimilatory NO_3^- reduction will then be enhanced.

Phytoplankton

Phytoplankton growth depends on several abiotic and biotic factors, of which temperature, light, nutrient availability, competition, and grazing are among the most important. P additions to a lake system may alter several of these factors, directly or indirectly, since P is the most common limiting nutrient for phytoplankton growth in Norwegian lakes (Faafeng and Hessen 1993).

Algae utilise available P very efficiently, even at the low P concentrations present in many Norwegian oligotrophic lakes. However, there is a strong competition between bacteria, phytoplankton, periphyton and macrophytes for available P. At low P concentrations, pelagic algae often contain high concentrations of the enzyme phosphatase, which ease the uptake of P from the lake water. Mixotrophy (combination of autotrophy and heterotrophy) is another strategy for algae to compete for P in oligotrophic waters. In addition to utilising inorganic P from the water column, mixotrophic species also have the ability to feed on P-rich bacteria (Bird and Kalff 1987). This is a successful strategy at low P concentrations, since pelagic bacteria are often very efficient competitors for P.

Examination of a large number of Norwegian lakes with different trophic status demonstrates that nutrient additions to a lake will bring both quantitative and qualitative changes in the phytoplankton community (Brettum 1989). Addition of P to an acidified, oligotrophic lake will thus increase both pelagic and littoral primary production. However, several factors will determine the qualitative and quantitative response of the phytoplankton community:

- *Competition:* The competitive relationship between phytoplankton, bacteria, periphyton and macrophytes will affect what proportion of the added P that will enter the phytoplankton compartment.
- *Light* can also be a limiting factor in humic lakes and in clearwater lakes if dense phytoplankton populations develop after P addition.
- *Limitation of other elements than P:* When adding P to a freshwater system, other elements can become limiting. As a rough estimate, phytoplankton will be increasingly N-limited as the N/P molar ratio decrease below 16 (Redfield ratio) in the water masses. At such low N/P ratios there is a risk for mass development of N-fixing Cyanobacteria (blue-green algae). Other elements that can be limiting are silica (for diatoms) and iron (Løvstad 1984). In acidified clearwater lakes there is often a shortage of inorganic carbon (Schindler 1986, Fairchild and Sherman 1992), which might hamper the uptake of P by the pelagic phytoplankton, and cause a shift towards growth of periphyton close to the lake bottom where carbon is supposedly more available.

- *P addition strategy*: Frequent, low level P additions during the production season tend to favour small, fast-growing species, and prevent development of large colony-forming Cyanobacteria (Stockner and Shortreed 1988, Olsen 1988), which are little affected by zooplankton grazing (Porter 1973).
- *Bioavailability of P*: It is somewhat unclear how the bioavailability of P is affected/changed in acidified lakes (Stokes 1986, Fairchild and Sherman 1992). According to Jansson *et al.* (1981b) P bioavailability is reduced due to precipitation with aluminium. In a recent review, Olsson and Petterson (1993) found no conclusive evidence for the oligotrophication of acidified water due to reduced bioavailability of P. Recent investigations, however, found good evidence for increased phosphatase activity and rapid phosphate turnover rates in acidified water (Mulholland *et al.* 1986, Münster 1994, 1995). This would ensure efficient P utilisation in acidified water.
- *Sedimentation and grazing* will suppress the phytoplankton biomass. A high grazing pressure tends to favour small phytoplankton species with high turnover rates. This leads to high phytoplankton production even if the biomass is low. In some cases a high grazing pressure favours large, inedible or non-digestible species, which will lead to an accumulation of phytoplankton biomass. Whether grazing will favour small vs. large phytoplankton species is dependent on size and species composition of the zooplankton community, as well as a number of other factors (Lyche 1995).
- *Toxic elements*: Inorganic aluminium (Al_i) present in the acid lake before treatment may be transformed to less toxic organic Al-fractions due to the increased production of organic matter. A decrease in the Al_i -concentration will be beneficial for invertebrates and fish, which indirectly will influence the phytoplankton community.

Due to these factors, it is difficult to predict the phytoplankton response to different levels of P additions. A survey of 355 Norwegian lakes in 1988 revealed a considerable variation in chlorophyll at equal tot-P concentrations (Faafeng *et al.* 1990). However, morphometric calibration of empirical P loading models shows that some of the variation is reduced, when considering either shallow lakes or deep lakes separately. There is still considerable variation left in the chlorophyll response in different lakes at similar P concentrations, due to inter-lake differences in food web structure, and other factors. Lakes with an efficient grazer food chain will have less algal biomass than lakes with a very low grazing pressure.

P addition up to a tot-P concentration of 15 µg/l in lake Nedre Lundetjenn will yield a phytoplankton biomass of roughly 6-8 µg chl a/l, corresponding to a total phytoplankton volume of 1 mg/l, and a secchi depth of 3 m, following the predictions from the shallow lakes empirical model (Berge 1987). This is roughly an order of magnitude higher than the present algal biomass in lake Nedre Lundetjenn (Brettum unpubl. data). This prediction will hold only if P is the limiting nutrient. A large part of the phytoplankton production will probably not be grazed, due to lack of large efficient grazers, and will thus sink to the sediments, and thereby increase N retention. If grazing increases over time, the chlorophyll-level will be < 6-8 µg/l and the secchi-depth > 3m at the same level of tot-P concentration. To what extent these predictions will hold for acidic lakes is uncertain, however.

Several P addition experiments, designed for different purposes, have been performed in lakes throughout the world. Collectively, these experiments have generated a huge literature on P additions and the resulting biogeochemical and biological responses. Many of the experiments have been performed in Canada; in the Experimental Lakes Area (ELA) in northwestern Ontario (Schindler *et al.* 1973), in the Sudbury region in southern Ontario (Scheider and Dillon 1976, Dillon *et al.* 1979), and in British Columbia (Stockner and Shortreed 1988). In Norway, large-scale P addition experiments have been performed in lakes by Langeland (1982), Johannessen *et al.* (1984), and Skar (1986). In 1997, a new lake-fertilisation experiment (the Limnocult-project) was started in Finnmark, northern Norway.

All fertilisation experiments lead to increased primary production, but the effects on phytoplankton community structure are diverse. In some cases fertilisation led to small qualitative changes (Johannessen *et al.* 1984, Skar 1986), in others to shifts to cyanophytes and chlorophytes (Schindler *et al.* 1973), even at low tot-P concentrations ($< 15 \mu\text{g P/L}$) (Dillon *et al.* 1979). During four years of nutrient additions to lake 227, ELA, Schindler *et al.* (1973) noticed dominance by different phytoplankton groups in different years of fertilisation. As can be seen from these few examples, phytoplankton response to different levels of lake fertilisation is rather complex. In acidic lakes however, the probability for cyanobacterial dominance should be low, even after P addition, since this group of phytoplankton rarely dominate at pH-levels < 7.0 (Brettum 1989). One exception is the cyanophyte *Merismopedia tenuissima*, which is most often found in lakes with pH-levels from 5-7 (Brettum 1989). Phytoplankton groups normally dominating in acidic lakes are dinoflagellates (i.e. *Peridinium inconspicuum*), mixotrophic chrysophytes and some chlorophytes (i.e. *Mougeotia spp.*) (Brettum 1989). Since P addition probably will not raise pH above 6.0, it is likely that these groups will continue their dominance also after P addition, maybe with reappearance of some cryptophytes like *Rhodomonas spp.* (Brettum pers. comm.)

Whole-lake experiments and measurements in lakes of different acidic status do not generally show declines in phytoplankton biomass or production as lakes acidify (Schindler 1994). Lakes susceptible to acidification tend to be low in ionic strength, and often low in P (Dillon *et al.* 1979). Thus, suggested correlations between pH and phytoplankton biomass may be more readily explained by the nutrient levels than by lake pH (op. cit.).

Zooplankton

Changes along the P gradient:

There is a weak positive relationship between zooplankton biomass and tot-P in lakes (Faafeng *et al.* 1990), with zooplankton biomass increasing from $< 100 \mu\text{g DW/l}$ in oligotrophic lakes to $> 200 \mu\text{g DW/l}$ in eutrophic lakes (Rognerud and Kjellberg 1984, Jeppesen and Faafeng unpubl. data), due to increased food supply of phytoplankton and bacteria. In most eutrophic lakes fish predation on zooplankton is intensive, and causes a lower increase in zooplankton biomass upon further nutrient addition. Data on zooplankton biomass from eutrophic systems without fish are more scarce, but theoretical models (Andersen 1993) as well as limited empirical data (Benndorf 1987) suggest that zooplankton biomass becomes unstable, and tends to bust and boom with time in an unpredictable pattern, if P loading exceeds $100 \mu\text{g P L}^{-1} \text{ yr}^{-1}$.

The number of zooplankton species in Norwegian lakes seems to increase with increased nutrient supply up to a moderately eutrophic level ($< 50 \mu\text{g P/l}$) (Schartau *et al.* in press), probably due to increased phytoplankton production and diversity (Brettum *et al.* in press). Limited data indicate that the number of species decreases again in highly eutrophic lakes (Schartau *et al.* in press). The species composition changes with increased P concentration from large cladocerans and copepods in oligotrophic lakes to a dominance of rotifers, smaller cladocerans and copepods in eutrophic lakes with a high fish predation (Lyche 1990). Eutrophic lakes with low fish predation often tend to be dominated by large *Daphnia* species during parts of the summer season.

Changes along the acidity gradient:

The effects of acidification on zooplankton biomass are not well described in the literature. Some acid-sensitive species, like *Daphnia*, disappear, whereas others, like the calanoid copepods often dominate the zooplankton communities in acidic clearwater lakes (Hobæk and Raddum 1980, Stenson *et al.* 1993). These changes in species composition, including the disappearance of many fast-growing cladoceran species, indicate that the zooplankton biomass should decrease with acidification (Hessen, personal communication). The effects of acidification on the food resources are complex, however, and literature data on acidification responses in the communities of phytoplankton and bacteria are contradictory (Olsson and Petterson 1993, Bell and Tranvik 1993). Fish predation decrease in acidified

lakes, whereas invertebrate predation from *Chaoborus* or *Notonecta* may increase. The net effect of these changes on zooplankton biomass is difficult to predict.

Zooplankton diversity, however, is clearly reduced in acidified lakes. This is due to a chemical intolerance to low pH-levels and high aluminium-concentration in several species, but may also be related to food web changes such as decreased fish predation and more intensive interspecific competition. Acidic humic lakes have more species than acidic clear-water lakes, but fewer species than less acidic lakes (Hobæk and Raddum 1980). The species composition changes from a community where most of the main zooplankton taxa are present, to a community dominated by calanoid copepods. The most sensitive taxa to acidification are the daphnids and also most of the cyclopoid copepods, whereas the cladocerans *Holopedium* and *Bosmina longispina* are more tolerant along with many calanoid copepod-species (Hobæk and Raddum 1980, Schartau *et al.* in press). The disappearance of daphnids probably reduce the zooplankton grazing on the phytoplankton, and creates a less efficient pelagic food web in terms of carbon and energy transfer to higher trophic levels. A larger proportion of the pelagic primary production thus will sediment down to the lake bottom, and either be buried in the sediments or be regenerated and used by the benthic algae (see section 5.2).

Expected zooplankton community response to moderate P addition and pH increase in a small Norwegian clearwater lake:

From the patterns outlined above, both biomass and species diversity in the zooplankton community is expected to increase with moderate P addition and pH increase, but the magnitude of the increase is difficult to predict.

Whether the daphnids will reappear in the community or not is hard to predict, since empirical data shows that *Daphnia* sometimes reappears rapidly (Hörnström *et al.* 1993), and sometimes slowly after liming in acidic lakes (Stenson and Svensson 1994). Whether the delay in reappearance of daphnids in limed lakes is due to exhaustion of the seed bank of ephippia in the sediments, to food limitation, P limitation, predation or other factors is not known. If the time-lag is due to food or P limitation, the re-establishment may be faster in a lake added a moderate amount of P, than in a limed lake. With an expected pH raise to only 5.5, however, it is uncertain whether daphnids will reappear in the lake, since these species seem to depend upon pH-levels > 5.5 to maintain normal reproduction (Locke 1991).

The soft-water-adapted cladoceran *Holopedium* may, however, be expected to increase its biomass significantly, along with *Bosmina longispina* and *Cyclops scutifer*. The calanoid copepods may also be expected to increase in biomass. The biomass of rotifers will probably stay low due to an increase in the biomass of invertebrate predators on the rotifers, such as cyclopoid copepods, carnivorous cladocerans (*Bythotrephes*, *Polyphemus* and *Leptodora*) and *Chaoborus* larvae. These changes will most likely cause a moderate increase in the grazing rate, as opposed to the large increase in grazing rate that would occur if large *Daphnia*-species reappear. The increased zooplankton biomass will also contribute to increased N retention through natural mortality and sinking, especially if calanoid copepods continue to dominate, since calanoid copepods have a high specific N content (> 10% of dryweight) (Andersen and Hessen 1990, Hessen and Lyche 1991).

If planktivorous fish is restocked in the lake after the P addition, the change in the zooplankton community will most likely be a decreased biomass, an increased biodiversity (Schartau *et al.* in press) and a decreased grazing pressure on the phytoplankton, as the large and efficient grazers are preferred by the fish. Stocking the lake with brown trout only, may have less impact on the zooplankton community, since this is not an efficient planktivorous fish species. Introduction of brown trout to a Swedish limed lake, however, caused reduced populations of invertebrate predators like *Chaoborus* and *Corixids*, and an considerable increase in *Daphnia longispina* (Stenson and Svensson 1994).

Stocking with brown trout may thus have a positive effect on the restoration of *Daphnia* and thereby a positive effect on the grazer control on phytoplankton.

6.2 Benthic flora

Periphyton

Periphyton, is a practical term for algae, bacteria, fungi and small organisms, such as ciliates, flagellates etc., living attached to-, or in close contact with a substratum in the water. Aquatic mosses are also included in the periphyton. The primary producers, attached algae and aquatic mosses, are generally the major constituents of the periphyton. Like phytoplankton, they depend on several biotic and abiotic factors for growth. Temperature, light, nutrients, competition and grazing are the most important. In the many nutrient-poor watercourses in Norway there is a strong competition for available nutrients between the periphyton and the phytoplankton. In most nutrient-poor acidified lakes, the availability of P is so low that it will limit the production of both phytoplankton and periphyton.

When a lake becomes acidified, increased standing crop of periphyton is often reported (Stokes 1986, Howell *et al.* 1990, Turner *et al.* 1991). There is also a shift in primary production from the pelagic zone to the lake bottom and the littoral. The mechanisms that govern this are reported to be several:

- reduced microbial activity causes reduced decomposition of organic matter and accumulation of particulate organic matter on the lake bottom, which thereby becomes a nutrient sink (Grahn *et al.* 1974, Stokes 1981, Jackson *et al.* 1990)
- reduced grazing activity by invertebrates causes reduced recycling of organic matter and reduced bioturbation at the lake bottom, and the nutrient sink effect is strengthened (Økland and Økland 1986, Stokes 1986)
- increased light penetration in the lake due to decreased phytoplankton biomass (Hultberg and Andersen 1982), reduced colouring of the humic substances (Gjessing *et al.* 1976) and increased sedimentation of the humic substances (Dickson 1978) enhances the primary production in the layers close to the lake bottom (Turner *et al.* 1991)
- the availability of dissolved inorganic carbon, a nutrient that may limit primary production in acidified waters (Schindler 1986, Turner *et al.* 1991, Fairchild and Everett 1988, Fairchild and Sherman 1992) is higher at the interface between open water and the lake bottom, where the major part of the decomposition of organic matter takes place. In addition, there is a leakage of bicarbonate and other inorganic carbon compounds from the sediments, which will be utilised by the periphyton rather than by the phytoplankton (Schindler and Turner 1982)
- a shortage of the essential nutrient, inorganic carbon, in acidified clearwater lakes might hamper the uptake of P by the pelagic phytoplankton and cause a shift towards growth of periphyton close to the lake bottom where carbon is supposedly more available

Two Norwegian large-scale fertilisation experiments include periphyton data:

One experiment was conducted in the small naturally acidic, humic Lake Skjervatjern (Lydersen *et al.* 1996). Artificial acidification with sulphuric acid and ammonium nitrate, also fertilised the lake and caused a shift from primarily N limitation to P limitation. In humic lakes the P supply may be higher than in clearwater lakes, due to a relatively large dissolved organic P fraction, suggesting that N limitation may be more common in humic lakes than in clearwater lakes. The production and standing crop of both phytoplankton and periphyton in Lake Skjervatjern increased after addition of ammonium nitrate, but the increase was most pronounced for periphyton (Brettum 1996, Lindstrøm 1996). This might be attributed to better growth conditions for periphyton in acidified lakes.

In the other experiment, which was designed to increase fish production, inorganic N and P was added to two small, ultraoligotrophic neutral lakes in Finnmark. The weight-ratio between the added N and P

was kept above the Redfield ratio (Redfield 1958), to reduce the probability for N limitation, and possible development of N-fixing Cyanobacteria. The preliminary results suggest that after a rapid increase in phytoplankton production, the periphyton was most affected by the nutrient addition and had the highest increase in biomass. The primary production rates of the two communities are so far not compared. After a month of nutrient addition, a dense cover of periphyton developed on the aquatic macrophytes. This appeared to reduce the nutrient availability and the light conditions for the macrophytes.

It is hypothesised that:

1. P addition will contribute to increased standing crop and production of periphyton and thereby increase the N retention in the lake
2. The effect of P addition on periphyton production and standing crop will be at least as pronounced as on phytoplankton
3. Increased periphyton production will increase the benthic fauna, mainly by providing a better food supply for the herbivorous invertebrates, but also by increasing the pH through increased primary production and NO_3^- assimilation.

According to Axler *et al.* (1994) optimal conditions for primary production will be achieved when the N to P rates, measured as DIN/tot-P ratios are between 1.5 and 4. This is in agreement with the results obtained in lake Skjervatjern. The lake tend to be P-limited at DIN/tot-P ratios around 5-6 and N-limited at DIN/tot-P ratios below 2. DIN/tot-P ratios constantly below 1.5 might promote the growth of N-fixing cyanobacteria. This must be considered when the P additions are calculated.

Macrophytes

Community biomass and diversity along gradients of P and H⁺:

The aquatic macrophytes (here including higher plants, aquatic mosses and charophytes) are as other primary producers in fresh waters generally regarded as being growth limited by P (cf. Wetzel 1983). This implies that a P enrichment of waters often leads to an increased growth and density of submersed macrophytes. In Norway this is well documented in some case studies from (strongly) eutrophicated rivers (Brandrud *et al.* 1989), and from eutrophicated lakes infested with *Elodea canadensis* (Mjelde 1997a). However, in acid soft-water lakes P rarely seems to be growth limiting (Roelofs *et al.* 1996). In these lakes, bicarbonate is no longer available and the CO_2 concentrations are frequently low (except in humic lakes). The vegetation therefore generally appears to be C-limited. Plants using CO_2 as their sole source for inorganic carbon such as bulbous rush (*Juncus bulbosus* = *J. supinus*) dominate, and there is substantial experimental and field evidence that their growth is primarily correlated with the C and N levels, and not the P levels (Roelofs *et al.* 1994, 1996). Within such lakes, areas with soft, organic bottoms might have a high production of CO_2 and NH_4^+ , and in such areas, P might possibly be limiting. There are indications from some eutrophicated, humic soft-water lakes that increased P inputs leads to an increased growth of the dominating vegetation of nymphaeids (floating leaf plants) (cf. Brandrud 1990).

The biodiversity of macrophytes is often highest in slightly enriched (mesotrophic) waters (Brandrud and Aagaard 1997, Mjelde 1997b), but this is probably mainly due to the higher ionic content and not the enhanced P levels in these lakes. In hyper-eutrophic lakes with tot-P > 50-100 $\mu\text{g/l}$, the diversity is strongly decreased. Also the production declines, and the submersed vegetation might disappear completely in heavily P-loaded lakes with severe algal blooms, due to reduced light transparency (cf. Mjelde and Faafeng 1997).

Acidification leads to a number of effects in the macrophyte community, the most important being the decrease in biodiversity due to the disappearance of plants using bicarbonate. Furthermore, acidification in some cases also leads to a substantial growth increase in some CO_2 plants such as

Juncus bulbosus and *Sphagnum auriculatum* coll. In Norway this increase is seen mainly in southeastern areas in slightly humic lakes with fairly organic sediments (Brandrud and Mjelde 1993).

Expected community response to moderate P addition and H⁺ increase:

Moderate P addition will probably lead to little macrovegetation response in most acidified lakes in Norway since most of these lakes are characterised by soft and clear water, and normally has a C-limited plant growth. This applies especially to the isoetid vegetation which is a character element more or less confined to soft-water lakes (species such as *Isoetes* spp. and *Lobelia dortmanna*). If the P addition leads to eutrophication and anoxic conditions in the sediments, this can in the long term lead to a decrease in the isoetid vegetation due to lack of seed germination in reducing sediments (cf. Roelofs *et al.* 1996).

Some other vegetation elements of soft-water lakes, such as bulbous rush (*Juncus bulbosus*) and *Sphagnum auriculatum* might in some cases probably have a more positive growth response. When these vegetation elements occur in more humic lakes with soft organic bottoms and high CO₂ and NH₄⁺ levels, they might be at least temporarily P-limited, and might also show an increased growth at moderate P addition levels. An increase in pH from (below) 5.0 to 5.5 will give possibilities for the re-establishment of soft-water, acid-sensitive species (mainly *Myriophyllum alterniflorum* and some *Potamogeton* spp.). The effects will probably be comparable to those of moderate liming (Brandrud and Roelofs 1996), which can lead to an increase of 20-30% of the macrophyte diversity.

7. Summary

N retention

The most important mechanisms contributing to N retention in lakes are assimilation, sedimentation, and denitrification. As a rough theoretical estimate, P additions can give a 40% reduction in NO_3^- outputs from Lake Nedre Lundetjenn during the growing season and a 15% reduction on a yearly basis. Since the relative contribution from riverine sources to available nutrient concentrations in the coastal areas is highest during summer (Hessen *et al.* 1997b), however, the 40% reduction in NO_3^- loading estimated for the growing season may both contribute to reduced algal biomass in near-shore coastal areas during summer periods with N-limited algal growth, as well as to a lower N/P ratio, which will reduce the probability for development of toxic dinoflagellate blooms (Skjoldal 1993).

Deacidification

Theoretical considerations and limited empirical data suggest that the base production following P treatment will be enough to increase the pH from 5.0 to 5.5 during the growing season in a non-buffered system. During the dormant season the pH-increase will be less (e.g. from 5.0 to 5.1). The P addition method will work best in moderately acidified lakes with initial pH-values above ~5.2. In more acidic lakes it may be difficult to raise pH above 5.5 without use of additional neutralising agents. However, such a pH-increase during the growing season may still be sufficient to allow survival and recolonization of many acid-sensitive species in the lake, who are able to avoid the acidic surface water during the dormant season. The stream biota may not be expected to recover as much as the lake biota, due to the low pH in the streams during the dormant season and early spring.

P addition will significantly increase NO_3^- -retention in acid lakes during the growing season, whereas traditional neutralising methods such as liming will have little or no effect on NO_3^- -retention. P addition will also stimulate aquatic production and improve the resource base for fish production, whereas liming has little or no effect on aquatic production *per se* (although biodiversity will increase after liming). To obtain both increased NO_3^- -retention and sufficient pH-increase to restore aquatic life in highly acidified lakes and streams, a combination of liming and moderate P addition may thus be the optimal management tool.

Bacteria

Due to increased supply of organic carbon from increased phytoplankton production, the pelagic bacterial biomass is expected to increase slightly with moderate P addition, following the general pattern with increasing biomass with increasing tot-P concentration. The bacterial activity in the sediments may also increase after P addition due to enhanced supply of autochthonous organic carbon. This may increase the mineralization of organic matter in the sediments, and reduce the oxygen level on the sediment surface. Dissimilatory NO_3^- reduction will then be enhanced.

Phytoplankton

According to an empirical model for shallow Norwegian lakes (Berge 1987), P addition up to a tot-P concentration of 15 $\mu\text{g/l}$ in lake Nedre Lundetjenn will yield a phytoplankton biomass of roughly 6-8 $\mu\text{g chl a/l}$. There is, however, considerable variation in the chlorophyll response in different lakes at similar P concentrations, due to inter-lake differences in food web structure, and other factors. Lakes with an efficient grazer food chain will have less algal biomass than lakes with a very low grazing pressure. Initially, a large part of the phytoplankton production in Lake Nedre Lundetjenn will probably not be grazed, due to lack of large efficient grazers, and will thus sink to the sediments, and thereby increase N retention.

The probability for cyanobacterial dominance should be low after P addition to acidic lakes, since this group of phytoplankton rarely dominates at pH-levels < 7.0 (Brettum 1989). Phytoplankton groups normally dominating in acidic lakes are dinoflagellates (i.e. *Peridinium inconspicuum*), mixotrophic chrysophytes and some chlorophytes (i.e. *Mougeotia spp.*) (Brettum 1989). Since P addition probably will not raise pH above 6.0, it is likely that these groups will continue their dominance also after P addition, maybe with reappearance of some cryptophytes like *Rhodomonas spp.* (Brettum pers.comm.)

Zooplankton

Both biomass and species diversity in the zooplankton community is expected to increase with moderate P addition and pH increase, but the magnitude of the increase is difficult to predict. The soft-water-adapted cladoceran *Holopedium gibberum* may be expected to increase its biomass significantly, along with *Bosmina longispina* and *Cyclops scutifer*. The calanoid copepods may also be expected to increase in biomass. These changes will most likely cause a moderate increase in the grazing rate, as opposed to the large increase in grazing rate that would occur if large *Daphnia*-species reappear. The increased zooplankton biomass will also contribute to increased N retention through natural mortality and sinking, especially if calanoid copepods continue to dominate, since calanoid copepods have a high specific N content (Andersen and Hessen 1990, Hessen and Lyche 1991).

Periphyton

P addition will contribute to increased standing crop and production of periphyton and thereby increase the N retention in the lake. The effect of P addition on periphyton production and standing crop will be at least as pronounced as on phytoplankton. Increased periphyton production will increase the benthic fauna, mainly by providing a better food supply for the herbivore invertebrates, but also by increasing pH through increased primary production and NO₃⁻ assimilation.

Macrovegetation

Moderate P addition will probably lead to little macrovegetation response in most acidified lakes in Norway since most of these lakes are characterised by soft and clear water, and normally have a C-limited plant growth. An increase in pH from (below) 5.0 to 5.5 will give possibilities for the re-establishment of soft-water, acid-sensitive species (mainly *Myriophyllum alterniflorum* and some *Potamogeton spp.*). The effects will probably be comparable to those of moderate liming, which can lead to an increase of 20-30% of the macrophyte diversity.

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Technical solutions in an ecological perspective.

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1. Summary

P additions can alleviate acidification problems in watersheds exposed to high nitrogen loads. Available global P reserves are, however, limited and must be utilised accordingly, implying that P fertilisation strategies must be developed within strict ecological frameworks. A holistic approach in which scientific tools as well as nutrient cycle technology is utilised to maximise the effects of added P, must therefore be developed. It is so far concluded that both refuse and wastewater have significant amounts of P which can be utilised at relatively low costs. Changing policies regarding P removal from sewage, making wastewater treatment demands recipient dependent, is presently the most efficient and easily implemented measure both from an ecological and economical perspective. New strategies to recover P from various waste streams must be implemented as ecologically sound sources of P. It also appears that existing advanced ecological treatment plants, implemented in relevant locations, may serve as model systems to study the influence of P on pH, N removal, entropy reduction, food and plant production potential.

2. Introduction

Davison *et al.* (1995) showed that controlled P additions to a small lake in the UK clearly reduced the NO₃ concentration, and also lead to an increase in lake pH through assimilation (See previous main chapter). This has not influenced the "official attitude" to P release to rivers and lakes, even though the knowledge of the mechanisms involved have been known for quite a while (Dillon *et al.*, 1979; Scheider and Dillon, 1976): P removal from wastewater is, for example, still required by 'default' in Norway, regardless of the status of the recipient, while N removal is hardly implemented. P in our waste streams are in many ways dealt with as if it was a toxin or represented a general environmental hazard, and most of it ends up on landfills. Some P is returned to agriculture as sewage sludge, but chemical coagulants making it generally unavailable to plants, and, therefore, of no value to the farmers. In other words, society thereby waste money, energy, chemicals and efforts to remove P where it could be beneficiary.

Superfluous phosphorous in run-off, effluents and wastes from various human activities ought to be utilised to the benefit of our environment, such as to buffer and regulate biological production in waters exposed to acid rain. This will require a new, holistic, multi-disciplinary quest focused on process integration, and something like an ideal "closed loop production" approach in the agroecosystem². The challenges are significant since certain steps in this case, such as acid rain and plant production, are intrinsically open. The potential rewards in "closing loops" are, however, great, yielding a variety of products, including enhanced food production, while reducing pollution and effects of pollution beyond our control.

² The term agroecosystem stems from 'agricultural-socioeconomic-ecological system', and is defined by Mc Cracken *et al.* (1988) as an ecological system partly modified by man to produce food, fiber or other agricultural products.

2.1 Goal

The goal of this work is to establish strategies to utilise phosphorous in wastes to alleviate environmental strain due to acid rain. To approach this objective, it is necessary to:

- Establish status concerning mass and energy flow in surface run-off, wastewater, sludge, and refuse.
- Improve technology for treatment of effluents to water and atmosphere, focused on resource recovery through separation, conversion and reuse.
- Improve control/overview of the anthropogenic nutrient cycle associated with agro- industrial society.
- Establish strategies to select the optimal combination of processes based on ecological and economic models.
- Develop advanced model-based control systems for process lines where the surrounding environment is included.
- Verification through real and virtual pilot projects.

The general purpose of this effort is to utilise scientific tools to establish better strategies for efficient development of sustainable solutions, including process integration in a larger ecosystem perspective. The traditional engineering approach, based on trial and error, is inadequate to solve the waste recycle challenges and growing global resource crisis. The alternative scientific and holistic approach can contribute in adapting technology to complicated ecological demands.

3. Methods

This study is primarily a literature review of possible technological solutions to the ecological challenges of 'NITRAP'. The primary scientific criterion applied to evaluate various solutions and strategies at this stage is: Maximise entropy reduction at a minimum of energy expenditures. All parameters in this thermodynamic optimisation criterion is not easily quantifiable at the moment, but it may still be a powerful tool to select appropriate solutions while sorting out inappropriate.

The energy potential, Gibbs free energy, G , can be applied to describe a systems status based on the definition:

$$\Delta G = \Delta H - T\Delta S$$

where: ΔH = energy loss in the process
 ΔS = entropy change in the process

A prerequisite for a process to occur is a negative ΔG . Energy must, therefore, be added to the system to obtain reduced entropy. Entropy reduction obtainable is limited according to:

$$\Delta H > - T\Delta S$$

The source of the energy added to the system is a key issue of this evaluation. Consumption of fossil fuels are, for example, not desirable (and easily quantifiable), while use of 'free energy' such as solar radiation for primary production or chemically bound energy in the wastes are desirable. Entropy reduction is harder to quantify, but it is at least possible for most relevant processes to determine whether entropy increase or decrease. A process in which dissolved nitrogen (e.g. NO_3) is assimilated

and incorporated in algae biomass, is an example of reduced entropy. It appears that an evaluation of the trophic structure of the influenced ecosystem can be used for a more detailed analysis.

4. Results and discussion

4.1 Sources

Four 'sources' of P are considered to be relevant; ¹fertilisers as applied in agriculture, ²non-point source runoff from fertilised arable land, ³wastewater (sewage) and ⁴organic wastes, including sludge and manure. A schematic presentation of the general 'flow of P' is presented in Figure 1, in which the arrows going to 'permanent loss' in landfills are interrupted with an arrow going to nutrient cycle technology (NCT). The processes presented in this figure are the main topics of the remainder of this paper.

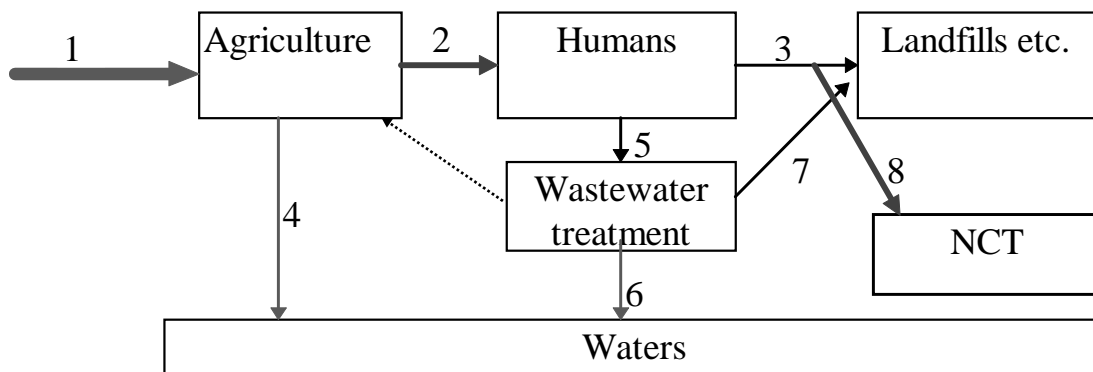


Figure 1. A simplified schematic presentation of the general 'flow of P' in our society: **1-** fertilisers applied in agriculture, **2-** food for human consumption, **3-** food wastes to landfills, **4-** non-point source runoff from fertilised land, **5-** wastewater (sewage) and **6-** wastewater to recipient, **7-** sewage sludge to landfills, and **8-** nutrients recovered through nutrient cycle technology.

Fertiliser

A large portion of the P which is introduced in our agroecosystem stems from fertilisers applied in agriculture. P plays an essential role as a potentially limiting factor in our agriculture as in all forms of life. High quality P ore is, however, a scarce resource, which, at the present rate of consumption, will be depleted within a few hundred years, putting the human culture, as we know it, in jeopardy. Utilisation of commercial fertilisers as P source in waters exposed to acid rain must be evaluated in this perspective, for example, requiring food production yields equal to or greater than in agriculture.

Non-point sources

Only 5-10% of fertiliser P added to arable land is actually taken up by crops in the year of application (Loehr, 1974). Typical runoff from fertilised grassland is $175 \text{ g P da}^{-1} \text{ yr}^{-1}$ and $6 \text{ kg N da}^{-1} \text{ yr}^{-1}$ (Undheim, 1988). Nutrients in runoff are not easily recoverable, and can therefore not play a key role as P source. *In situ* ecological measures to convert these nutrients to biomass may still be relevant (see Treatment parks).

Wastewater

Typical sewage contain $2.5 \text{ g P pe}^{-1} \text{ day}^{-1}$ and $12 \text{ g N pe}^{-1} \text{ day}^{-1}$ (SFT, 1983), implying that there is almost 1 kg P available per person, or $\sim 4000 \text{ tons P yr}^{-1}$ in Norwegian wastewater. A significant portion of this P is removed from the wastewater through chemical precipitation and deposited on

landfills, 'lawns' and arable land. Hardly any of this P is utilised, even though most of it is deposited on productive land, as it is strongly bound to the chemical precipitant. Wastewater represents, in other words, a significant source of P, which can be utilised (see Wastewater treatment).

Refuse

Organic wastes in private refuse is roughly estimated to contain $\sim 200 \text{ g P pe}^{-1} \text{ yr}^{-1}$, representing a significant P source, which, presently, to a large extent ends up on landfills. There are, however, legislative moves towards restricting this practice. There is, in addition, a significant amount of organic wastes from industry containing varying amounts of P. The extent of P recovery if and when land fill deposition and refuse incineration is abandoned depends on the 'logistic' and technological solutions established (see Refuse utilisation).

4.2 Technological solutions

Treatment parks

Wetlands and other ecological treatment systems are constructed to treat runoff from non point sources, primarily to avoid eutrophication, removing both P and N, producing biomass, reducing entropy, etc. (Bakke *et al.*, 1995; Hagman *et al.*, 1996). Such treatment systems are designed, using a multi-disciplinary approach, to also serve as parks, and are therefore termed *treatment parks*. They may include tree production, spawning grounds for trout, bird habitat etc.

Nitrogen is removed through ¹⁾assimilation in biomass (micro-organisms, plants and animals), and mainly through ²⁾desimilation (denitrification). Assuming persistent anoxic degradation Leonardsen (1994) estimated the denitrification potential in wetlands to be approximately 500 - 1000 kg N/ha·y, which may provide the downstream system with 100 - 200 kg alk/y. P is also removed through assimilation, but is also retained in the treatment system, representing thereby a future or additional 'nitrogen removal capacity'. Such treatment systems are relevant from three perspectives:

1. They may enhance the positive effects of P containing runoff from farmland to rivers and lakes influenced by acid rain.
2. They may provide protonic buffering zones by internal assimilative but mainly dissimilative processes.
3. They may serve as research objects to study the effects of relatively high P loads on N-rich ecosystems (non controversial objects as no additional P is required; some have been established for quite some time; significant variations in design).
4. They may serve as model systems to establish the most cost effective strategies to add P to N-rich watercourses.

Such treatment parks score high on the proposed thermodynamic evaluation, producing biomass and a more ordered ecosystem (less entropy) with a minimum of energy expenditures beyond that which the treatment system itself is able to harvest from solar radiation. Such treatment parks are, thereby, quite ideal measures for 'solar powered entropy reduction' (SPER).

Wastewater treatment

Most Norwegian wastewater treatment is designed to remove P through chemical precipitation, irrespective of the P needs of the recipient waters. Significant amounts of chemical precipitants are also lost to the recipient, due to the intrinsic inefficiency of such chemical treatment processes, binding naturally occurring P, making it unavailable to biological assimilation, buffering, NITRAP etc. Approximately 70% of the P rich sludge removed from wastewater is spread on farmland, but yield no significant fertilisation due to the strong chemical P binding. This general strategy requires significant input of energy (i.e. fossil fuels for transportation), while probably causing entropy

increase in the local ecosystem, especially when the recipient waters are oligotrophic. This strategy, in which P is contaminated with precipitants (e.g. AlPO_4), is also questionable from an ethical point of view, since P is a scarce resource. Some aluminum species are known to be toxic at lowered pH values.

Alternative strategies to treat wastewater, in which focus is shifted to resource recovery and/or utilisation is required, as a move towards sustain ability. Methods to selectively remove nitrogen at a reasonable cost, while controllable degrees of P is either released to the recipient or removed by biological means, are, therefore, developed (Horntvedt et al., 1997; Ingebretsen *et al.*, 1997). The aim is to develop strategies to apply environmental technologies that yield optimal nutrient cycles, strengthen production chains and convert pollution to products. Theoretical analysis and experience reveal a significant potential in the integration of treatment technology for regeneration of components in effluents (Helland *et al.*, 1997; Hagman *et al.*, 1997).

The two main moves in wastewater treatment technology relevant to NITRAP are: 1) improved bioreactor control through which consortia of micro-organisms can be cultivated to selectively remove nutrients as desired. 2) 'natural treatment systems' (see Metcalf and Eddy 1991 for general descriptions) which can be used both to assimilate and desimilate nitrogen, either as 'stand alone solutions' or as tertiary treatment processes to 'polish' effluents from bioreactors. Such biological treatment systems will have a variable degree of ecological quality (evaluated based on our thermodynamic criterion) depending on the local solution; e.g. degree of consumption of electrical energy for aeration, degree of energy utilisation based on biogas from the organics in the wastewater, degree of utilisation of the nutrients to enhance bioproduction and produce buffer.

Wastewater treatment plants can become self sufficient in energy while nutrients can be recovered and utilised as fertilisers in agriculture or directly in the recipient waters. Direct P utilisation in recipient waters to stimulate growth and alkalinity production, where appropriate, appears to be an ideal solution, minimising transport, energy consumption etc. The main hindrance to implementation of this strategy, at the moment, is tradition and questionable enforcement of existing environmental regulation (Effluent requirements are, officially, recipient dependent, while P removal by default is still reality).

Technology by which resources in wastewater can be utilised constructively in a holistic ecological perspective, is available, but ought to be further developed and adapted to the challenges imposed by acid rain. A total of 4000 tons relatively low grade P available, however, a relatively low fraction may be ecologically recoverable by present technological solutions. Strategies by which these resources are managed, in an optimal manner, by our environmental bureaucracy, must also be developed.

Assuming that one mole PO_4 has a buffer capacity equivalent of 8 moles CaCO_3 , it is estimated that 4000 tons P in sewage has a buffer capacity similar to 88000 tons CaCO_3 . It is certainly not realistic to utilised all P from wastes as buffers, but this calculation illustrates that wastes represents a significant P source in this respect. Anoxic decomposition internal may increase the effective P generated buffering capacity to approximatly 100 mol base/mol P (Davidson et.al., 1995).

Refuse utilisation

Organic refuse contain nutrients and energy as organic components which ought to be utilised, similarly to wastewater. Present situation and future perspectives are also similar to that of wastewater, and the same criteria ought to be utilised to select the optimal solutions. The purity of P separated from refuse will, however, typically be higher than for wastewater sludge, yielding higher value and greater interest for application in food production.

4.3 Distribution

P containing waste streams are typically not in abundance along watercourses suffering from acid rain. Logistics and technological solutions must bear this in mind, striving towards a minimum of energy expenditures for transport. There are, however, some P containing waste streams in areas suffering from acid rain, which should be utilised locally. Local utilisation of available P in waste streams in exposed areas is, according to the evaluation criteria in this evaluation, the most ecologically sound measures available.

4.4 Optimisation criteria

The entropy evaluation applied here is a useful tool to analyse ecological consequences of various solutions. It also appears that this entropy approach may be evolved to encompass the key ethical issue regarding food production and P utilisation, since food production is yield entropy reduction based on energy from solar radiation.

Criteria to decide on P application (where, when and how much) may be developed based on the ethics and the entropy evaluation, in addition to more traditional water quality criteria (e.g. avoid eutrophication). It may, for example, be required that: Food production in water courses due to P addition must be equal to, or better than in agriculture to be acceptable. Such a requirement will not be hard to fulfil in most cases where the source of P is sewage.

The way in which P is distributed in the local environment will also be of significance as far as fulfilling the above proposed criterion. P addition can give local effects such as salmon and trout reproduction (eg. remediate lost spawning grounds), which can influence larger areas and enhance food production beyond the immediate area.

It is also important to see P addition strategies relative to the quality of the P containing fertiliser. Addition of low grade P (e.g. from wastewater sludge) to bio-fuel production fields consuming N (and CO₂), may be evaluated based on other criteria than food production. Low grade P with heavy metal content above acceptable limits for food production may for instance be permanently immobilised in wood, together with N.

Mechanistic mathematical modelling is presently utilised as a key tool to design ecological technology, modelling the interaction between various cultures and physical and chemical processes. Such models ought to be developed further to predict effects in rivers and lakes and to design 'ideal interaction' between the treatment systems and the recipients.

5. Conclusions

A holistic approach in which scientific tools as well as nutrient cycle technology is utilised to maximise the effects of added P, can be developed. Both refuse and wastewaters have significant amounts of P which can be utilised at relatively low cost, both from a strict economic perspective and from a global ecological perspective. The main short term challenge is not technological but appears to be political or cultural/psychological, as P removal from sewage is still practised almost regardless of the recipient. Making wastewater treatment recipient dependent, removing particulate matter, BOD (Biochemical oxygen demand) and nitrogen, but not P (in relevant locations), is presently the most efficient and easily implemented measure. New strategies and technologies to recover P from various waste streams can be implemented, yielding ecologically sound sources of P. It also appears that existing advanced ecological treatment plants, implemented in relevant locations, may serve as model systems to study the influence of P on pH, N removal, entropy reduction, food and plant production

potential. Various scientific tools, such as thermodynamic and mechanistic mass balance models, ought to be utilised and developed further to develop optimal solutions efficiently.

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