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Phosphorus fertilizer leaching from drained ombrotrophic peatland forests: empirical studies and modelling

Mika Nieminen

VANTAAN TUTKIMUSKESKUS - VANTAA RESEARCH CENTRE

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Academic dissertation

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ABSTRACT

Empirical studies and a literature review were performed to understand and estimate the three primary processes controlling phosphorus (P) fertilizer leaching, that is: (1) the rate of dissolution of various P fertilizers, (2) the accumulation of dissolved P in vegetation biomass and litter, and (3) the adsorption of dissolved P by peat. A simulation model of fertilizer-P leaching from drained ombrotrophic peatland forests was developed in which the fertilizer dissolution, biological accumulation and adsorption of P are considered. The daily leaching of fertilizer-P was then modelled for two sites at which ditch outflow P concentrations had been determined in previous studies. The model estimates daily ditch water P concentrations where the fertilizer dose is similar to that used in practical peatland forestry (40-45 kg ha⁻¹), and assumes that all the added P enters the soil, i.e. the direct deposition of fertilizer granules to ditches and transport with the overland flow to ditches are negligible.

Comparison with measured data indicated that the changes in ditch water P concentrations were satisfactorily explained by the proposed model within the ranges of the model parameter values. Running the model for up to about 20 years after fertilization indicated that although the P concentrations in the ditch outflow peaked at different times and at different levels for fertilizers of differing solubility, the total leaching losses over the 20 year period were the same. It was therefore concluded that the rate of fertilizer dissolution is of minor importance in restricting leaching losses. The results indicated that the factors affecting the total leaching of fertilizer are the P adsorption capacity of the peat and the effectiveness of trees and understorey vegetation in accumulating the added P. The risk for high leaching rates of P fertilizer from drained ombrotrophic peat soils is related to their very low P adsorption capacity and incomplete accumulation of fertilizer-P in trees and understorey vegetation.

Keywords: fertilizer dissolution, phosphorus adsorption, phosphorus leaching, phosphorus uptake.

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LIST OF ORIGINAL PAPERS

The thesis is based on this summary report that proposes a simple model for fertilizer-induced leaching of phosphorus from drained ombrotrophic peatlands, and the following original papers, which are referred to in the text by their Roman numerals.

- I Nieminen, M. 1997. Properties of slow release phosphorus fertilizers with special reference to their use on drained peatland forests - A review. *Suo* 48(4): 115-126.
- II Nieminen, M. & Jarva, M. 1999. Dissolution of phosphorus fertilizers of differing solubility in peat soil: A field experiment on a drained pine bog. *Scandinavian Journal of Forest Research*. (accepted).
- III Finér, L. & Nieminen, M. 1997. Dry mass and the amounts of nutrients in understorey vegetation before and after fertilization on a drained pine bog. *Silva Fennica* 31(4): 391-400.
- IV Nieminen, M. & Jarva, M. 1996. Phosphorus adsorption by peat from drained mires in southern Finland. *Scandinavian Journal of Forest Research* 11: 321-326.

The authors' contribution

Paper II: Mika Nieminen was responsible for planning the study, carrying out the field work, performing the statistical analyses, and interpreting the results. He also wrote the first draft version of the manuscript. Maija Jarva participated in writing the section "Material and methods" and was responsible for carrying out the laboratory analyses.

Paper III: Leena Finér was responsible for the field work and the laboratory analyses. Mika Nieminen performed the statistical analyses, and participated in the interpretation of the results and preparation of the manuscript.

Paper IV: Mika Nieminen planned the study. He carried out the field work, the statistical analyses, and interpreted the results. He also wrote the first draft version of the manuscript. Maija Jarva was responsible for carrying out the laboratory analyses and participated in writing the section "Laboratory analysis".

DEFINITIONS

Biomass, as used in this study, includes not only the mass of the living parts of the plants but also the dead tissues fixed to living individuals (e.g. bark, heartwood, dead branches). Biomass has the same meaning as dry mass (dried in 105 °C).

Total plant biomass refers to the biomass of all vegetation compartments present in a peatland ecosystem (i.e. the above-ground parts in the tree, bush, field, and bottom layers, and the below-ground parts in root systems).

Total leaching of fertilizer refers to the complete loss of the leachable portion of the totally dissolved fertilizer, and *total uptake of P-fertilizer* to the amount of P taken up (by plants) from the totally dissolved fertilizer. Total leaching and total P uptake of fertilizer therefore depends on the time taken for all the fertilizer to dissolve.

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1 INTRODUCTION

1.1 General overview

In the beginning of the 20th century, the area of pristine peatlands in Finland totalled about 10 million hectares, covering one third of the total land area. About half of this area has now been drained for forestry purposes. The present growth of peatland forests is estimated to be 17.7 mill. m³, accounting for about 23 % of the total growth of all Finnish forests (Tomppo 1998).

The growth of trees on drained peatlands is often limited by a deficiency of available phosphorus. According to the most recent nutrient status investigations of peatland forests by needle analysis (Moilanen 1992, Veijalainen 1992), about 60 % of the stands would increase their growth after P fertilization. However, the use of P-fertilizers has been very small during the past two decades (Metsätalous ja vesistöt 1996).

One reason why there has been so little use of P fertilization has been the concern over the possible leaching of P from fertilized peatlands and the consequent eutrophication of recipient water courses. Indeed, long-term leaching losses of fertilizer-P from drained peatlands have been observed in a number of studies (e.g. Harriman 1978, Kenttämies 1981, Ahti 1983, Malcolm & Cuttle 1983a, Nieminen & Ahti 1993, Saura et al. 1999), and the trophic state of a recipient water body was shown to have been altered after the application of P fertilizer to a drained peatland (Lepistö & Saura 1998). However, other investigations have indicated only minor leaching of applied P from drained peatlands (Karsisto 1970, Karsisto & Ravela 1971, Almberger & Salomonsson 1979, Jarva et al. 1995). To identify those situations where the risk for enhanced leaching is high, information about all the mechanisms controlling the leaching of fertilizer-P is needed.

1.2 Mechanisms controlling the leaching of fertilizer-P from drained peatlands

1.2.1 Timing and method of application

When fertilizers were spread on the top of a >50 cm thick snow cover during winter, much of the fertilizer residues still remained in the surface 0-10 cm snow layer at the beginning of snowmelt (Paavilainen 1969). This finding

indicated that fertilizer residues might be carried to ditches with the overland flow of the snowmelt and hence caused great concern about possible water quality effects. Adverse results of P fertilizing during the winter period were published by Nieminen and Ahti (1993). They found substantially higher leaching losses from peatland areas where the fertilizers had been applied to the snow compared with those areas where the fertilizers had been spread on the bare ground after snowmelt. However, other investigations indicated insignificant changes in P outflow after spreading P-fertilizers on snow cover (Karsisto 1970, Karsisto & Ravela 1971).

The aerial application of fertilizer results in part of the fertilizer granules falling directly into the ditches. This may cause substantial P leaching to water courses. However, the effect of aerial application on P leaching from drained peatlands has not been studied.

1.2.2 Fertilizer dissolution

Phosphorus fertilizers that have been commonly used in Finland, either for practical peatland forestry purposes or for research purposes, include: superphosphate, Moroccan phosphate rock, Siilinjärvi apatite, and two commercial PK-fertilizers known under the trade names of "Rakeinen Suo-PK" and "Metsän-PK". Siilinjärvi apatite is a Finnish fluoroapatite of igneous origin while Moroccan phosphate rock is a carbonate apatite of sedimentary origin. "Rakeinen Suo-PK" is manufactured from Moroccan phosphate rock and potassium chloride and "Metsän-PK" from Siilinjärvi apatite and potassium chloride. The P in Siilinjärvi apatite, Moroccan phosphate rock and "Metsän-PK" is water-insoluble while about 16 % of total P in "Rakeinen Suo-PK" and 80 % of that in superphosphate is water-soluble. Water-soluble fertilizer-P is liable to leach to water courses immediately after fertilizer application. Phosphorus in water-insoluble fertilizers has first to be converted into a water-soluble form by chemical processes in soil before becoming available to plants or liable to leaching.

The effects of different P fertilizers on tree production on drained mires have been studied extensively in Finland (Karsisto 1968, 1977, Penttilä & Moilanen 1987, Kaunisto et al. 1993, Silfverberg & Hartman 1998). However, only one laboratory study has dealt with the dissolution of different P-fertilizers in peat soil (Yli-Halla & Lumme 1987). To fully understand the effects of fertilizers on the growth of peatland forests or the leaching of fertilizer-P from drained

peatlands the dissolution of different P-fertilizers under field conditions needs to be known.

Phosphate rock dissolution has been studied fairly extensively under field conditions in agricultural soils (Rajan 1987, Rajan et al. 1991, Rajan & Watkinson 1992). Substantial differences in the rates of dissolution between phosphate rocks of different origin have been shown (Rajan 1987). The rate of dissolution was closely related to soil pH and the fertilizer dose (Rajan et al. 1991). The release of P from phosphate rocks is also known to depend on the P and Ca sorption capacity of the soil (Mackay & Syers 1986), soil moisture (Bolland & Gilkes 1995), and Ca uptake by different plant species (Flach et al. 1987). In forest soils, mycorrhizal fungi may also play an important role in the release of P from slow-release fertilizers (Wallander et al. 1997).

If the peat P adsorption capacity is low, slowly-soluble P fertilizers are recommended in restricting P leaching to water courses. Under conditions of low peat P adsorption, however, the use of slowly soluble fertilizers will significantly restrict the total leaching of fertilizer-P only if the peatland vegetation accumulates more P than from easily soluble fertilizers. Several investigations have shown no significant differences in the total tree growth between sites where fertilizers with differing P solubilities have been used (Karsisto 1968, 1977, Penttilä & Moilanen 1987, Kaunisto et al. 1993, Silfverberg & Hartman 1998). These results imply that the total uptake of P-fertilizer by trees is not dependent on fertilizer solubility. It is not known, however, whether the uptake of fertilizer-P by peatland vegetation other than trees depends on the solubility of the fertilizer.

1.2.3 Uptake of fertilizer-phosphorus by vegetation

Finér (1991b) found that the amount of P bound-up in the understory vegetation plus tree stand on an ombrotrophic pine bog was lower than the amounts of P fertilizer used in practical peatland forestry (40-45 kg ha⁻¹). In well-developed unfertilized tree stands on drained mires, the annual uptake of P by the tree stand is only 1-3 kg ha⁻¹ (Finér 1989, 1991a, 1991b), of which about half is released back to soil as litterfall (Finér 1991b). On this basis, all of the P applied in practical peatland forest fertilization is unlikely to be bound up by the trees and other vegetation biomass. However, the fertilizer-induced changes in biomass P accumulation on drained peatlands are poorly known. Several studies have been carried out to investigate the effect of fertilization on the accumulation

of P in one or more vegetation compartments (i.e. in the tree, bush, field and bottom layers, and root systems) present in a drained peatland ecosystem (e.g. Haaveraen 1967, Braekke 1977, 1988, Paavilainen 1980, Malcolm & Cuttle 1983b, Finér 1989, 1991a). But investigations regarding the changes caused by fertilization in the amounts of P in total plant biomass (including all compartments) are scarce.

1.2.4 Adsorption of fertilizer-phosphorus by peat

In mineral soils, phosphate P from fertilizer is tightly bound to the soil by certain compounds, Al or Fe oxides and hydrous oxides in particular (Partiff 1978). Because of the low content of these compounds, some peat soils, especially acid *Sphagnum* peats, have been shown to have a very low P adsorption capacity (Kaila 1959, Rannikko & Hartikainen 1980). Cuttle (1983) estimated the P adsorption capacity of the least sorptive peat soils to be only 0.04 mg P 100 cm⁻³ (equivalent to 0.8 kg P ha⁻¹ in the 0-20 cm peat layer). Under conditions of low adsorption capacity and low P uptake by the vegetation, there is a substantial risk for the outflow of the fertilizer-P.

Some of the fertilizer-P may also be taken by microbes. Under conditions of high P addition, however, the microorganism phosphate uptake is of minor importance in reducing P leaching from peat soils (Richardson 1985).

1.2.5 Climatic conditions and hydrological properties of peat

Harriman (1978) and Ahti (1983) reported an equal increase in ditch outflow P concentrations from drained peatlands after P-fertilization (0.1-0.2 mg P l⁻¹). However, because of the much smaller annual precipitation and consequent runoff in Ahti's (1983) Finnish study, the annual amounts of P leached remained considerably smaller (< 500 g ha⁻¹) than the average annual loss of 1-2 kg ha⁻¹ reported by Harriman (1978) for peatlands in Scotland.

There is no information about the effects of different temperature conditions on the leaching of fertilizer-P from drained peatlands. However, the outflow of fertilizer-P may be expected to be the highest in areas where unfavourable temperature conditions restrict plant growth and therefore also the uptake of fertilizer. Temperature may also affect P leaching by either increasing or decreasing the rate of P release from slowly soluble fertilizers. However,

temperature was not found to significantly affect phosphate rock dissolution in tropical soils (Chien et al. 1980). High P concentrations in ditch outflow after fertilization may be observed in areas subjected to prolonged high-temperature droughts. This is because of the concentration effect caused by the loss of water in evapotranspiration.

Anaerobiosis in the peat may increase the leaching of phosphate ions for at least two reasons. Firstly, anaerobic conditions are likely to reduce plant growth and thereby also the P uptake by vegetation. Secondly, anaerobiosis inhibits P adsorption due to the reduction and redistribution of Fe (Armstrong 1975). Due to the high water retention capacity of peat (Päivänen 1973), anaerobic conditions tend to prevail in the subsurface peat layers of most peat soils.

The changes in the P concentrations in ditch outflow after fertilization are also affected by the rate of water flow through peat. Relatively rapid changes in P concentrations are to be expected from the soils consisting of slightly decomposed *Sphagnum* peat. This is because of the higher hydraulic conductivity of such soils (Päivänen 1973). Low hydraulic conductivity is typical for highly decomposed peats. In such soils, there may be a substantial delay before any leaching of P fertilizer occurs.

1.3 Aims of the study

The objective of this study was to determine the effects of (1) varying dissolution of different P-fertilizers, (2) the accumulation of P in vegetation biomass and litter, and (3) the adsorption of P by peat on the leaching of P from drained ombrotrophic peatland forests. Empirical studies and a literature review were first performed to understand and estimate these three processes. To determine the fate and transport of fertilizer-P via these processes, a simple model of fertilizer-P leaching from drained ombrotrophic peatlands was developed. The model was then applied to the two sites at which fertilizer-P leaching had been determined in previous studies. Finally, the impact of the processes affecting P leaching were investigated using sensitivity analysis and various scenarios.

2 SUMMARY OF ORIGINAL PUBLICATIONS

In this summary report, the results of the three empirical studies (II-IV) are used to determine model parameter values. The main results of the studies concerning the fate of P fertilizer on drained ombrotrophic peatlands are therefore given in the parameterization section (3.3) and in connection with the interpretation of the model parameter values (3.6.3). However, a brief summary of the studies II-IV is given below. Detailed descriptions of the material and methods used, the results obtained, and the interpretation of the results are given in the original publications. The first original paper (I) reviews the properties, manufacture, and behaviour in agricultural and peat soils of various P-fertilizers. It was made as background information to the fertilizer dissolution study (II).

The fertilizer dissolution study (II) was performed on a drained pine bog in southern Finland (61°51'N; 25°59'E, 131 m a.s.l.). The experiment consisted of five fertilization treatments with three replicates. The treatments were: (1) Superphosphate, (2) Mire-PK (Finnish: Rakeinen Suometsien PK), (3) Moroccan phosphate rock, (4) Siilinjärvi apatite, and (5) Forest-PK (Finnish: Metsän PK). In each of 15 plots, unfertilized and fertilized sampling quadrates were systematically located. Peat samples from the unfertilized quadrates were taken at the beginning of the experiment in August 1996. Peat samples from the fertilized quadrates were taken about 2, 12, 20, and 24 months after fertilization. The measurements of the amount of residual (undissolved) fertilizer-P were used to investigate the dissolution of the studied fertilizers. Dried (70 °C) and milled samples (1 g) were first pre-extracted with 0.5 M NaCl/TEA and 1 M NaOH to remove dissolved fertilizer-P. The amount of the residual fertilizer-P was then estimated as the difference in the amount of P dissolved in a mixed acid digestion (HNO₃, HCl, H₂SO₄) between fertilized and unfertilized samples. Phosphorus concentrations in the digests were determined by ICP/AES, ARL 3580. The dissolution of the studied fertilizers, calculated as the proportion of the amount of fertilizer-P added, ranged from 44 % (Forest-PK and Moroccan phosphate rock) to 93 % (Superphosphate) over the two years covered in the study (Fig. 3 in publication II).

The effects of PK and NPK fertilization on the dry mass and nutrient accumulation in understorey vegetation (III) were studied on a drained low-shrub pine bog in eastern Finland (62°14'N; 29°50'E, 81 m a.s.l.). A 3 x 3 Latin square design was used. The treatments were: (1) unfertilized, (2) fertilized with PK(MgB), and (3) fertilized with NPK(MgB). The understorey vegetation was sampled prior to fertilization and at about 2.5 years after fertilization. The understorey vegetation was divided into bush, field and bottom/litter layers. The bush layer vegetation was very sparse and have therefore been ignored in

the study. Litter accumulated on and between bryophytes and lichens was not separated from the living bottom layer vegetation and is why the layer was referred to as the bottom/litter layer. Above-ground parts of the layers were harvested from 20 sampling quadrates (0.25 m²) on each plot (1500 m²), and the root systems were extracted by hand from the peat samples taken down to a depth of 40 cm. Total nutrient concentrations in the samples were determined according to Halonen et al. (1983), and nutrient amounts were calculated by multiplying the dry masses with the nutrient concentrations. The results of an earlier study (Finér 1991a) carried out at the same site on the tree layer were combined with those of study III on the understorey vegetation and litter. About 33 % of the added P (53 kg ha⁻¹) had accumulated in the total plant biomass (field and bottom/litter layers + tree layer) after 2.5 years on the PK-fertilized plots, and about 25 % on the NPK-fertilized plots (Table 4 in publication III).

Peat samples from 20 sites were collected from different parts of southern Finland (between latitudes 60°N and 62°N) to study the adsorption of P by peat and those soil properties likely to influence it (IV). The samples were first used to determine P adsorption isotherms. For this, samples of moist peat (equivalent to 1 g dry weight) were added to bottles containing solutions with increasing amounts of P (from 0.0 mg P l⁻¹ to 40.0 mg P l⁻¹). After equilibration (23 h) and filtration (first through a glass fibre paper and then through a membrane filter) the concentration of P remaining in solution was measured (ICP/AES, ARL 3580). Phosphorus that had disappeared from the solution was considered to have been adsorbed, and the amount of P adsorbed was plotted against the equilibrium P concentration to obtain the adsorption isotherms (see Fig. 1 in publication IV). To determine maximum adsorption, the P adsorption index values (PSI) and the total P adsorption capacity (PAC) values were also calculated. The PSI values, determined from one addition of 150 mg P (100 g)⁻¹ dry weight of peat, were calculated as: $X/\log C$, where X is the quantity of P adsorbed (mg P (100 g)⁻¹ dry weight of peat) and C is the concentration of P in the equilibrium solution (Bache & Williams 1971). For the calculation of the total P adsorption capacity (PAC), the X term in the quotient $X/\log C$ was multiplied by the bulk density of the peat sample and the adsorption was expressed as kg P sorbed ha⁻¹. Adsorption was strongly correlated to the Fe content of the peat (Table 2 and Fig. 2 in publication IV). PAC for several of the soils studied was substantially lower than the amount of P fertilizer (40–45 kg ha⁻¹) applied to Finnish peatlands in practical peatland forestry (see Table 3 in publication IV).

The following statistical methods were used in the empirical studies: Pearson correlation analysis (IV), regression analysis (II, IV), analysis of variance for repeated measures designs (II), and analysis of variance for Latin square designs and Tukey's test (III).

3 MODELLING

3.1 Model structure

In this section, a simple model for fertilizer-P leaching from drained ombrotrophic peatlands is presented (Fig. 1, Table 1). In the model, the peat deposit is divided into three layers. In the uppermost active layer, a certain amount of fertilizer-P (DP_t) dissolves each day. A fraction (a) of the dissolved fertilizer-P is adsorbed by the peat and another fraction (u) is accumulated in the vegetation biomass and litter. The remaining fraction ($1-(a+u)$) leaches to the runoff layer and to the ditch from where it is exported from the basin. The bottom passive layer is assumed to have no significant effect on the leaching behaviour of the fertilizer-P. The fraction of P going to leaching is assumed to be completely and evenly mixed with the daily volume (W_t) of water present in the runoff layer. The concentration of fertilizer-P in runoff is calculated by dividing the amount of fertilizer-P in the runoff layer by the volume of water in the runoff layer (i.e. RP_t/W_t), and the ditch outflow of fertilizer-P (OP_t) is simply given by the product of the concentration of fertilizer-P in the runoff layer and the runoff water flow (i.e. $(RP_t/W_t)q_t$).

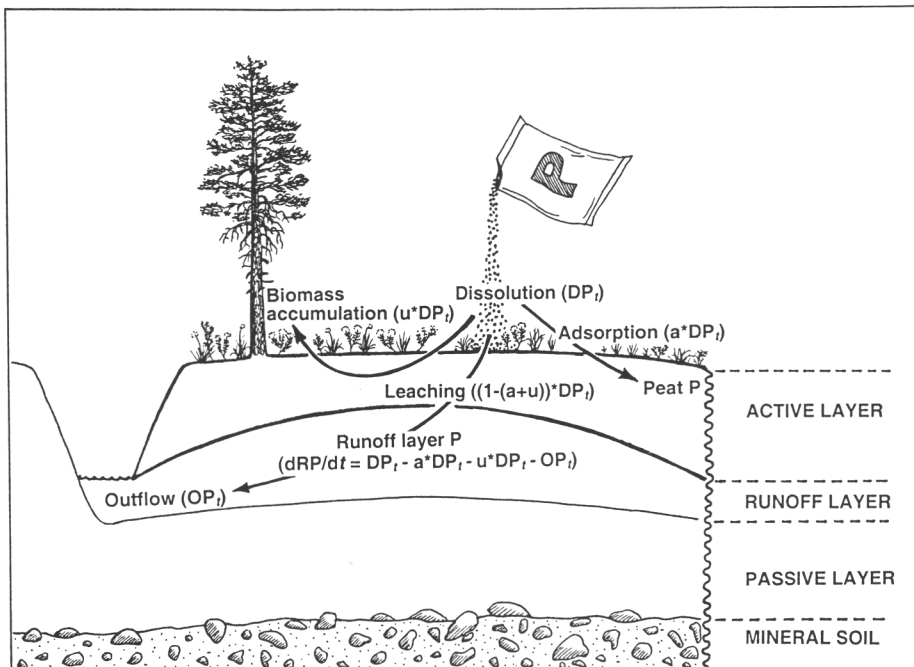


Fig. 1. Schematic presentation of the fertilizer-P leaching model.

Table 1. State variables and equations for fertilizer-P leaching model.

$$dRP/dt = DP_t - a * DP_t - u * DP_t - OP_t$$

$$OP_t = (RP_t / W_t) * q_t$$

$$TP_t = (RP_t / W_t) * 1000 * d + BP$$

RP_t = amount of fertilizer-P in runoff layer at time t ,
g ha⁻¹

DP_t = dissolution of fertilizer-P, g ha⁻¹ d⁻¹

a = coefficient for rate of adsorption of
fertilizer-P by peat

u = coefficient for rate of accumulation of fertilizer-P
in vegetation biomass and litter

OP_t = outflow of fertilizer-P, g ha⁻¹ d⁻¹

W_t = water volume in runoff layer at time t , l ha⁻¹

q_t = runoff, l ha⁻¹ d⁻¹

TP_t = total P concentration in runoff at time t , mg l⁻¹

d = dilution coefficient

BP = background P concentration in runoff, mg l⁻¹

t = time, d

The proposed model assumes that all the applied P enters the soil and that the direct deposition of fertilizer granules to the ditches and the transport with the overland flow to ditches are negligible. Therefore, the model should not be applied to sites where the fertilizer has been applied from the air nor where it has been applied on snow.

3.2 Related data

In addition to the results of the original publications II-IV, data from two previous leaching experiments were used for the definition of model parameter values. The two studies had been carried out at Liesineva (Ahti 1983) and Kivisuo (Ahti & Paarlahti 1988, Nieminen & Ahti 1993). The results from these studies were also used for model application and verification. The experiments are briefly described below and more detailed descriptions are to be found in the previously mentioned publications.

The Kivisuo experiment (61°53'N, 25°58'E, 125 m a.s.l.) was drained and partly fertilized in 1967. The area is divided by ditches into 16 artificial small basins (area 1.2 or 2.0 ha) which differ from each other with respect to ditch spacing and original ditch depth (Fig. 2). The original 40 cm deep ditches were cleaned in 1976. The original site type in basins 1-8 varied from cotton grass pine bog to small sedge pine bog, and in basins 9-16 from small sedge pine bog to *Sphagnum fuscum* bog (Heikurainen & Pakarinen 1982). The thickness of the peat layer at the time of ditching was 1.5-2.5 m throughout. Some chemical properties of the surface peat at Kivisuo are given in Table 2.

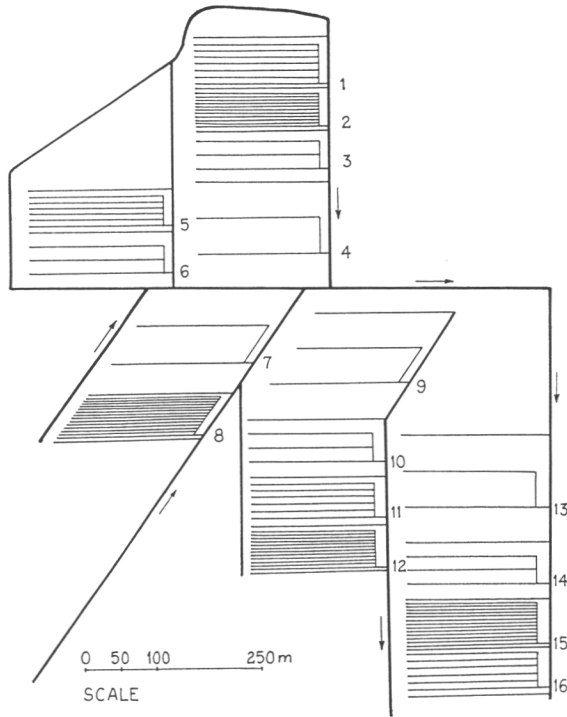


Fig. 2. The experimental layout at Kivisuo showing basin areas 1-16. Ditch spacing = 5, 10, 20 or 50 m. Original ditch depth: Areas 1-4 and 13-16 = 0.8 m, and areas 5-12 = 0.4 m. Fertilization: Areas 2, 3, 5 and 7 = application on snow 9.-13.3.1987, areas 1, 4, 6 and 8 = application on bare ground 19.-20.5.1987, and areas 9-16 = control.

During the period 9.-13.3.1987, basins 2, 3, 5 and 7 were broad cast fertilized by spreading 500 kg ha⁻¹ of a commercial PK-fertilizer (P 8.7 %, K 16.6 %, the fertilizer is known under the trade name “Rakeinen Suo-PK” in Finland, and is here after referred to as Mire-PK), and 215 kg ha⁻¹ of urea on to the snow pack. During the period 19.-20.5.1987, a similar application was spread on bare

Table 2. Some background information about peat properties at Kivisuo and Liesineva (the surface 0-15 cm peat layer).

	Kivisuo	Liesineva
Ash content ¹⁾ , %	1.39	3.30
P _{tot} ²⁾ , mg kg ⁻¹	524	1066
K _{tot} ²⁾ , mg kg ⁻¹	388	701
Ca _{tot} ²⁾ , mg kg ⁻¹	1466	2092
Mg _{tot} ²⁾ , mg kg ⁻¹	362	379
Al _{tot} ²⁾ , mg kg ⁻¹	451	1777
Fe _{tot} ²⁾ , mg kg ⁻¹	805	2120

Methods used:

¹⁾ Halonen et al. (1983)

²⁾ Dry digestion in HCl (Halonen et al. 1983); ICP/AES

ground after snowmelt at basins 1, 4, 6 and 8. Basins 9-16 were used as unfertilized controls. Phosphorus in the Mire-PK fertilizer originates from water-insoluble Moroccan phosphate rock. Due to the addition of nitric acid during granulation while being manufactured, about 16 % of the total P is converted into water-soluble form.

The runoff samples were collected from the overflow of a rectangle-notched overfall weir installed in the outlet ditch of each basin area. Results showed that there was a considerable increase in P concentrations in the outflow from the fertilized basins compared to the unfertilized control basins, particularly in the case of the basins where the fertilizer had been applied on to the snow pack (Nieminen & Ahti 1993). Some 9 kg P ha⁻¹ of the P-fertilizer was lost over 1.5 years after fertilizer application on to the snow pack. The corresponding loss was about 3 kg P ha⁻¹ for the basins where the fertilizer had been applied on bare ground.

As the model is not applicable to sites where the fertilizer has been applied on snow, the model verification data comes only from the basins 1, 4, 6 and 8. The tree stand was dominated by Scots pine (*Pinus sylvestris*), and the volume of the stand measured in 1982 was 28.8, 15.8, 11.7, and 4.3 m³ ha⁻¹ in basins 1, 4, 6, and 8, respectively.

The Liesineva experiment (61°59' N, 23°15' E, 150 m a.s.l.) had been drained already in 1915, but the present ditch network originates from 1955 (Fig. 3). Ditch spacing varies from 5 to 100 meters, and the original ditch depth was 0.8 m. The original site type was cotton grass pine bog with patches of ordinary small sedge bog (Heikurainen & Pakarinen 1982). The original thickness of the peat layer was over 2 m. Some chemical properties of the surface peat at Liesineva are given in Table 2. The tree stand was dominated by Scots pine (*Pinus sylvestris*), and the volume of the stand measured in 1979 varied with spacing as shown in Table 3.

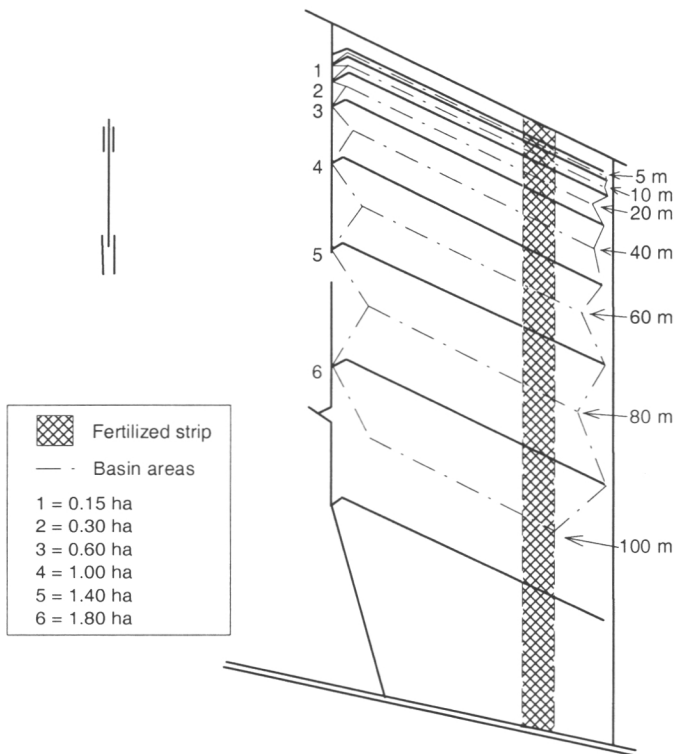


Fig. 3. The experimental layout at Liesineva showing basin areas 1-6. Ditch spacing: 5-100 meters. Size of basin area: 0.15-1.80 ha.

N, P and K fertilizations were performed at Liesineva already in 1961 and 1965 (Ahti 1983). However, the model verification data comes from a later fertilization experiment. In 1977, a strip comprising 10 % of the experimental area was fertilized with 500 kg ha⁻¹ of a commercial PK-fertilizer (P 8.3 %, K 15.8 %, P as Moroccan phosphate rock, K as potassium chloride) and 400 kg ha⁻¹ of ammonium nitrate fertilizer (N 27.5 %). Compared to the pre-fertilization period, the P concentrations in ditch outflow were 0.1-0.2 mg l⁻¹ higher during the period 1977-1982 (Ahti 1983).

Table 3. Volume of the tree stand measured in 1979 in relation to ditch spacing at Liesineva.

	Ditch spacing, m						
	5	10	20	40	60	80	100
Stand volume, m ³ ha ⁻¹	98.1	93.1	73.4	52.7	35.4	24.2	25.7

The Liesineva ditch runoff samples were collected from V-shape gutters installed in the bottom of the ditches. No damming up of runoff water was induced by this sampling method and samples could be collected during somewhat drier periods than would have been possible if sampling had taken place from the overflow of V-notch weirs. Samples from very low flow periods showed higher variation in P concentrations than those from wetter periods (Fig. 4). No explanation was found for the high variation in runoff P concentrations during dry periods. However, very low flows have little effect on the overall leaching of fertilizer-P (calculated as g P ha⁻¹) compared to the influence of very high spring and autumn flows. Samples taken when the runoff was < 0.015 l s⁻¹ ha⁻¹ were therefore excluded from the Liesineva verification data. Some of the sampling occasions lacked information about runoff, usually as the result of cessation in runoff flow during the sample collection or immediately after it. The samples with no information about runoff were also excluded from the Liesineva data.

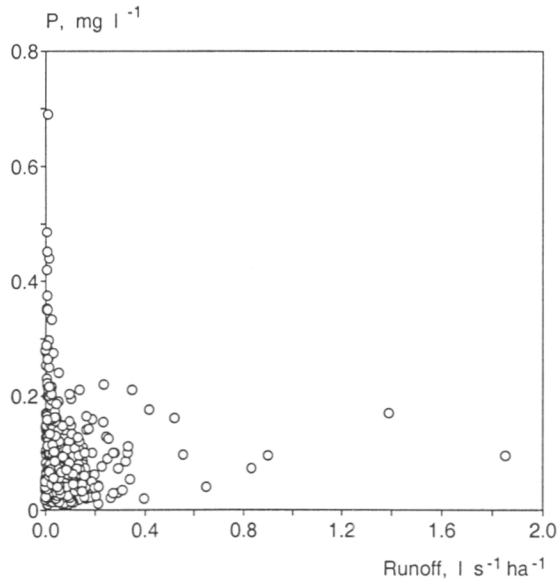


Fig. 4. Ditch water P concentrations as a function of runoff flow at Liesineva. Ditch water samples from all sampling occasions during 1977-1982 at each of the six basin areas are included.

The location of the water divide between basin areas in experiments such as Liesineva varies over time due to watertable fluctuation (Ahti 1983). The area contributing to the runoff therefore varied between ditch water sampling occasions. This source of variation has not been taken into consideration, and fixed sizes of the basin areas were assumed (Fig. 3).

3.3 Parameterization

3.3.1 Fertilizer dissolution

The dissolution (DP_t , see Table 1) of the P-fertilizers used at Liesineva (Moroccan phosphate rock) and Kivisuo (Mire-PK) were estimated on the basis of the dissolution curves presented in Fig. 3 in publication II. The study period in publication II covered the first two years after fertilization. For model application to the Liesineva leaching experiment, however, information was needed about the dissolution of Moroccan phosphate rock for 6 years after fertilizer application. In the model, the daily dissolution rate of Moroccan phosphate rock after the first 2 years is assumed to be the average of the second year ($0.0289\% \text{ d}^{-1}$ of the amount added). It is also assumed in the model that there is no fertilizer dissolution during the period when the soil is frozen (from the beginning of November to the end of April) and that dissolution is enhanced for one month after the winter-period. The rates of dissolution of the most soluble P-compounds in the fertilizers were also assumed to differ from those suggested by the regression models presented in publication II. The original dissolution curves from publication II and the curves used in the model are illustrated in Fig. 5.

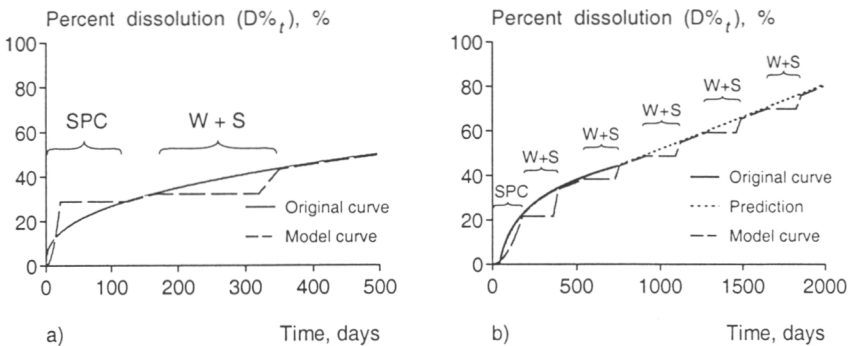


Fig. 5. The original dissolution curves from publication II for (a) Mire-PK and (b) Moroccan phosphate rock, and predicted dissolution for Moroccan phosphate rock after the first 2 years after application, and the dissolution curves adopted for the model. $W + S$ = no dissolution during the winter-period and an enhanced dissolution period in spring. SPC = dissolution of the most soluble P-compounds, (see text).

In the model, the rate of fertilizer dissolution ($D\%$) illustrated in Fig. 5 is converted into the amount of fertilizer-P dissolved during time t (DA_t , $g\ ha^{-1}$):

$$DA_t = (D\%/100) * A, \quad (1)$$

where A =dose of application, $g\ ha^{-1}$. The daily dissolution in $g\ ha^{-1}\ d^{-1}$ (DP_t , see Table 1) is then calculated as the difference between the amount of P dissolved at time t and that at time $t-1$:

$$DP_t = DA_t - DA_{t-1} \quad (2)$$

The DP_t curves calculated using Equation 2 are presented in Fig. 6.

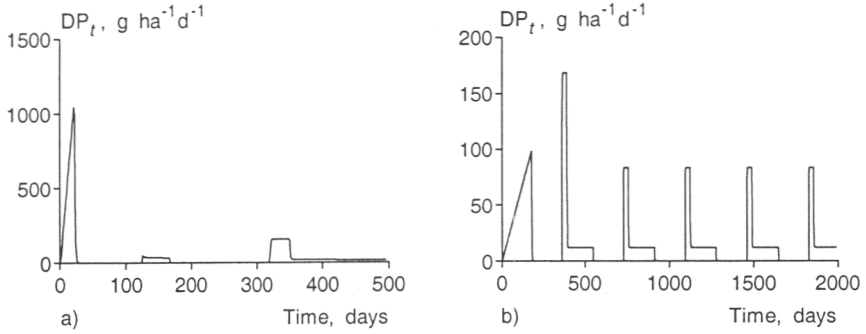


Fig. 6. Dissolution (DP_t , $g\ ha^{-1}\ d^{-1}$) of (a) Mire-PK and (b) Moroccan phosphate rock calculated using Equation 2, (see text).

3.3.2 Accumulation of fertilizer-phosphorus in vegetation biomass and litter

The daily accumulation of fertilizer-P in the vegetation biomass and litter (ACCUM) is given as:

$$ACCUM = u * DP_t, \quad (3)$$

where u is the coefficient for the rate of accumulation of fertilizer-P in vegetation biomass and litter and DP_t is the dissolution of fertilizer-P from Equation 2.

Information about the accumulation of fertilizer-P in the vegetation biomass and litter comes from publication III. The average biomass accumulation of P (P given as Moroccan phosphate rock with an application dose of $53\ kg\ ha^{-1}$)

over the about 2.5 year study period was 15.3 kg ha⁻¹ (13.3 kg ha⁻¹ for the NPK-fertilized plots, and for the PK-fertilized plots, 17.3 kg ha⁻¹). About 48 % of P in Moroccan phosphate rock was estimated to be released in a plant available form over 2.5 years (Fig. 5b). The coefficient for the rate of accumulation of fertilizer-P in the vegetation biomass and litter (u) is thus calculated as:

$$u = 15.3 / (48/100) * 53 \quad (4)$$

The accumulation of fertilizer-P in the biomass and litter is therefore given by:

$$ACCUM = 0.6 * DP_t \quad (5)$$

3.3.3 Adsorption of fertilizer-phosphorus by peat

The daily adsorption of fertilizer-P by peat (ADSORP) is given as:

$$ADSORP = a * DP_t \quad (6)$$

where a is the coefficient for the rate of adsorption of fertilizer-P by peat and DP_t is the dissolution of fertilizer-P from Equation 2.

The P adsorption isotherms of the surface 0-15 cm peat layer were used in the estimation of the peat adsorption of fertilizer-P (Fig. 1 in publication IV). Under conditions of low concentrations of P in equilibrium solution (< 10 mg l⁻¹), the P adsorption isotherms of the surface 0-15 cm peat samples were negative or only slightly positive in each of the 6 ombrotrophic peat soils studied (samples 14-17 and 19-20). Except for sample 19, the adsorption of P by peat was also very low under conditions of high concentrations of P in equilibrium solution (> 30 mg l⁻¹). Phosphorus adsorption isotherms tend to overestimate the real P adsorption in the field (Richardson 1985, IV). The adsorption of P by peat is therefore probably of little consequence to the fate of fertilizer-P in ombrotrophic peat soils. The coefficient for P-adsorption in the model was thus set zero.

The adsorption of fertilizer-P by peat is thus given as:

$$ADSORP = 0.0 * DP_t \quad (7)$$

In the particularly Fe-rich peat soils, however, the adsorption of P is likely to significantly affect the fate of fertilizer-P (IV).

3.3.4 Other parameters

The runoff data (q , in Table 1) for the frost-free period comes from manual measurements performed usually 3-5 times weekly, but sometimes only once a week. Both the Kivisuo experimental area and the Liesineva area lack winter runoff measurements. Runoff for winter period was estimated using the nearby small basin areas of the former National Board of Waters (NBW). Estimation was done by first calculating linear regression equations for the relationship between monthly means of frost-free period runoff values in different basin areas at Liesineva and Kivisuo and respective values in the nearby NBW areas. The missing runoff values for Liesineva and Kivisuo were then estimated using these equations and measured winter runoff values in the NBW areas. The correlations between the frost-free period runoff values in different basin areas at Liesineva and Kivisuo and respective values in the NBW areas were high ($r=0.88-0.96$) and statistically significant ($p<0.001$). Runoff from different basins at Kivisuo and Liesineva during the study periods used in the model are given in Fig. 7. In the model, the runoff values are in $l\ ha^{-1}\ d^{-1}$ (Table 1).

The background P concentrations (BP in Table 1) were calculated as the average of P concentrations in runoff samples taken during the pre-fertilization periods (4.6.-20.11.1976 at Liesineva; 27.5.-2.11.1986 at Kivisuo). The background P concentrations are assumed to represent the concentrations that had existed in each basin area if the fertilizations had not been performed (Table 4). At the Kivisuo basin 8, however, the P concentrations of the runoff samples collected in 27.5.-2.11.1986 were about $0.25\ mg\ l^{-1}$ lower than those of the samples collected just prior to fertilizer application in 1.-18.5.1987. The very high runoff P concentrations prior to fertilizer application may be because some fertilizer-P was accidentally spread on basin area 8 in connection with fertilization of the basin areas 2, 3, 5 and 7 in 9.-13.3.1987 (Fig. 2). It is also possible that some fertilizer-P was leached to basin 8 from basin 7. Whatever the reason for this “excess input” of P, it was thought important enough to be accounted for in the model. The Kivisuo basin 8 background P concentration for the period 19.5.-2.11.1987 was therefore set at $0.30\ mg\ l^{-1}$.

If only a part of the basin area is fertilized, as was the case at Liesineva, the outflow waters from the fertilized part of the basin are mixed with waters from the unfertilized part. In the model, the fertilizer-induced changes in runoff P concentrations are therefore multiplied by a dilution coefficient (d in Table 1), which is the ratio of the fertilizer-treated area to the whole basin area (1.0 for Kivisuo, and 0.1 for Liesineva).

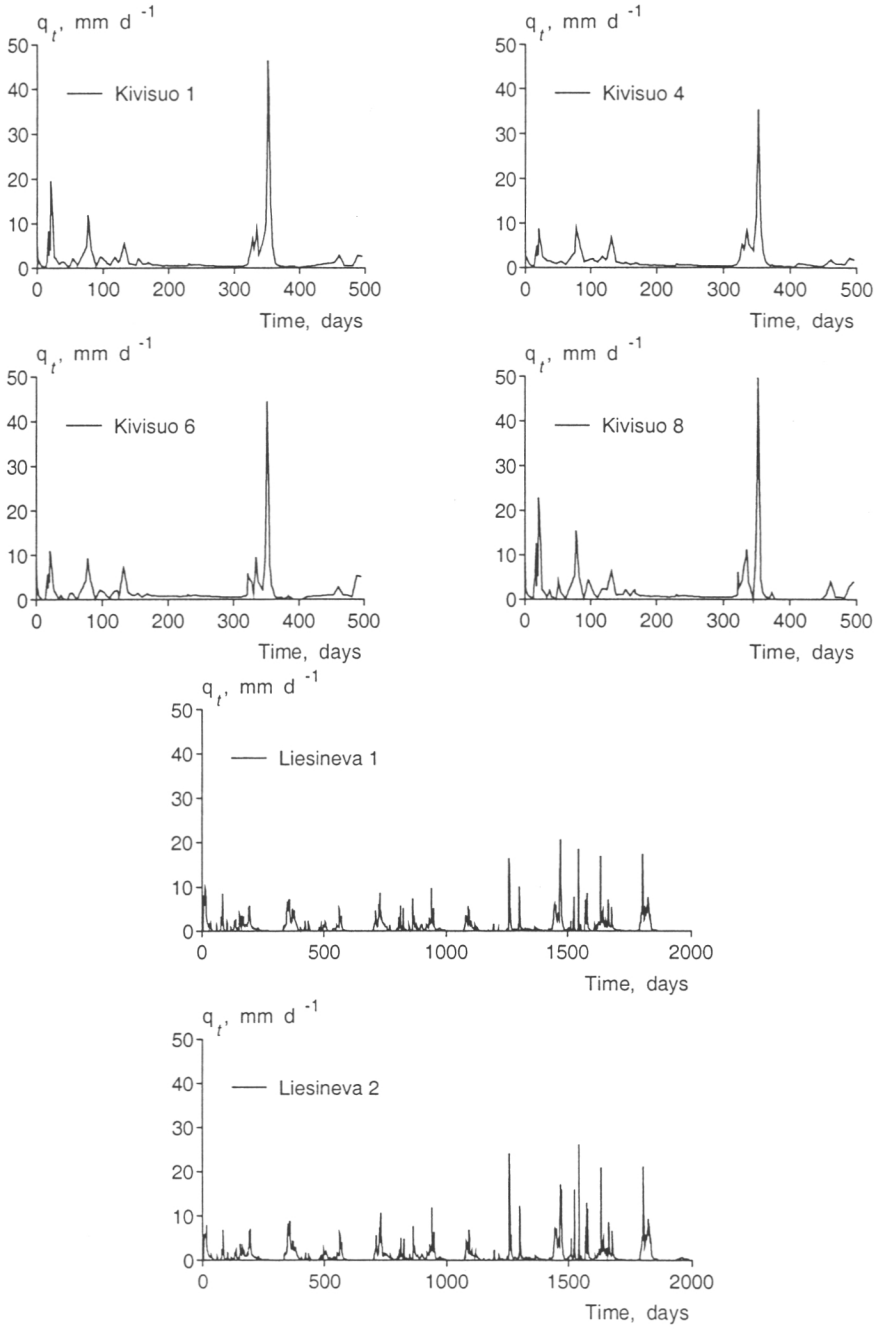


Fig. 7. Daily runoff from each Kivisuo basin 1.5 years and Liesineva basin 6 years since fertilization.

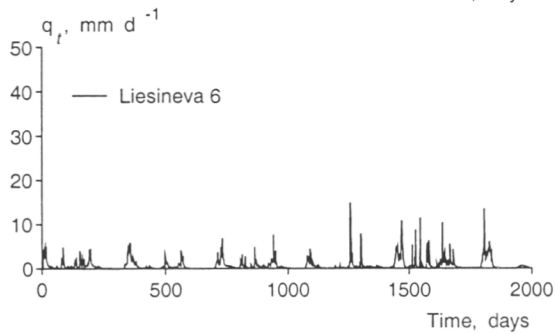
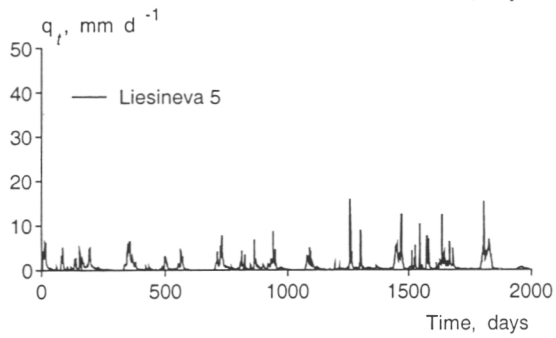
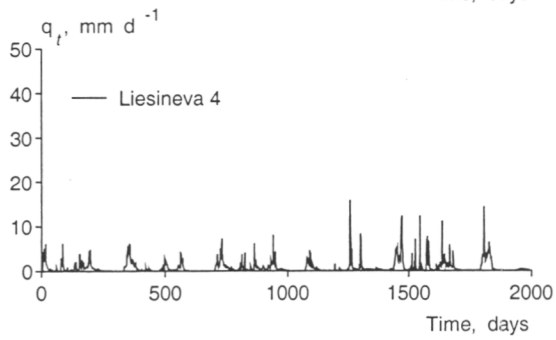
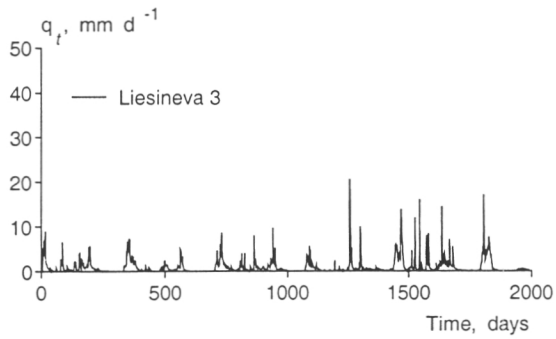


Fig. 7. continues

Table 4. Background P concentrations in ditch runoff from Kivisuo and Liesineva.

Experiment	Basin	P, mg l ⁻¹
Kivisuo	1	0.051
	4	0.041
	6	0.046
	8	0.055 ^{a)}
Liesineva	1	0.023
	2	0.034
	3	0.062
	4	0.017
	5	0.012
	6	0.009

^{a)} 0.30 mg P l⁻¹ in 19.5.—2.11.1987

In the estimation of the water volume in the runoff layer (W_t in Table 1), two basic assumptions were made: (1) the location of the divider between the active layer and the runoff layer varies due to fluctuations in the watertable level, and (2) the divider between the runoff layer and the passive layer is located at the same depth as the bottom of the ditches (Fig. 1).

The thickness of runoff layer (RL_t , mm) at time t is therefore calculated as:

$$RL_t = D - GW_t \quad (8)$$

where D =ditch depth, mm; GW_t =watertable level at time t , mm (= the vertical distance between soil surface and watertable).

The water volume (W_t , mm) in the runoff layer at time t is then calculated as:

$$W_t = RL_t * (PW/100), \quad (9)$$

where PW =water content of the peat at saturation, %.

Ditch cleaning in 1976 at Kivisuo basins 6 and 8 (original ditch depth=400 mm) somewhat increased the depth of the ditches. Ditch depth (D) for these basins was therefore set at 600 mm. No ditch cleanings were performed at the other basins however, and the ditch depth was set at the same depth as the original ditch depth (800 mm). In the case of the Kivisuo experimental area, the data for watertable level (GW_t) during the frost-free period comes from manual measurements made at 1-2 weeks intervals. However, no watertable measurements were made at Liesineva. The level of watertable for the snowless period (1.6.-30.9) in the different basins at Liesineva were estimated using the measured runoff data and curves derived by Ahti (1987) showing the relationship between runoff and watertable level (Fig. 8). For the period in winter when the soil was frozen, the watertable level was set at 100 mm for those basins with an average ditch spacing of ≤ 30 m, 50 mm for those basins with an average ditch spacing of >30 -50 m, and 10 mm for those basins with an average ditch spacing of >50 m. The water content of the peat at saturation (PW) was set at 92 % (based on measurements for undecomposed *Sphagnum* peat by Päivänen, 1973). The water volumes in the runoff layer during the study periods are given in Fig. 9. For use in the model, these values were converted to $l\ ha^{-1}$ (Table 1).

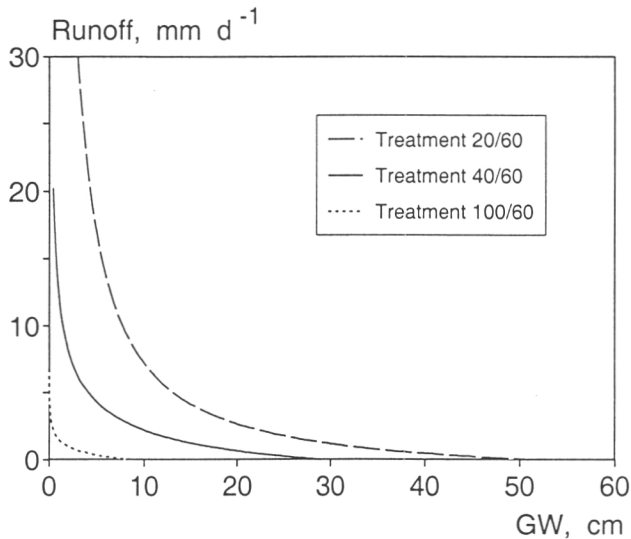


Fig. 8. The relationship between runoff and watertable level over the period 1977-1981 (redrawn from Ahti, 1987). The first number in the treatments gives ditch spacing (m) and the second number ditch depth (cm). The curve from the 20/60 treatment was used to estimate the watertable level for basin 1, 2 and 3 at Liesineva, and that from the 40/60 treatment for the basin 4. The level of watertable at the Liesineva basins 5 and 6 was estimated using the curve from the 100/60 treatment.

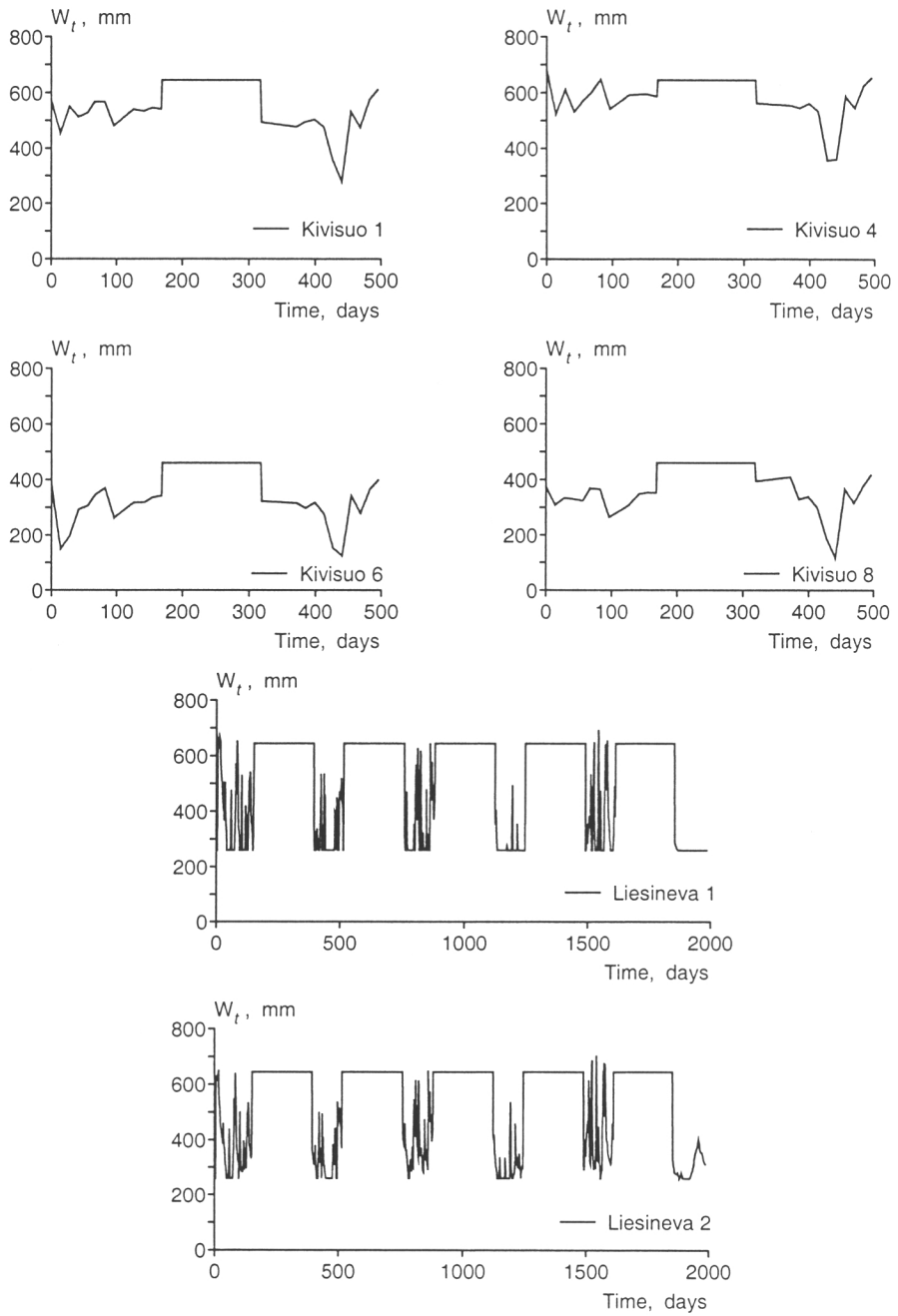


Fig. 9. Daily water content of the runoff layer at each Kivisuo basin 1.5 years and Liesineva basin 6 years since fertilization.

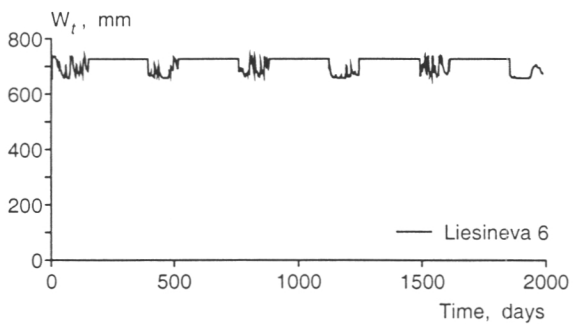
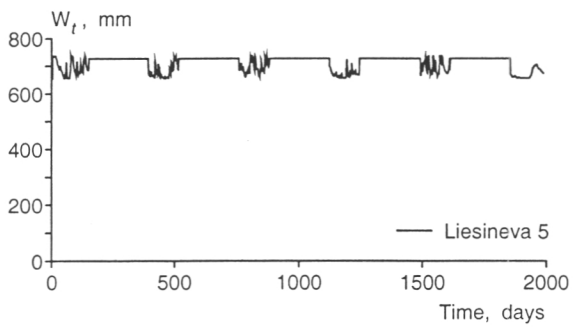
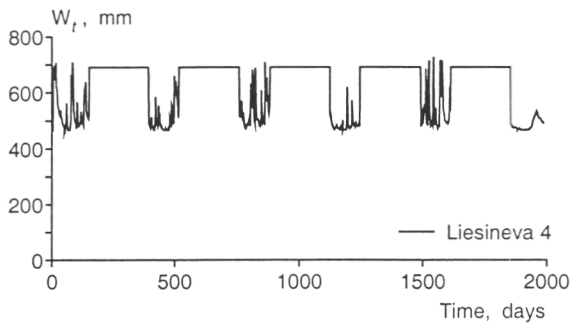
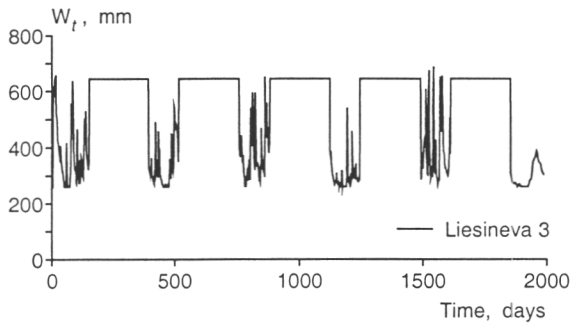


Fig. 9. continues

3.4 Calculations

Model verification was done by checking the model's output with P concentrations in ditch outflow from each of the 4 basin areas at Kivisuo (basins 1, 4, 6, and 8, see Fig. 2), and 6 basin areas at Liesineva (Fig. 3). Sensitivity analysis was done by studying the response of the model's output to changes in the values of one parameter at a time or the simultaneous changes in the values of two parameters. For the sensitivity analysis and various scenarios, the model was run for up to about 20 years after fertilization.

3.5 Results

3.5.1 Model verification

No systematic deviations between the modelled and measured ditch water P concentrations were found (Fig. 10). The general structure and parameterization of the model were therefore judged satisfactory. The fit of the model's output with the measured data from Liesineva, particularly in the case of the basins 1 and 6, was the worst. At Liesineva basin 1, the measured runoff P concentrations were lower than the modelled concentrations during the third and the fourth year after fertilizer application, and during almost the whole study period at Liesineva basin 6. For Liesineva basin 3, the measured runoff P concentrations were often higher than the modelled concentrations during the last two years after application.

3.5.2 Sensitivity analysis and scenarios

To determine the sensitivity of the model's output to changes in parameter values and to calculate alternative scenarios of P leaching, a number of simulations were performed by altering parameter values. Table 5 gives a brief description of these simulations. Total amounts (kg ha^{-1}) of P leaching from the fertilization area are also given for the different simulations in Table 5.

The model's output was rather sensitive to changes in the values of each of the four parameters tested (Figs. 11-15). The maximum P concentrations in ditch outflow and the duration of P leaching were significantly affected by the fertilizer dissolution rate (Fig. 11). The maximum P concentrations for the dissolution rates $0.0274*t$, $0.0584*t$, $0.0822*t$, and $0.1096*t$ were 0.44, 0.87,

Table 5. Simulations for sensitivity analysis and scenarios. The dilution coefficient (d) was set to 1.0, the background P concentration (BP) to 0.00 mg l⁻¹, and the fertilizer dose to 40 kg P ha⁻¹. For each simulation, the model was run for 8 000 days after fertilizer application.

Number	Percent dissolution (D% _t)	Adsorption Plus Accumulation (a+u)	Water content in runoff layer (W _r , mm)	Runoff (q _r , mm d ⁻¹)	Total leaching (kg P ha ⁻¹)
Ia	=0.0274*t ^{a)}	0.60	400	1.0	16.0
Ib	=0.0548*t ^{b)}	0.60	400	1.0	16.0
Ic	=0.0822*t ^{c)}	0.60	400	1.0	16.0
Id	=0.1096*t ^{d)}	0.60	400	1.0	16.0
IIa	=0.0274*t ^{a)}	0.00	400	1.0	40.0
IIb	=0.0274*t ^{a)}	0.30	400	1.0	28.0
IIc	=0.0274*t ^{a)}	0.60	400	1.0	16.0
IIId	=0.0274*t ^{a)}	0.90	400	1.0	4.0
IIIa	=0.0274*t ^{a)}	0.60	200	1.0	16.0
IIIb	=0.0274*t ^{a)}	0.60	400	1.0	16.0
IIIc	=0.0274*t ^{a)}	0.60	600	1.0	16.0
IIId	=0.0274*t ^{a)}	0.60	800	1.0	16.0
IVa	=0.0274*t ^{a)}	0.60	400	0.5	16.0
IVb	=0.0274*t ^{a)}	0.60	400	1.0	16.0
IVc	=0.0274*t ^{a)}	0.60	400	1.5	16.0
IVd	=0.0274*t ^{a)}	0.60	400	2.0	16.0
Va	=0.0274*t ^{a)}	0.60	200	0.6	16.0
Vb	=0.0274*t ^{a)}	0.60	400	0.8	16.0
Vc	=0.0274*t ^{a)}	0.60	600	1.0	16.0
Vd	=0.0274*t ^{a)}	0.60	800	1.2	16.0

a) D%_t = 100 % for t ≥ 3650 days

b) D%_t = 100 % for t ≥ 1825 days

c) D%_t = 100 % for t ≥ 1217 days

d) D%_t = 100 % for t ≥ 913 days

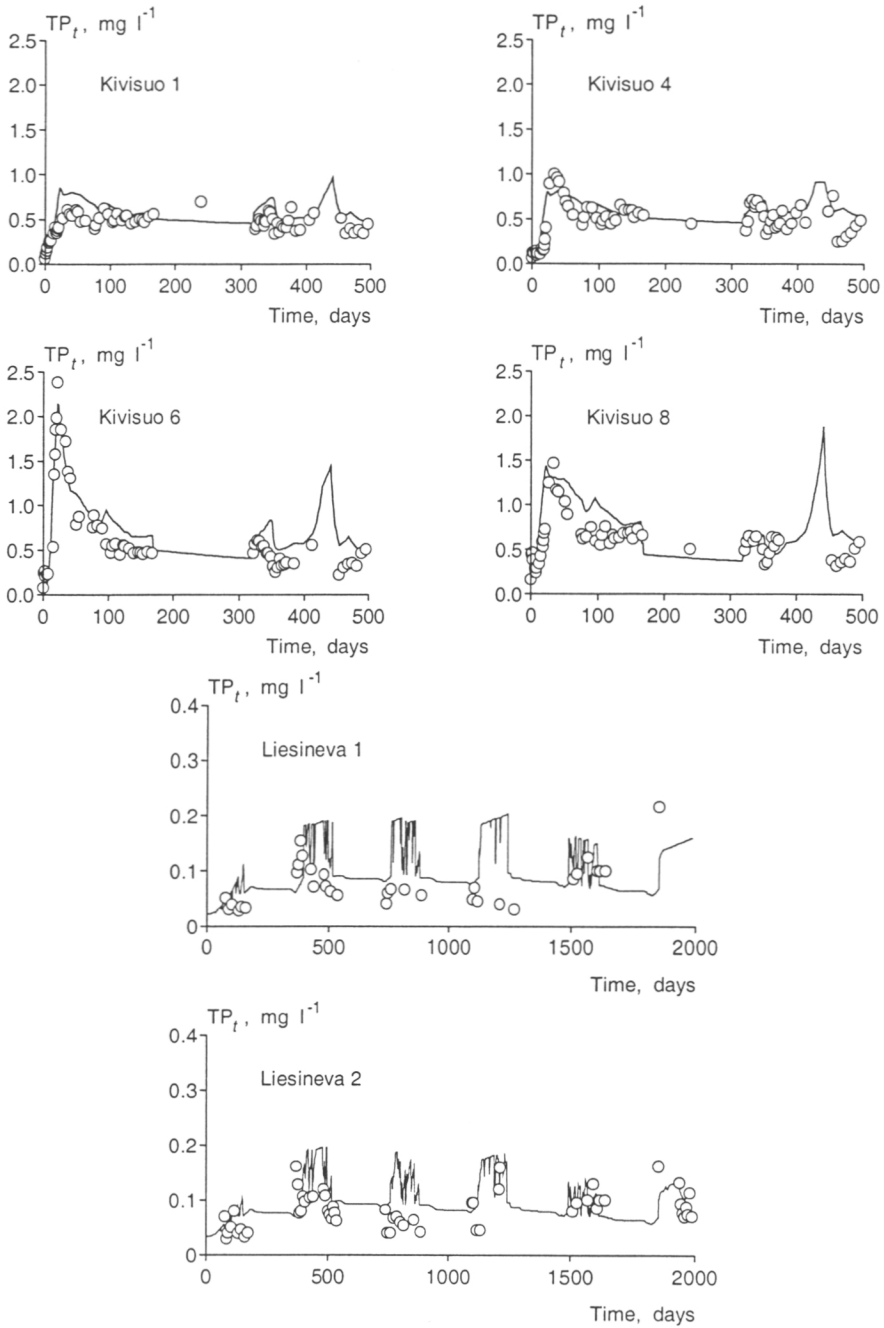


Fig. 10. Measured (circles) and modelled total P (TP_t in Table 1) concentrations in ditch runoff from each Kivisuo basin 1.5 years and Liesineva basin 6 years since fertilizer application.

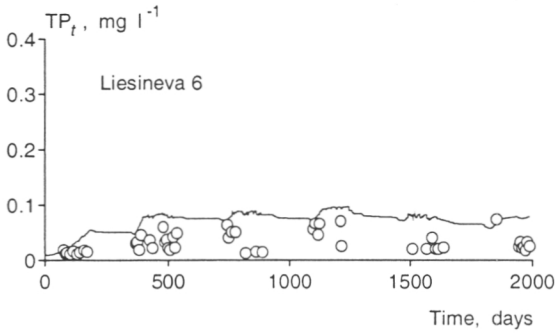
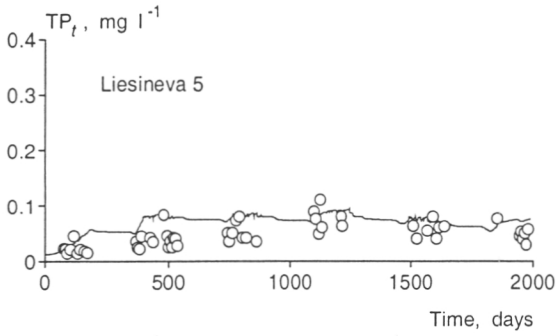
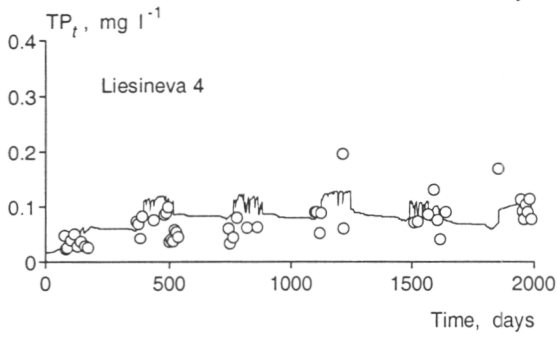
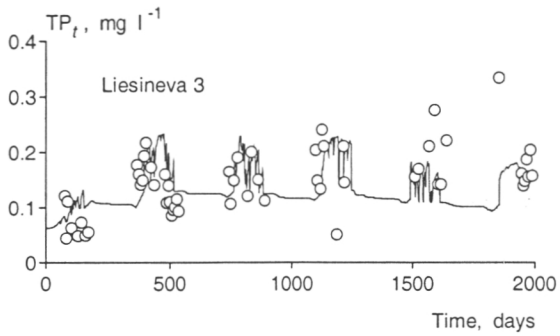


Fig. 10. continues

1.25, and 1.57 mg l⁻¹, respectively. A 0.3 unit increase in the coefficient for biomass P accumulation and P adsorption by peat (a+u) caused a 0.33 mg l⁻¹ decrease in the maximum P concentration in ditch outflow (Fig. 12). The P concentrations in ditch outflow were also significantly affected by the volume of water in the runoff layer (Fig. 13), and the runoff (Fig. 14). The maximum P concentrations for the runoff values 0.5, 1.0, 1.5, and 2.0 mm d⁻¹ were 0.87, 0.44, 0.29, and 0.22 mg l⁻¹. For the very dry conditions (low runoff and small water volume in the runoff layer) the maximum P concentrations in ditch outflow were significantly higher than for the wet conditions (Fig. 15). The maximum P concentrations for the simulations Va, Vb, Vc, and Vd were 0.73, 0.55, 0.44, and 0.36 mg l⁻¹, respectively. Although the P concentrations in ditch outflow and the duration of leaching were sensitive to changes in the rate of fertilizer dissolution (Fig. 11), and the water volume of the runoff layer and the runoff (Figs. 13-15), the total amounts of P leached over the period of about 20 years were the same (Table 5). The only factors affecting the total P leaching would be the peat P adsorption capacity and the effectiveness of the trees and understorey vegetation in accumulating added P (Table 5).

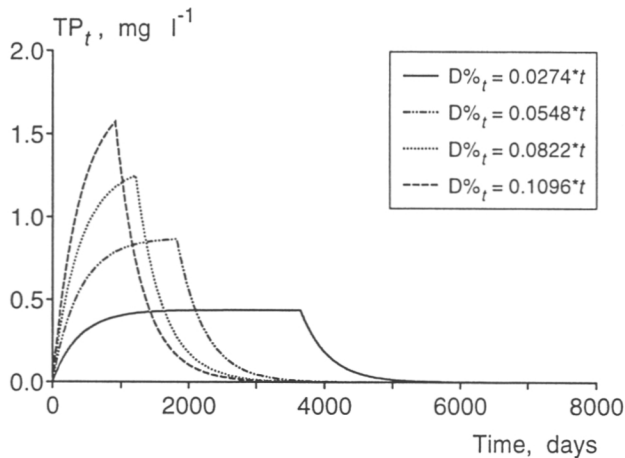


Fig. 11. Modelled ditch water P concentrations in response to changes in the dissolution of fertilizer-P ($D\%_t$). For details of simulation parameters, see Table 5.

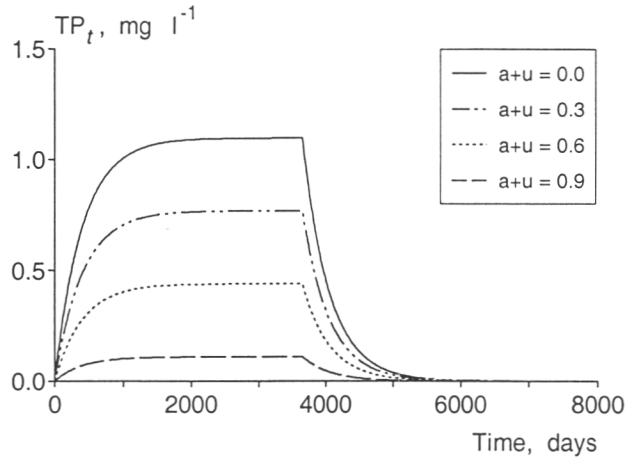


Fig. 12. Modelled ditch water P concentrations in response to changes in the adsorption of fertilizer- P by peat (a) plus accumulation in the vegetation biomass and litter (u). For details of simulation parameters, see Table 5.

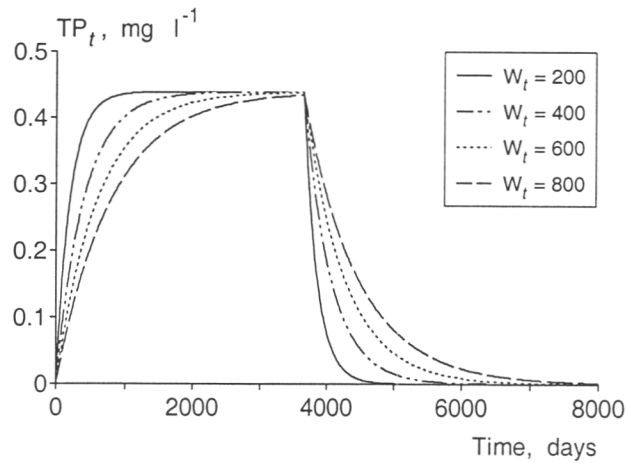


Fig. 13. Modelled ditch water P concentrations in response to changes in the water volume of the runoff layer (W_t). For details of simulation parameters, see Table 5.

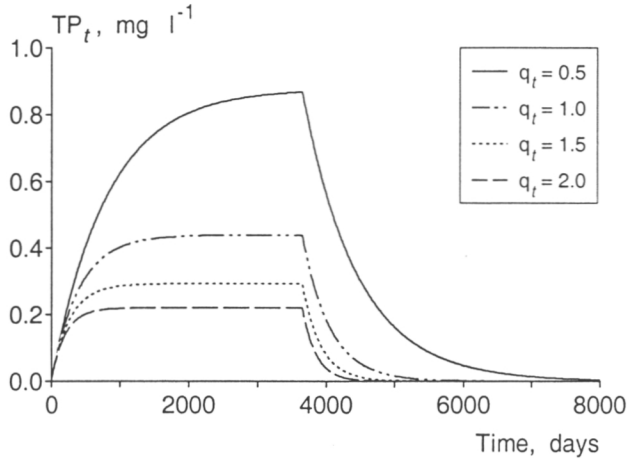


Fig. 14. Modelled ditch water P concentrations in response to changes in the runoff flow (q_t). For details of simulation parameters, see Table 5.

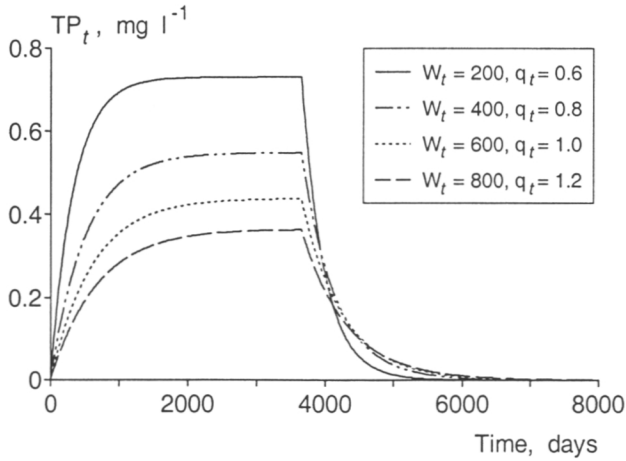


Fig.15. Modelled ditch water P concentrations in response to changes in the water volume of the runoff layer (W_t) and the runoff flow (q_t). For details of simulation parameters, see Table 5.

3.6 Discussion

3.6.1 Verification data

The Liesineva data are not completely satisfactory for verification purposes. One reason for this is that the locations of the water divide between basin areas varies over time due to watertable fluctuation (Ahti 1983). Exact sizes of the basin areas can therefore not be determined. In the case of the basin 6, for example, a significant part of the fertilizer-P may have leached to southern ditch outside the basin area boundary assumed in Fig. 3, and not to the ditch with the sampling point.

Another weakness in the Liesineva data for verification purposes is that most of the runoff samples were taken during low runoff flows in the summer-time. Due to the lack of the runoff samples from maximum spring and autumn flows, the model's behaviour could not be tested during the most critical P outflow events, i.e. when the daily outflow of fertilizer-P is likely to be the greatest.

The runoff samples from the very low flows ($< 0.015 \text{ l s}^{-1} \text{ ha}^{-1}$) were excluded from the Liesineva verification data. Even though the high variation in runoff P concentrations (Fig. 4) could not be explained, it should be noted that very little P is leached during these very low flow periods. For example, if the daily average runoff flow is $0.010 \text{ l s}^{-1} \text{ ha}^{-1}$ and the runoff P concentration is 0.3 mg l^{-1} , the amount of P leaching is $< 0.3 \text{ g ha}^{-1} \text{ d}^{-1}$. During a maximum spring flow (e.g. $2.0 \text{ l s}^{-1} \text{ ha}^{-1}$), a similar runoff P concentration would correspond to $> 50 \text{ g ha}^{-1} \text{ d}^{-1}$ in the amount of P leaching. It should also be noted that during dry periods the Liesineva runoff samples were often taken from almost stagnant water rather than from clearly flowing water, as is normal practice in nutrient outflow experiments. Sometimes the runoff flow ceased totally during or after sample collection.

With fixed basin sizes and frequent sampling of runoff also during high flow periods, the Kivisuo experimental area is more suitable for the verification of the P-outflow model than the Liesineva experiment. However, due to some unexplained excess input of P, the Kivisuo basin 8 is not as satisfactory as the data from the other basins.

The ditch water samples were analysed for the total dissolved P (ICP/AES, ARL 3580) at Kivisuo, and for the dissolved reactive P (ascorbic acid-molybdenum blue method) at Liesineva (for the definition "reactive P", see

Ekholm, 1998). Both the total dissolved P and the dissolved reactive P can contain a number of different forms of inorganic and organic P. Water-soluble phosphate is likely to be the main fertilizer-derived P component in ditch outflow from drained ombrotrophic peatlands however. Increases in P leaching from drained ombrotrophic peatlands following clear-cutting have been shown to be mainly due to increased concentrations of water-soluble phosphate (Nieminen 1999).

The fit of the model to Liesineva data was not as good as that to Kivisuo data. In addition to the reasons mentioned above, this may also be because the fertilizer-induced changes in runoff P concentrations were significantly lower at Liesineva than at Kivisuo. The runoff P concentrations therefore remained lower at Liesineva. Factors not considered in the model (e.g. atmospheric P deposition) are thus likely to have relatively more effect on runoff P concentrations at Liesineva than at Kivisuo.

3.6.2 Model structure

In the model, the peat deposit is divided into three layers, (1) the active layer, from where dissolved phosphate ions are adsorbed by the peat and taken up by plant roots, (2) the runoff layer, which controls the leaching of dissolved phosphate ions not sorbed by peat and not taken up by the vegetation, and (3) the passive layer, the remainder of the peat deposit which does not affect the fate of fertilizer-P (Fig. 1). This division of the peat deposit with respect to the behaviour of fertilizer-P closely resembles the division of peat into the acrotelm and catotelm (Ivanov 1981, Ingram 1983, Damman & French 1987). The acrotelm is the surface peat layer above the lowest watertable level, and the catotelm is the permanently anaerobic peat layer below this level (Fig. 16). The acrotelm is further divided into two layers, an upper aerobic layer above the highest watertable level, and a lower acrotelm layer between the lowest and highest watertable levels. Thus, as in the model presented here, three hydrologically and ecologically different layers are defined. In the model, the uptake and adsorption of fertilizer-P occurs in the uppermost active peat layer, where there is sufficient aeration and where most of the biological activity takes place (would correspond to the upper level of the acrotelm). The leaching of phosphate ions to the ditch occurs from the runoff layer where the water level fluctuates (would correspond to the lower level of the acrotelm). The permanently anaerobic passive layer, where water movement is negligible, corresponds to the catotelm.

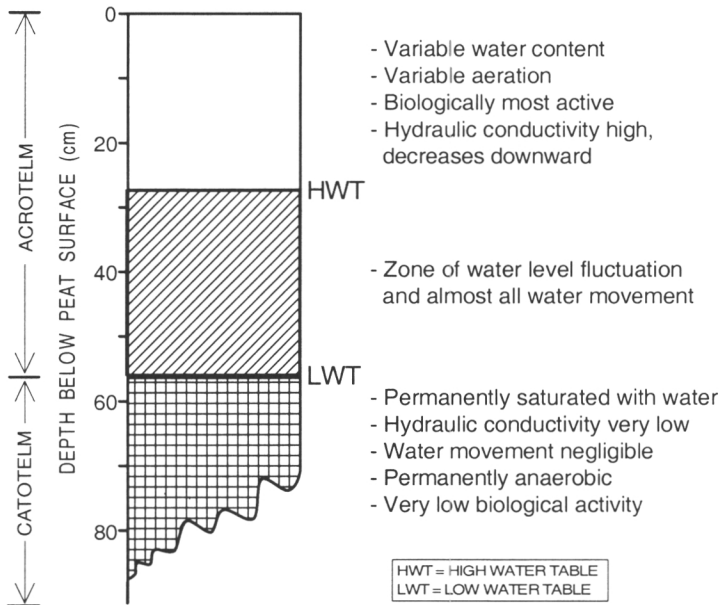


Fig. 16. Properties of the acrotelm and catotelm of a bog (redrawn from Damman & French, 1987).

The boundary between the runoff layer and the passive layer (i.e. the acrotelm and the catotelm) was assumed to be at the same level as the bottom of the ditches. It is reasonable to assume that ditching increases water movement in the peat layer above the level of the bottom of the ditches. In drained peatlands, the division between the acrotelm and the catotelm may therefore be expected to be approximately at the same level as the bottom of the ditches. In areas with very shallow or highly decomposed peat deposits however, there may be a nearly water-impermeable soil layer above the level of the bottom of the ditches. In such areas, the division between the acrotelm and catotelm is likely to be above the level of the bottom of the ditches.

In the model, the fraction of fertilizer-P going to leaching ($1-(a+u)$) was assumed to be mixed with the total volume of water in the saturated layer above the level of the bottom of the ditches (i.e. in the runoff layer). No empirical data are available to support this assumption. The model's output was very sensitive to changes in the water volume (W_r) in the runoff layer however (Fig. 13). Different water volume estimates in the model would therefore have given significantly different model results.

No significant delay was assumed between the dissolution of P-fertilizer in the active layer and the leaching of dissolved phosphate ions to the runoff layer. This is probably true for sites like Kivisuo and Liesineva, where the surface peat layers consist of slightly decomposed *Sphagnum* peat. In such sites, the rate of water flow through the surface peat is rapid. The water permeability of highly decomposed peat is low. A substantial delay may therefore occur before the dissolved phosphate ions move through the surface peat layers and appear in the runoff layer. In a laboratory study by Sarasto (1963), the vertical water flow in slightly decomposed *Sphagnum* peat was about 64 cm h⁻¹. For highly decomposed peat, the corresponding value was only 0.64 cm h⁻¹.

Soil and the soil water freezing are likely to change water flow pathways during the winter and upon snowmelt. These changes may be expected to influence the leaching of fertilizer-P. However, frozen soil parameters were not included in the model due to a lack of information about their significance and because the number of runoff samples collected during the frozen soil period was very limited.

There is no information about the effects of different application doses on fertilizer-P leaching from drained peatlands. As the model was based on application doses similar to those used in practical peatland forestry (i.e. 40-45 kg ha⁻¹), its results should not be compared to sites where the application dose markedly differs from that used in practice.

The fertilizer-P leaching model was based on empirical data collected from nutrient-poor ombrotrophic peatland sites. The leaching of fertilizer-P from the nutrient-rich minerotrophic sites is likely to differ from that of the nutrient-poor ombrotrophic sites. This is because such sites differ from each other with respect to the factors (e.g. the peat P adsorption capacity, IV) affecting leaching. Although the results of this study are applicable to a limited range of peatland types, over one million hectares of such ombrotrophic peatlands have been drained for forestry purposes in Finland (Tomppo 1998). The model was based on data from only a few sites, however, and further investigations are needed.

3.6.3 Parameter definition

3.6.3.1 Fertilizer dissolution

The estimation of fertilizer dissolution (DP_i) for the first two years after fertilization was based on publication II. For model application to the Liesineva

leaching experiment, however, information was needed about the dissolution of Moroccan phosphate rock for 6 years after fertilization. In the model, the daily dissolution of Moroccan phosphate rock in years 3-6 after application was assumed to be the average of the second year. Tree growth tends to steadily increase in years 2-6 after the application of Moroccan phosphate rock (Karsisto 1968, 1977, Penttilä & Moilanen 1987, Kaunisto et al. 1993). This steady increase in tree growth supports the assumption of a uniform dissolution rate for the second to sixth year after the application of Moroccan phosphate rock. Sudden high increases or decreases in the rate of dissolution of Moroccan phosphate rock in years 2-6 after application would most probably be seen in tree growth.

The original dissolution curves from publication II were not directly adopted for use in the model. It is assumed in the model that there is no dissolution during the winter-period when the soil is frozen and there is no free water for dissolution reactions. An enhanced dissolution period in spring is assumed in the model. This was because the fertilizer granules are likely to be broken down into finer particles by freeze-thaw processes during the winter, and this disintegration of the granules may be expected to increase their dissolution. However, it is still unknown if the rates of dissolution of the most soluble P-compounds in Moroccan phosphate rock and Mire-PK are as assumed in Fig. 5. To describe the seasonal and other short-term changes in the rates of dissolution of different P-fertilizers, shorter sampling intervals than those in the publication II (2-10 months) should be used.

In the leaching experiments used for model application and verification, urea was added together with Mire-PK at Kivisuo, and potassium chloride and ammonium nitrate together with Moroccan phosphate rock at Liesineva. However, in publication II, which was used to estimate fertilizer dissolution for the model, only Mire-PK or Moroccan phosphate rock were applied. Nitrogen and potassium fertilizer salts have been shown to increase phosphate rock dissolution (I and the references therein). The actual dissolution rates at Kivisuo and Liesineva may therefore have been higher than those used in the model. The proportion of phosphate rock that dissolves correlates negatively with the dose of phosphate rock (Rajan et al. 1991). The doses of fertilizer given in the dissolution experiment (II) were higher than those used in the Kivisuo and Liesineva leaching experiments. The dissolution rates used in the model may therefore have underestimated the real dissolution of the fertilizers at Kivisuo and Liesineva.

3.6.3.2 Accumulation of fertilizer-phosphorus in vegetation biomass and litter

Using the results from publication III to determine the value of u (coefficient for the accumulation of fertilizer-P in the vegetation biomass and litter) is associated with at least two possible errors. Firstly, if the addition of fertilizer-P and other fertilizer nutrients increases the mineralization of peat P, part of the fertilizer-induced accumulation may be due to the uptake of peat P. It was assumed, however, that the increases in P accumulation in vegetation biomass and litter presented in publication III were solely due to accumulation of fertilizer-P. Secondly, as was speculated in publication III, the vegetation samples may still have contained residual unreactive phosphate rock at the time of sampling. Thus, the results of publication III may somewhat overestimate the real P accumulation in vegetation biomass. Isotopic labelling methods could give more reliable information about the rate of accumulation fertilizer-P in vegetation biomass and litter.

The accumulation of fertilizer-P in the vegetation biomass and litter was assumed not to depend on the rate at which the fertilizer dissolves, i.e. the coefficient u was assumed to be the same for all fertilizers regardless of solubility. This assumption is supported by the fact that a number of investigations have shown no significant differences in the total tree growth between P sources of differing solubility (I and the references therein). This indicates that the total uptake of P-fertilizer by trees does not depend on fertilizer solubility, which is in agreement with the assumption. It is not known, however, whether the uptake of fertilizer-P by peatland vegetation other than trees depends on the solubility of the fertilizer.

In the model, the accumulation of P in the total plant biomass was also assumed not to depend on the volume of the tree stand, i.e. though different amounts of fertilizer-P may be expected to allocate to different vegetation compartments (tree, bush, field, and bottom layers, and root systems) in areas with differing tree stand volume, the accumulation in the total plant biomass (sum of all compartments) is assumed to be the same. In a study by Päivänen (1970) carried out on a treeless low-sedge pine bog, about 7 % of P in a phosphate rock fertilizer had accumulated in the above-ground vegetation biomass (field layer vegetation) after three years. On a treeless upland bog in England, the corresponding value was 9.9 % (Malcolm & Cuttle 1983b). Calculations with the data presented by Paavilainen (1980) showed that the average accumulation of P in the above-ground vegetation biomass (field layer + tree layer) after three years had been about 6 % of the amount applied with a phosphate rock

fertilizer (dwarf shrub pine bog with tree stand volume $\approx 95 \text{ m}^3 \text{ ha}^{-1}$). Calculations with the results presented by Finér (1991a), and those in the publication III showed that the fertilizer-induced (Moroccan phosphate rock) accumulation in the above-ground biomass (field layer + tree layer) was 6-8 % after three years (low-shrub pine bog with tree stand volume $\approx 80 \text{ m}^3 \text{ ha}^{-1}$). These results indicate that the accumulation of fertilizer-P in the total plant biomass is of the similar magnitude for peatland areas with significantly different tree stand volumes.

In addition to the results in publication III, only one study was found concerning the accumulation of fertilizer-P in the total plant biomass and litter of ombrotrophic peatlands (Vasander 1981). However, there was no replication of the fertilization treatments in Vasander's study and the treatments differed not only with respect to fertilization but also with respect to drainage (the control site was a pristine bog, whereas the fertilized site had been drained 4 years before fertilization). Vasander's (1981) estimates for the accumulation of fertilizer-P in vegetation and litter must therefore be regarded with caution.

3.6.3.3 Adsorption of fertilizer-phosphorus by peat

In the estimation of the adsorption of fertilizer-P by peat, P adsorption isotherms of the surface 0-15 cm peat layer were used (IV). These isotherms indicated that ombrotrophic peat soils have very little ability to retain P against leaching. The adsorption coefficient (a) in the model was therefore set to zero. However, results of publication IV showed rather high P adsorption for the subsurface 15-30 cm peat layer in most of the studied ombrotrophic soils. The P adsorption isotherms were determined under aerobic conditions in the laboratory. Under field conditions, however, anaerobic conditions tend to prevail below the uppermost peat layers during most of the year. Anaerobiosis is known to inhibit P adsorption due to reduction and redistribution of Fe (Armstrong 1975). High P adsorption values as determined in the laboratory for the 15-30 cm peat samples may therefore not be realised under field conditions. Phosphorus adsorption values may also be overestimated because the samples are thoroughly mixed in the laboratory. This mixing results in the close contact with the peat and the phosphate ions. Under field conditions, however, the movement of water and phosphate ions is mainly confined to the large pores and channels and there is little contact with a large portion of the soil matrix (Richardson 1985).

Laboratory studies with soil samples placed in leaching columns probably better estimate P adsorption under field conditions. Results from such leaching column

studies (e.g. Fox & Kamprath 1971) indicate very low P adsorption capacity for organic soils with low amounts of inorganic colloids.

The low P adsorption capacity of ombrotrophic peat soils is related to their low Fe content (IV). Applying compounds rich in Fe can therefore be used to increase the P adsorption capacity of peat and thereby reduce P leaching losses (Scheffer & Kuntze 1989). According to Scheffer et al. (1986), much of the phosphate sorbed by Fe remains available to plants. Thus, tree production would necessarily not be decreased by an application of Fe. The effect of P+Fe fertilization on the growth of peatland forests and the leaching of P from drained peatlands should therefore be investigated.

4 CONCLUSIONS

The aim of the study was to determine the effects of P-fertilizers of varying dissolution rate, the adsorption of P by peat, and the accumulation of P in vegetation biomass and litter on the leaching of P from drained ombrotrophic peatland forests. The results indicated that although the P concentrations in ditch outflow and the duration of leaching varied between the P-fertilizers of differing solubility, the total leaching losses over the period of about 20 years were the same. The results suggest that the factors restricting the total leaching of fertilizer are the P adsorption capacity of the peat and the effectiveness of trees and understorey vegetation in accumulating the added P. Ombrotrophic peat soils have very low capacity to adsorb P however. This is related to low contents in peat of P-sorbing compounds, Fe in particular. Compared with amounts of P fertilizer used in practical peatland forestry (40-45 kg ha⁻¹), the accumulation of P in trees and understorey vegetation is also low. Due to low peat P adsorption capacity and P accumulation in trees and understorey vegetation, the risk for high leaching rates of applied P from drained ombrotrophic peatlands is consequently substantial. The use of application doses of less than 40-45 kg ha⁻¹ and P-fertilizers including P-sorbing compounds (especially Fe) in reducing phosphate leaching to water courses should therefore be investigated.

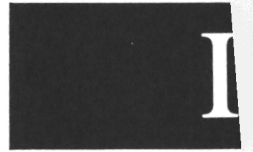
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Properties of slow-release phosphorus fertilizers with special reference to their use on drained peatland forests. A review

Hidasliukoisten fosforilannoitteiden ominaisuudet ja käyttökelpoisuus suometsien lannoituksessa. Kirjallisuuteen perustuva tarkastelu

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Slow-release phosphorus fertilizers have long been considered as a primary fertilization option on drained peatland forests in Finland. There has also been growing interest in using slow-release P-fertilizers as a better alternative to water-soluble fertilizers on agricultural land. Manufacture of different P-fertilizers, and those fertilizer and site properties which affect the rate of P release, are reviewed. The effects of slow-release P-fertilizers on plant growth and the liability to be leached into waterways are also discussed. In particular, the behaviour of slow-release P-fertilizers on drained peatland forests is considered.

Key words: fertilizer dissolution, peatland forestry, phosphate minerals, phosphorus outflow

INTRODUCTION

The use of slow-release phosphorus (P)-fertilizers instead of water-soluble forms is attractive from the viewpoint of both economy and environmental protection (slow-release P-fertilizer is a generic term and refers here to products which contain higher amounts of sparingly soluble components than traditional water-soluble fertilizers). Slow-release P-fertilizers are much cheaper than totally water-soluble ones (Sanches & Salinas 1981), costing as little as one-fifth the price of a single superphosphate. The concentration of P in slow-release P-fertilizers is also often greater than in water-soluble fertilizers, thus leading to savings in transport and application. Many develop-

ing countries have indigenous phosphorus deposits, the use of which significantly decreases the cost of food production compared with the use of imported water-soluble fertilizers (Sale & Mokuwunye 1993). Water-soluble P-fertilizers are most often produced by the acidulation of phosphate rocks with phosphoric acid. Each ton of phosphoric acid used results in 2.2 tons of phosphogypsum, a byproduct the disposal of which is a great environmental problem (Rajan et al. 1994). Use of totally water-insoluble P-fertilizers eliminates this problem. For some soils and in some environments, slow-release P-fertilizers have also been shown to better match plant demand than water-soluble ones (Rajan & Watkinson 1992, Dahana-yake et al. 1995). This should both increase eco-

nomical efficiency and reduce leaching of fertilizer-P to watercourses.

Slow-release P-fertilizers have long been considered as a primary option on drained peatland forests in Finland, and the effects on tree production of P-fertilizers of differing solubility have been studied fairly extensively (Karsisto 1968, 1977, Penttilä & Moilanen 1987, Kaunisto et al. 1993, K. Silfverberg & M. Hartman unpubl.). There has also been a growing interest in the use of slow-release P-fertilizers as a better alternative to water-soluble fertilizers on agricultural land (Bolan et al. 1993, Hagin & Harrison 1993, Sale & Mokwunye 1993). The purpose of this paper is to summarize the information known about the properties of slow-release P-fertilizers in order to be able to answer the following questions:

- What are the different types and characteristics of slow-release P-fertilizers?
- How do fertilizer properties affect the release of P from fertilizers?
- How do site characteristics affect the release of P from fertilizers?
- Are the slow-release P-fertilizers likely to better match plant demand than water-soluble ones?
- Are the slow-release P-fertilizers likely to be less liable to be leached into watercourses than water-soluble ones?

The last three questions are discussed with special reference to the use of slow-release P-fertilizers on drained peatland forests.

ORIGIN AND MANUFACTURE OF P-FERTILIZERS

All P-fertilizers are produced from various mineral deposits of phosphorus. These include: Fe-Al phosphates (e.g. variscite and strengtite), Ca-Al-Fe phosphates (e.g. crandallite and millisite), and Ca phosphates (apatites) (McClellan & Gremillion 1980). Apatite is the tenth most abundant mineral in the earth's crust, and the major source of commercial phosphate.

On the basis of their geological formation, phosphate minerals are classified to igneous, sedimentary and metamorphic (Khasawneh & Doll 1978, McClellan & Gremillion 1980). Igneous

rocks are formed by crystallization of primary minerals from hot molten magma. Sedimentary rocks contain significant amounts of organic phosphorus, and metamorphic rocks are transitional in chemical nature between igneous and sedimentary rocks. Sedimentary apatites of commercial interest are collectively known as phosphate rock (PR), and account for about 80% of the world's phosphate production. PRs have also received the greatest research interest and most of the information reviewed here comes from these studies.

The typical phosphate mineral in igneous and metamorphic depositions is fluoroapatite, while sedimentary deposits are composed of carbonate apatite (francolite) (McClellan & Lehr 1969, McKelvey 1973). Moroccan phosphate rock used earlier on drained peatland forests in Finland is an example of a carbonate apatite-type PR, while the present peatland forest fertilizer, Siilinjärvi apatite, is a fluoroapatite of igneous origin.

There are several possible ways to use phosphate minerals in agriculture and forestry. They can be applied directly, as is done in the case of Siilinjärvi apatite on drained peatland forests in Finland, for example. Direct application has been extensively used for tree crops also in Asia (Chien & Menon 1995). Total and citric acid-soluble P contents of some commercial PR materials are given in Table 1. The materials with citric P > 30% are usually regarded as possible alternatives to water-soluble P-fertilizers for direct application to agricultural land, while materials with citric P < 30% are considered too unreactive to be directly applied.

In order to increase their solubility, P minerals can be heated (thermally treated phosphates) or acidulated with mineral acids such as sulphuric acid, phosphoric acid, or nitric acid (Fig. 1). The high energy consumption in the manufacture of thermally treated phosphates makes them expensive forms of P-fertilizer. Nevertheless, a large number of experiments have been carried out on agricultural land in Australia and New Zealand evaluating the suitability of thermal phosphates as slow-release fertilizers (Bolland & Gilkes 1987, 1991, 1995).

Traditionally, P has been applied to agricultural land in the form of completely acidulated water-soluble fertilizers, such as single superphosphate, triple superphosphate and diammonium-

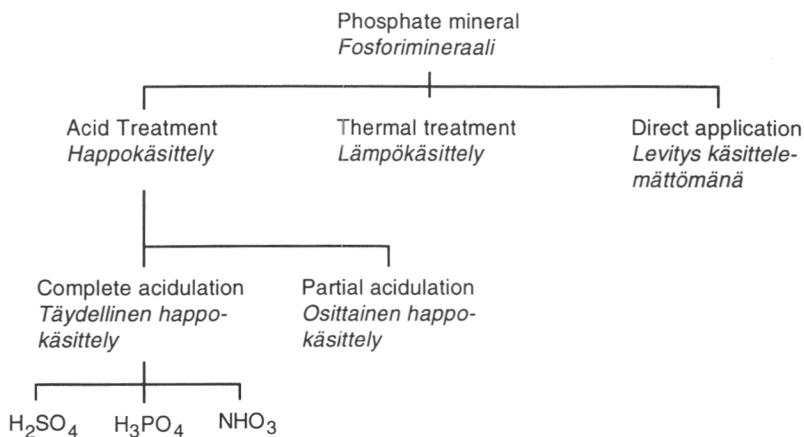


Fig. 1. Phosphate mineral is the primary source of phosphorus fertilizers. Reproduced from Bolan et al. (1993).

Kuva 1. Fosforilannoitteiden valmistus fosforimineraaleista. Muunnettu julkaisusta Bolan ym. (1993).

phosphate. However, partially acidulated phosphorus fertilizers have recently become of great interest as low-cost fertilizers on agricultural land. Partially acidulated P-fertilizers are produced by either direct acidulation of phosphorus minerals with less acid than that required for complete acidulation, or indirectly, by mixing different portions of fully acidulated and unacidulated P-fertilizers (Bolan et al. 1993).

The wide variation in the chemical composition of different phosphate minerals, and the number of alternative methods in the manufac-

ture of P-fertilizers, cause significant difficulties in predicting the behaviour of P-fertilizers under field conditions, unless the mechanisms controlling the release of P are known.

FERTILIZER PROPERTIES CONTROLLING THE RELEASE OF P

The most informative fertilizer property controlling the rate of dissolution of fertilizer-P is, of course, the amount of water-soluble P. Water-solu-

Table 1. Total P and 2% citric acid-soluble P contents of some commercially available phosphate rock materials. Source: Bolan et al. (1993).

Taulukko 1. Eräiden raakaosfaattien kokonaisfosforipitoisuus ja 2% sitruunahappoon liukeneva fosfori. Lähde: Bolan ym. (1993).

Phosphate rock <i>Raakaosfaattilaji</i>	Origin <i>Alkuperä</i>	Total P (%) <i>Kokonais-P</i>	Citric P (% of total P) <i>Sitruunahappoliukoinen P (% kokonais-P:stä)</i>
Christmas Island A	Christmas Island	16.4	23
Christmas Island C	Christmas Island	11.6	19
Duchess	Australia	13.5	6
Nauru	Nauru	15.6	22
Central Florida	USA	14.6	20
Khouribga	Morocco	14.4	26
Jordan	Jordan	15.0	26
Youssafia	Morocco	13.8	27
Egyptian	Egypt	13.0	33
Arad	Israel	14.4	30
Moroccan	Morocco	14.0	32
Chatham Rise	New Zealand	9.0	23
Sechura	Peru	13.2	43
Gafsa	North Africa	13.0	33
North Carolina	USA	12.8	32

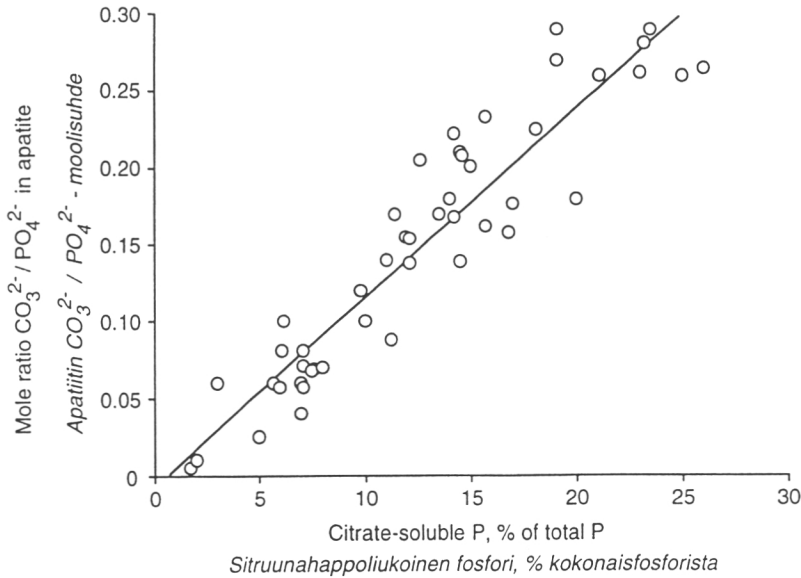


Fig. 2. Relationship between citrate solubility of apatite and its composition as indicated by the CO_3/PO_4 mole ratio. Source: Lehr and McClellan (1972).

Kuva 2. Apatiittimineraalien sitruunahappoliukoisuuden ja kiderakenteen CO_3/PO_4 -moolisuhteen välinen riippuvuus. Lähde: Lehr ja McClellan (1972).

ble P is not only readily available to plants, but can also increase the release of fertilizer-P from water-insoluble PR residues (Rajan & Watkinson 1992). However, this effect has not been shown in all experiments (Rajan 1987). High leaching rates of P were observed following the application of a PK-fertilizer with 20% of total P in a water-soluble form (Nieminen & Ahti 1993, Saura et al. 1995). This is why fertilizers with high amounts of water-soluble P are nowadays considered inappropriate for use on drained peatland forests in Finland.

For carbonate apatite-type PRs, the key-factor determining the reactivity of water-insoluble PR is the degree to which isomorphic substitution of phosphate by carbonate has occurred within the apatite crystal structure (Bolan et al. 1993, Chien 1993, Hagin & Harrison 1993, Sale & Mokwunye 1993). Because PO_4^{2-} ions have a tetrahedron structure and CO_3^{2-} a planar structure, CO_3^{2-} substitution for PO_4^{2-} results in structural instability making PRs more reactive (Fig. 2). Because the $\text{CO}_3^{2-}/\text{PO}_4^{2-}$ molar ratio in an apatite molecule is difficult to measure, the reactivity of different PRs is normally measured with neutral ammonium citrate, 2% citric acid or 2% formic acid (Chien 1993).

Great differences in reactivity between PRs of different origin are normal (Table 1). Moroccan phosphate rock used earlier on drained peat-

land forests in Finland is one of the PRs considered as 'reactive' (citric P > 30% of total P) by agricultural standards (e.g. Bolan et al. 1993). The citric acid solubility of the present peatland forest fertilizer, Siilinjärvi apatite, is only 1–2%.

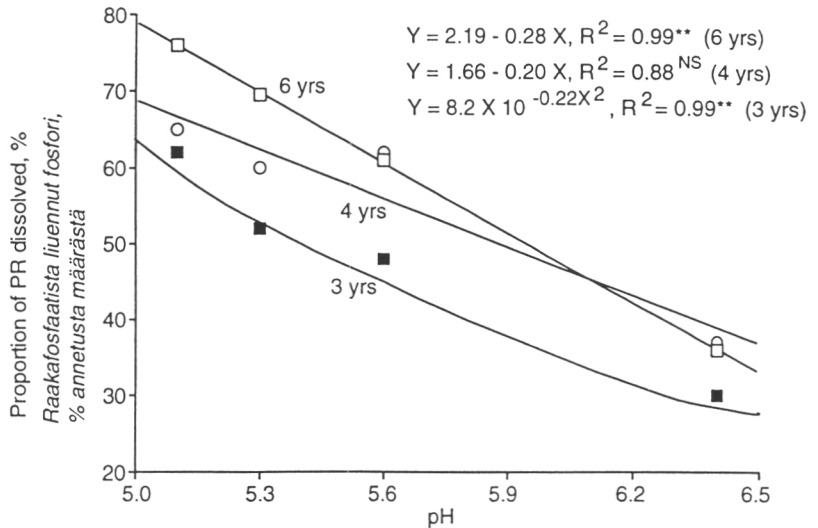
Phosphorus deposits can contain other minerals in addition to apatite. Some of these (e.g. siliceous minerals) may depress P release from fertilizers, whereas some (e.g. calcite) have no effect on P reactivity in the soil (Hammond et al. 1986).

Perhaps surprisingly, the particle size of phosphorus fertilizers has only a limited influence on P dissolution. Reducing particle size firstly increases reactivity, but fine grinding to a size of less than 100 mesh (150 μm) is not advisable, since finer particles do not increase reactivity greatly (Khasawneh & Doll 1978). In the case of long intervals between sequential fertilizer applications (e.g. forest fertilization), as plant root systems develop and fertilizer granules physically break into finer particles, the effect of granules on plant growth may be similar to powdered fertilizers (Gillion et al. 1979, Penttilä & Moilanen 1987).

The granulation technique also affects the reactivity of the fertilizer. In granulation, small amounts (2–5%) of binding agents, e.g. mineral acids (Stangel 1978), are added to improve the physical characteristics of the granules. It is to be noted that use of mineral acids as binding agents

Fig. 3. Effect of soil pH on the proportion of added phosphate rock dissolved 3, 4 and 6 years after application. Source: Rajan et al. (1991).

Kuva 3. Raakafosfaatista 3:ssa, 4:ssä ja 6:ssa vuodessa liuennut fosfori ja sen riippuvuus maan happamuudesta. Lähde: Rajan ym. (1991).



not only produce granules with good physical characteristics but also produce small amounts of water-soluble P. Nitric acid was added in the granulation of "Suo-PK", a commercial PK-fertilizer used earlier on drained peatlands in Finland. This is why Suo-PK also contained water-soluble P and nitrogen (2%).

SITE CHARACTERISTICS CONTROLLING THE RELEASE OF P

The dissolution of a slow-release phosphorus fertilizer, using fluoroapatite as an example, can be described by the following equation:



From the equation it is seen that the driving force for the dissolution of a slow-release P-fertilizer is the ability to maintain high concentrations of H^+ ions but low concentrations of Ca^{2+} and H_2PO_4^- ions in the soil solution. Several studies have shown that low soil pH enhances PR dissolution (Fig. 3). Drained peatlands, which have highly acidic surface peat layers ($\text{pH} < 4-5$), certainly have the ability to provide H^+ ions to promote dissolution.

As low levels of Ca^{2+} ions in soil solution promote fertilizer-P dissolution, plant species having a high Ca^{2+} uptake benefit the most from fertilizations with slow-release fertilizers (Flach et al.

1987). High concentrations of Ca^{2+} ions in a soil solution are unlikely to significantly depress fertilizer-P dissolution on drained peatlands. Owing to the high cation exchange capacity (CEC) of peat (Pättilä & Nieminen 1990), and the ability of organic matter to provide chelating substances that reduce Ca^{2+} ion activity in the soil solution (Chien 1979), drained peat soils most probably have the ability to maintain low concentrations of Ca^{2+} ions in the solution.

High concentrations of H_2PO_4^- ions in a soil solution have less effect on PR dissolution than those of Ca^{2+} ions (Mackay & Syers 1986). However, high soil P-sorption capacities have been shown to promote PR dissolution (Smyth & Sanchez 1982, Syers & Mackay 1986). The P-sorption capacities of Fe- and Al-poor peat soils can be extremely low (Cuttle 1983, Nieminen & Jarva 1996), which might depress the rate of P release. However, the high water content of peat and water movement through the surface soil are likely to rapidly remove the released phosphate ions away from the surfaces of fertilizer particles, and so promote additional fertilizer-P dissolution. Furthermore, peatland forests are often severely P deficient (Moilanen 1992, Veijalainen 1992), which is likely to result in high fertilizer-P uptake from the soil solution.

Application of non-P-fertilizers together with slow-release P sources may change the activity of H^+ , H_2PO_4^- or Ca^{2+} ions in the soil solution, and

thus alter fertilizer-P dissolution. Thus, N and K fertilizer salts were shown to increase PR availability to plants (Volk 1944, Jones 1948). This effect was probably because the N and K fertilizers increased the plant growth and thereby also the uptake of P from the soil solution (Chien 1979). The effect of other fertilizer nutrients on PR dissolution may, however, be also purely chemical. For example, the addition of urea hydrolyzes organic matter in the soil and the products of this hydrolysis increase the dissolution of PR by reducing the Ca^{2+} activity in the solution (Chien 1979).

Climatic factors are also important in affecting the dissolution of slow-release P-fertilizers. In areas with < 600 mm annual average rainfall in south-western Australia, the limited moisture supply severely depressed the dissolution of PR (Bolland & Gilkes 1995). However, due to the high water retention capacity of peat, the limited moisture supply probably seldom depresses P release on drained peatlands. Since flooding has not been shown to substantially affect dissolution in flooded rice soils (Hammond et al. 1986), excess moisture is also not likely to restrict P release from fertilizers.

Temperature has not been found to significantly affect PR dissolution in tropical soils (Chien et al. 1980). In regions with a distinct winter-period, however, below-zero temperatures and the frozen surface soil during the winter-period are unlikely to enable any fertilizer-P dissolution. Considerable dissolution during the winter-period, when there is no nutrient uptake by the vegetation, would be extremely harmful to recipient watercourses.

PLANT RESPONSE TO SLOW-RELEASE P-FERTILIZERS

The effects on plant yield of slow-release P-fertilizers have been studied extensively on agricultural land (e.g. Rajan & Marwaha 1993, Sale & Mokwunye 1993, Bolland & Gilkes 1995, Dahanayake et al. 1995). Due to variety in crop species, management practises, fertilizer and soil properties, it is difficult to generalise about the effectiveness of slow-release P-fertilizers. However, water-soluble and slow-release P-fertilizers

have most often been shown to be equally effective (Rajan & Marwaha 1993). Partially acidulated phosphate rocks (water-soluble P 40–50% of total P) were as effective as superphosphate in 86% of 109 field experiments conducted in Germany over the period 1961–1981 (Hagin 1985). McLean and Logan (1970) found that in 66% of 53 field trials partially acidulated Florida rock was as effective as superphosphate. It is generally accepted that unacidulated and partially acidulated phosphate rocks can be as effective as superphosphate for long-term or perennial crops, but not always for short-term and annual crops (Chien et al. 1990). The crop experiments where slow-release P-fertilizers have given better growth response than water-soluble fertilizers are scarce compared with those where slow-release fertilizers were equally or less effective (see, however, Hammond 1978, Khasawneh & Doll 1978, Garbouchev 1981, Hagin 1985, Rajan & Watkinson 1992, Dahanayake et al. 1995).

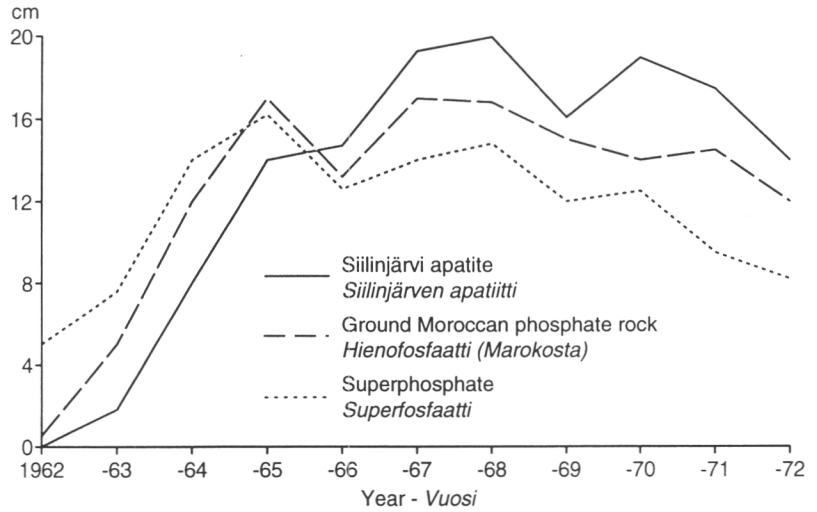
Fertilizations are usually repeated at 1–4-year intervals on agricultural land. For many fertilizers and environments, this time interval is probably far too short for all the applied slow-release P-fertilizer to be released in a plant-available form. Despite this, the agronomic effectiveness of water-soluble and slow-release P-fertilizers is often similar (see above). The time interval between sequential fertilizations is considerably longer in forestry (15–25 years), thus enabling all water-insoluble P to be released in a plant-available form. It is therefore not surprising that, in the long-term studies, different sources of P have affected tree production similarly on drained peatland forests (Karsisto 1968, 1977, Penttilä & Moilanen 1987, Kaunisto et al. 1993, K. Silfverberg & M. Hartman unpubl.). There is usually a more rapid response after fertilization with superphosphate (Fig. 4). However, the overall growth response is not affected by the solubility of the fertilizer, since the duration of response is longer for slow-release fertilizers.

LEACHING OF FERTILIZER-P INTO WATERWAYS

Agricultural land on acid peaty sands in high rainfall (> 800 mm annual average) areas of south-

Kuva 4. Increase in the annual height growth of Scots pine after fertilization in 1961 with different sources of P. Source: Karsisto (1977).

Kuva 4. Männyn vuotuisen pituuskasvun lisääntyminen eri fosforilannoitteilla vuonna 1961 tehdyn lannoituksen jälkeen. Lähde: Karsisto (1977).



western Australia have a high risk for fertilizer-P to be leached into waterways (Bolland et al. 1995). Peatlands drained for forestry in Finland pose a similar risk (Nieminen & Ahti 1993, Saura et al. 1995, Nieminen & Jarva 1996). Slow-release P-fertilizers have been considered as environmentally better alternatives to water-soluble P-fertilizers both in south-western Australia and in Finland. Because the yield effects of PRs and superphosphates were similar, Bolland et al. (1995) concluded that different sources of P are unlikely to reduce leaching of P into waterways from Australian acid peaty sands. As mentioned in the previous section, slow-release and water-soluble P-fertilizers have equal effects on the growth of trees on drained peatland forests, indicating that the uptake of fertilizer-P by trees is not related to the solubility of the fertilizer. However, it is not known whether the uptake of fertilizer-P by peatland vegetation other than trees depends on the source of P, but it is known that the adsorption of fertilizer-P by peat is not related to the solubility of the fertilizer (Kaunisto et al. 1993, K. Silfverberg & M. Hartman unpubl.). Thus, because slow-release P-fertilizers have not been shown to better match tree stand demand or to be more efficiently adsorbed by peat than water-soluble fertilizers, the uptake of fertilizer-P by understory vegetation is the only mechanism that can cause significant differences between water-soluble and slow-release P-fertilizers in overall P outflow to watercourses. If the fertilizer-P uptake by under-

storey vegetation does not depend on the source of P, the question arises, why have slow-release P-fertilizers been regarded as significantly less liable to be leached to watercourses than water-soluble fertilizers from drained peatland forests (Karsisto 1970, Karsisto & Ravela 1971, Almerger & Salomonsson 1979)?

The obvious answer is that the slow release of P from water-insoluble fertilizers has not been sufficiently accounted for in all P-outflow experiments. In the studies of Karsisto (1970), Karsisto and Ravela (1971), and Almerger and Salomonsson (1979), the monitoring of P outflow after fertilization with PR lasted only a few months. However, considerable changes in the leaching behaviour of slow-release P-fertilizers are unlikely to occur immediately after fertilization (Bolland et al. 1995, Jarva et al. 1995). For some fertilizers and in some environments, it may take even a few years before P outflow is significantly increased (Fig. 5). However, once slow-release P-fertilizers start to be lost to watercourses, P outflow continues for several years (Harriman 1978, Kenttämies 1981, Ahti 1983, Malcolm & Cuttle 1983).

CONCLUSIONS

The properties of phosphate minerals used for fertilizer manufacture differ significantly. Methods used to manufacture commercial P-fertilizers also vary significantly. It is thus difficult to un-

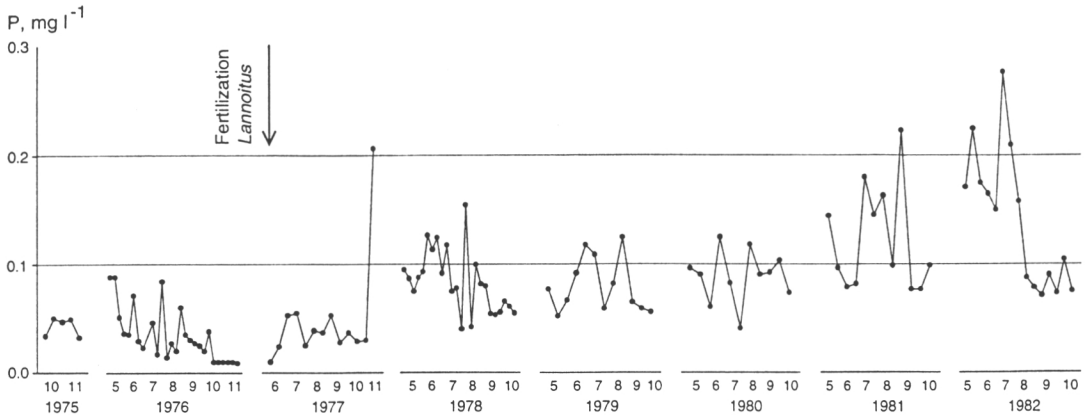


Fig. 5. Phosphorus concentrations of ditch water before (1975 and 1976) and after (1977–1982) fertilization with 500 kg ha⁻¹ of a commercial PK-fertilizer, including 8.3% of P as water-insoluble Moroccan phosphate rock. Only 10% of the area was fertilized. The values are the means of those presented by Ahti (1983) in appendices 1–3.

Kuva 5. Ojaveden fosforipitoisuudet ennen (1975 ja 1976) ja jälkeen (1977–1982) lannoituksen. Lannoitteena annettiin 500 kg ha⁻¹ kaupallista PK-lannoitetta, joka sisälsi 8,3% fosforia veteen liukenemattomassa muodossa (Marokkolaista raakaosfaattia). Vain 10% valuma-alueen pinta-alasta lannoitettiin. Kuvan arvot ovat keskiarvoja Ahdin (1983) liitteissä 1–3 esittämistä arvoista.

derstand or predict the behaviour of a particular P-fertilizer unless the fertilizer and site properties controlling the release of P are known.

The most important fertilizer properties controlling the release of P from fertilizers include: the amount of water-soluble P, the CO₃²⁻/PO₄²⁻ mole ratio of the apatite crystal structure, particle size, and granulation technique.

There is no experimental data about the site properties controlling the release of P from slow-release fertilizers on drained peatlands. However, because of high acidity and sufficient moisture supply, drained peatlands are likely to exhibit considerable fertilizer-P dissolution. Frozen soil during the winter-period is probably the factor most severely depressing P release in northern peatlands.

Slow-release P-fertilizers have not been shown to better match tree stand demand or to be more efficiently adsorbed by peat than water-soluble fertilizers on drained peatland forests. If the fertilizer-P uptake by peatland vegetation other than trees is also not related to the solubility of the fertilizer, there should be no major differences between water-soluble and slow-release P-fertilizers in overall P outflow to watercourses.

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TIIVISTELMÄ:

Hidasliukoisten fosforilannoitteiden ominaisuudet ja käyttökelpoisuus suometsien lannoituksessa. Kirjallisuuteen perustuva tarkastelu

Hidasliukoiset fosforilannoitteet (hidasliukoisuus tarkoittaa tässä yhteydessä sitä, että lannoitteessa on enemmän veteen liukenematonta fosforia kuin perinteisissä vesiliukoisissa fosforilannoitteissa) ovat kiinnostava vaihtoehto vesiliukoisille lannoitteille sekä taloudelliselta että ympäristönsuojelulliselta kannalta. Hidasliukoiset lannoitteet ovat selvästi vesiliukoisia fosforilannoitteita halvempia (Sanches & Salinas 1981). Hidasliukoisten lan-

noitteiden fosforipitoisuus on myös yleensä vesiliukoisia lannoitteita suurempi, mikä alentaa lannoitteiden kuljetus- ja levityskustannuksia. Vesiliukoiset fosforilannoitteet valmistetaan yleisimmin käsittelemällä erilaisia raakafosfaatteja fosforihapolla. Fosforihapon valmistuksessa syntyy sivutuotteena kipsijauhetta (Rajan ym. 1994), jonka varastointi ja hävittäminen on huomattava ympäristöongelma. Veteen liukenematonta fosforia

sisältävien lannoitteiden käytössä ei tätä ongelmaa ole. Joissakin tapauksissa hidasliukoisilla fosforilannoitteilla on myös saatu suurempia kasvunlisäyksiä kuin vesiliukoisilla lannoitteilla (Rajan & Watkinson 1982, Dahanayake ym. 1995). Tämä sekä lisää lannoituksen taloudellisuutta että todennäköisesti vähentää lannoitefosforin huuhtoutumista vesistöihin.

Tässä kirjallisuuskatsauksessa kootaan yhteen tutkimustuloksia fosforilannoitteiden alkuperästä ja ominaisuuksista sekä lannoitefosforin liukenemiseen vaikuttavista tekijöistä. Edelleen on tarkoitus verrata hidasliukoisilla ja vesiliukoisilla lannoitteilla saatuja kasvutuloksia ja liukoisuudeltaan erilaisten fosforilannoitteiden huuhtoutumista. Kirjallisuuskatsauksessa pyritään erityisesti arvioimaan hidasliukoisten fosforilannoitteiden käyttäytymistä ojitetuilla turvemaidella.

Kaikki fosforilannoitteet valmistetaan erilaisista fosforimineraaliesiintymistä. Näistä yleisimpiä ja tavallisimmin lannoitefosforin valmistuksessa käytettyjä ovat Ca-fosfaatit eli apatiitit. Muita fosforimineraaliesiintymiä ovat Ca-Al-Fe-fosfaatit ja Fe-Al-fosfaatit (McClellan & Gremillion 1980).

Geologisesti fosforimineraalit luokitellaan eloperäisiin, magmaattisiin ja metamorfisiin esiintymiin (Khasawneh & Doll 1978, McClellan & Gremillion 1980). Noin 80% kaikista fosforilannoitteista valmistetaan eloperäisistä esiintymistä. Eloperäistä alkuperää olevia, kaupallisesti kiinnostavia apatiittiesiintymiä kutsutaan yleisesti raakafosfaateiksi (= phosphate rocks). Eri alkuperää olevat fosforiesiintymät ovat yleensä huomattavan erilaisia kemialliselta koostumukseltaan. Taulukosta 1 nähdään, että esimerkiksi fosforin kokonaisuudet ja sitruunahappoliukoisuus vaihtelevat huomattavasti eri raakafosfaattiesiintymien välillä.

Fosforimineraaleja voidaan louhimisen ja jauhamisen jälkeen käyttää sellaisenaan kasvien fosforinlähteenä. Useimmiten fosforin liukoisuutta kuitenkin lisätään joko kuuma- tai happokäsittelyllä (Kuva 1). Osittain happokäsittellyt fosforilannoitteet ovat viime vuosina olleet tiiviin tutkimuksen kohteena maataloudessa, koska ne ovat perinteisiä vesiliukoisia fosforilannoitteita edullisempia.

Huomattava vaihtelu eri fosforimineraaliesiintymien kemiallisessa koostumuksessa ja lannoitteiden valmistusmenetelmissä aiheuttaa sen, että

fosforilannoitteiden käyttäytymistä kenttäolosuhteissa on vaikea ymmärtää tai ennustaa. Käyttäytymisen selvittämiseksi lannoitefosforin liukenemiseen vaikuttavat tekijät on kunnolla tunnettava.

Tärkein lannoitefosforin liukenemiseen vaikuttava lannoitelajista riippuva tekijä on lannoitteen sisältämän vesiliukoisen fosforin määrä. Vesiliukoista fosforia sisältäviä lannoitteita ei kuitenkaan viime vuosina ole suometsissä juurikaan käytetty.

Eloperäistä alkuperää olevien apatiittiesiintymien osalta veteenliukenemattoman fosforin liukenemisnopeus määräytyy suurelta osin apatiitin kiderakenteen $\text{CO}_3^{2-}/\text{PO}_4^{2-}$ -moolisuhteen perusteella (Kuva 2). Fosfaatin korvautuminen karbonaatilla aiheuttaa kiderakenteessa muutoksia, jotka lisäävät fosforin liukoisuutta (Hammond ym. 1986).

Koska apatiitin kiderakenteen $\text{CO}_3^{2-}/\text{PO}_4^{2-}$ -moolisuhteen mittaaminen on vaikeaa, veteenliukenemattoman fosforin liukoisuus määritetään yleensä neutraalilla ammonium nitraatilla, 2% sitruunahapolla tai 2% murahaishapolla (Chien 1993).

Raekoolla on myös vaikutusta fosforin liukenemiseen (Khasawneh & Doll 1978). Pitkäaikaisissa kokeissa (esim. suometsien lannoituksessa) raekoko ei kuitenkaan merkittävästi vaikuttane lannoituksen tehokkuuteen, koska murentuessaan rakeet alkavat ennenpitkää käyttäytyä kuten hienorakeisimmat lannoitteet (Gillion ym. 1979, Penttilä & Moilanen 1987).

Myös rakeistamisessa käytetty tekniikka vaikuttaa lannoitteen liukenemiseen. Rakeistamisessa lannoitteen lisätään 2–5% sitovia ainesosia (esim. mineraalihappoja) rakeiden fysikaalisten ominaisuuksien paranattamiseksi (Stangel 1978). Aiemmin suometsissä käytetyn PK-lannoitteen (Suo-PK) rakeistamisessa lannoiteseokseen oli lisätty typpihappoa, joka muuttaa osan fosforista vesiliukoiseen muotoon. Tästä syystä Suo-PK sisälsi jonkin verran vesiliukoista fosforia ja typpiä.

Tärkeimmät lannoitefosforin liukenemiseen vaikuttavat kasvupaikkatekijät selviävät yhtälöstä 1, joka kuvaa fluoroapatiitin liukenemista.

Yhtälöstä voidaan päätellä, että kasvupaikan kyky tuottaa maaveteen vetyioneja ja toisaalta pidättää maavedestä kalsiumia ja fosforia ovat ratkaisevia tekijöitä hidasliukoisten fosforilannoitteiden

den liukenemisessa. Happamuuden voimakas vaikutus veteenliukenemattoman fosforin liukenemiseen näkyy Kuvasta 3. Ojitetuilla turvemaiden maaveden vetyionipitoisuus (pH yleensä < 4–5) ei useinkaan rajoittane lannoitefosforin liukenemistä. Turpeen voimakas kationinvaihtokyky (Pätilä & Nieminen 1990) aiheuttaa sen, että myöskään korkeat maaveden Ca-konsentraatiot eivät yleensä liene esteenä lannoitefosforin liukenemiselle. Turvemaiden kyky pidättää maavedestä fosfaattia on sen sijaan heikko (Cuttle 1983, Nieminen & Jarva 1996). Veden suotautuminen pintaturpeen läpi kuitenkin todennäköisesti huuhtoo lannoitteista vapautuneet fosfaatti-ionit lannoiterakeiden pinnoilta syvempiin turvekerroksiin, jolloin maaveden fosfaattikonsentraatio lannoiterakeiden lähellä ei enää rajoittane fosforin liukenemistä.

Muita lannoitefosforin liukenemiseen vaikuttavia kasvupaikkatekijöitä ovat kasvupaikan hydrologia ja maan lämpötila. Kuivuus ei rajoittane lannoitefosforin liukenemistä suometsissä. Myöskään liiallinen kosteus ei estäne liukenemistä, koska riisipelloilla tulvittamisen ei ole havaittu vähentävän hidasliukoisen fosforin liukenemistä (Hammond ym. 1986). Sen sijaan maaveden jäätyminen talvella estää todennäköisesti kokonaan veteen liukenemattoman fosforin liukenemisen.

Fosforilannoitteiden liukoisuuden vaikutuksesta kasvien kasvuun on tehty useita tutkimuksia sekä maatalousmaalla että suometsissä. Maatalousmaalla tehtyjen tutkimusten perusteella on vaikea yksiselitteisesti päätellä hidasliukoisten fosforilannoitteiden tehokkuutta vesiliukoisiin lannoitteisiin verrattuna, koska viljelymenetelmät, kasvilajit ja lannoitteiden sekä maan ominaisuudet vaihtelevat eri tutkimuksissa. Useimmiten vesiliukoiset ja hidasliukoiset lannoitteet ovat kuitenkin olleet yhtä tehokkaita (McLean & Logan 1970, Hagin 1985, Rajan & Marhawa 1993). Maataloudessa lannoitukset toistetaan yleensä 1–4 vuoden välein. Monissa tapauksissa tämä ajanjakso on todennäköisesti liian lyhyt, jotta kaikki hidasliukoinen fosfori ehtisi muuttua vesiliukoiseen muotoon. Siksi ei ole yllättävää, että joissakin kokeissa vesiliukoiset fosforilannoitteet voivat olla hidas-

liukoisia tehokkaampia. Suometsätaloudessa lannoitusten aikaväli on sen sijaan huomattavasti pidempi (15–25 vuotta), joten kaikki hidasliukoinen fosfori todennäköisesti ehtii muuttua vesiliukoiseksi ennen lannoituksen uusimista. Siten ei ole yllättävää, että pitkäaikaisissa kokeissa lannoitusvaikutus on ollut samaa suuruusluokkaa liukoisuudeltaan erilaisilla lannoitteilla (Karsisto 1968, 1977, Penttilä & Moilanen 1987, Kaunisto ym. 1993, K. Silfverberg & M. Hartman julkaisematon). Yleensä vesiliukoiset lannoitteet kylläkin antavat nopeamman kasvunlisäyksen, mutta lannoitteen ominaisuudet eivät vaikuta kokonaistuokseen, koska hidasliukoisilla lannoitteilla lannoitusvaikutuksen kesto on pidempi (Kuva 4).

Lannoitefosforin huuhtoutuminen ojitusalueilta riippuu siitä, kuinka suuri osa levitetystä fosforista sitoutuu puustoon, pintakasvillisuuteen ja turpeeseen. Ojitusalueilla tehdyt tutkimukset ovat osoittaneet, että samoin kuin puuston kykyyn hyödyntää lannoitefosforia, lannoitteen liukoisuus ei vaikuta turpeeseen pidättyneen fosforin määriin (Kaunisto ym. 1993, K. Silfverberg & M. Hartman julkaisematon). Jos lannoitteen liukoisuus ei puuston ja turpeen lisäksi vaikuta myöskään aluskasvillisuuteen pidättyvän fosforin määriin, niin lannoitefosforin huuhtoutumisessa ei pitäisi olla merkittäviä eroja liukoisuudeltaan erilaisten fosforilannoitteiden välillä. Hidasliukoisia fosforilannoitteita on kuitenkin pidetty selvästi vähemmän huuhtoutumisalttiina kuin vesiliukoisia lannoitteita (Karsisto 1970, Karsisto & Ravela 1971, Almberger & Salomonsson 1979). Tämä käsitys voi hyvinkin aiheutua siitä, että em. huuhtoutumatutkimukset olivat hyvin lyhytaikaisia (seuranta vain muutama kuukausi lannoituksen jälkeen). Siten hidasliukoinen lannoitefosfori oli todennäköisesti vielä lähes kokonaan veteen liukenemattomassa muodossa kokeiden päättyessä. Pitkäaikaiset kokeet ovat osoittaneet, että myös hidasliukoiset fosforilannoitteet huuhtoutuvat ojitusalueilta (Harriman 1978, Kenttämies 1981, Ahti 1983, Malcolm & Cuttle 1983). Huuhtoutuminen alkaa usein kuitenkin lisääntyä merkittävästi vasta joitakin vuosia lannoituksen jälkeen (Kuva 5).

DISSOLUTION OF PHOSPHORUS FERTILIZERS OF DIFFERING SOLUBILITY
IN PEAT SOIL: A FIELD EXPERIMENT ON A DRAINED PINE BOG.

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Running headline: Dissolution of phosphorus fertilizers in peat soil

Nieminen, M. & Jarva, M. (Finnish Forest Research Institute, Vantaa Reserch Centre, P. O. Box 18, FIN-01301 Vantaa, Finland). Dissolution of phosphorus fertilizers of differing solubility in peat soil: a field experiment on a drained pine bog. Received May 25, 1999. Accepted October 16, 1999. *Scand. J. For. Res.* 00: 00-00, 1999.

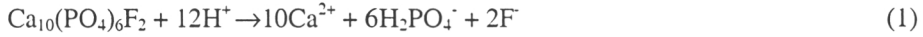
A 2-year field trial was conducted on a drained pine bog to measure the dissolution of five phosphorus (P) fertilizers of differing solubility. The rate of fertilizer dissolution was measured using a sequential fractionation which involved pre-extraction with 0.5 M NaCl/TEA followed by 1 M NaOH and a mixed acid ($\text{HNO}_3+\text{HCl}+\text{H}_2\text{SO}_4$) digestion. About 56 % of Siilinjärvi apatite, a hard magmatic rock phosphate, dissolved over the two years. For a commercial phosphorus+potassium fertilizer manufactured from Siilinjärvi apatite and potassium chloride (water-soluble P<0.1 %), the corresponding value was 44 %. For Moroccan phosphate rock, and a commercial fertilizer manufactured from Moroccan phosphate rock and potassium chloride (water-soluble P=15.8 %), the dissolution was about 44 % and 58 %, respectively. For superphosphate (water-soluble P=79 %), the corresponding value was 93 %.

Key words: drained peatlands, fertilizer residue, phosphorus, sequential fractionation, slow release fertilizers.

INTRODUCTION

In the beginning of the 20th century, the area of pristine peatlands in Finland totalled about 10 million hectares or about one third of the total land area. Over half of this area has now been drained for forestry purposes. It has been estimated that the present growth of peatland forests may be more than 25 % of the total growth of all Finnish forests (Tomppo 1998). However, phosphorus deficiency very often limits the growth of trees on drained peatlands. Application of P-fertilizers is therefore recommended on about 60 % of the drained peatland area (Moilanen 1992, Veijalainen 1992). Slow release P-fertilizers have long been considered as a primary fertilization option for drained peatland forests, and the effects on tree production of P-fertilizers of differing solubility have been studied extensively (Karsisto 1968, 1977, Penttilä & Moilanen 1987, Kaunisto et al. 1993, Silfverberg & Hartman 1998). However, only one study has dealt with the dissolution of different slow release P-fertilizers in peat soil (Yli-Halla & Lumme 1987). The results of their laboratory incubation study can not be directly converted to field conditions. To fully understand the effect of P fertilization on the growth of drained peatland stands, dissolution of different P-fertilizers in peat soil under field conditions needs to be known. Information about the dissolution of P-fertilizers of differing solubility can also be used to assess the risk of fertilizer-P leaching to surface waters.

The dissolution of a slow release P-fertilizer, using fluoroapatite as an example, can be described by the following reaction:



The methods proposed to measure the rate and extent of dissolution of slow release P-fertilizers are based on this reaction formula. In most studies, the extent of dissolution has been determined directly by measuring the amount of dissolved P (Mackay et al. 1986, Bolan & Hedley 1989, Mahimairaja et al. 1995) or Ca (Hughes & Gilkes 1984, 1994) in the soil. Under field conditions, however, a fraction of the dissolved P and Ca are likely to be removed by plant uptake and leaching and the amounts remaining in the soil would thus underestimate the extent of dissolution. Under field conditions, the decrease in the amount of residual fertilizer-P has provided an accurate estimate of phosphate rock dissolution (Rajan 1983, Rajan et al. 1991, Rajan & Watkinson 1992, Tambunan et al 1993).

The undissolved (residual) fertilizer-P is usually determined by pre-washing the soil samples from fertilized and respective unfertilized plots with either NaCl (Rajan 1983, McKay et al. 1986) or NaCl/TEA (Tambunan et al. 1993, Mahimairaja et al. 1995), and sequentially extracting with NaOH and either HCl (Bolan & Hedley 1989, Mahimairaja et al. 1995) or H₂SO₄ (Rajan 1987, Tambunan et al. 1993). NaCl and NaCl/TEA remove water-soluble and loosely bound P, and NaOH is assumed to remove inorganic and organic P associated with amorphous hydrous oxides of Al and Fe (Hedley et al. 1982). Extraction with HCl and H₂SO₄ dissolves calcium phosphate (apatite) and hence an increase in acid extractable P from fertilizer-P treated soil compared to untreated is a measure of the residual fertilizer-P. The assumptions

included are: (1) the Ca-P fraction is apatite phosphate because the NaCl or NaCl/TEA and NaOH solutions do not dissolve apatite, (2) the dissolution of apatite does not form any Ca-P compounds which are less soluble than apatite, and (3) the undissolved fertilizer residues do not move outside the soil sampling zone (Rajan 1987).

This paper reports a study to investigate the extent of P release from fertilizers of different solubility in peat soil under field conditions over a 2 year period.

MATERIAL AND METHODS

Site description and field work

The study site is located in southern Finland (61°51'N; 25°59'E, 131 m a.s.l.). The mean annual precipitation at the nearby meteorological station is 550 mm, and the mean annual temperature 3 °C. The peat layer was over 3 m thick and consisted almost entirely of *Sphagnum* peat. Some chemical properties of the surface peat layer are presented in Table 1. According to the peatland site type classification used in Finland (Heikurainen & Pakarinen 1982), the site was a Small-sedge pine bog with patches of *Sphagnum fuscum* bog. The site was drained in 1945-1947 with a 60 m ditch spacing. A naturally regenerated Scots pine (*Pinus sylvestris* L.) stand, with an average volume of about 10 m³ ha⁻¹, is growing on the site.

The field experiment was established during August 1996, and consisted of five fertilization treatments with three replicates. The treatments were as follows: (1) Superphosphate, (2) Mire-PK (Finnish: Rakeinen Suometsien PK), (3) Moroccan phosphate rock, (4) Siilinjärvi apatite, and (5) Forest-PK (Finnish: Metsän PK). Some chemical and physical properties of the fertilizers are given in Tables 2 and 3. Siilinjärvi apatite is a Finnish fluoroapatite of igneous origin, while Moroccan phosphate rock is a carbonate apatite of sedimentary origin. Mire-PK and Forest-PK are commercial P+K fertilizers used mainly on drained peatlands in Finland. Mire-PK is manufactured from Moroccan phosphate rock and potassium chloride, and Forest-PK from Siilinjärvi apatite and potassium chloride. In the manufacture of Mire-PK, nitric acid is added to

improve the physical properties of the granules and is why Mire-PK contains water-soluble P (15.8 % of total P) and N (2 %).

In each of 15 plots (10 m x 10 m) 9 circular patches (3.14 m²) were systematically located. In each of these patches there were 5 systematically located sampling quadrates (20 cm x 20 cm). Four of the quadrates were fertilized by evenly spreading the fertilizer (0.2 g P 100 cm⁻²) on the bottom layer vegetation of mosses and lichens, and one quadrate was left unfertilized. Peat samples from the unfertilized quadrates were taken at the beginning of the experiment in August 1996, and the samples from the fertilized quadrates about 2, 12, 20, and 24 months after fertilization. On each sampling occasion, a 10 cm x 10 cm core was taken from the middle of one systematically chosen quadrate from each of the 9 circular patches. The cores were divided into the 0-5 and 5-10 cm depth layers. The samples from each plot were combined by layers.

The shrub vegetation was cut away at a height of 2-3 cm from the soil surface prior to the sample collection. The bottom layer vegetation was, however, included in the peat sample. This was to ensure that the fertilizer residues would remain in the sampling zone.

Laboratory analyses and calculations

The samples were dried at 70 °C to constant mass and homogenized in a stainless steel mill (sieve mesh diameter 2.0 mm). The dissolution of the studied fertilizers was

investigated using a modification of the sequential P fractionation procedure described by Tambunan et al. (1993). The peat samples (1 g) were prewashed with 40 ml of 0.5 M NaCl/TEA (pH 7.0) to remove water-soluble and loosely bound P and exchangeable Ca. Removal of exchangeable Ca was carried in order to prevent the formation of $\text{Ca}(\text{OH})_2$ or CaCO_3 in the NaOH extracts and readsorption or co-precipitation of the dissolved P by these precipitates (Mackay et al. 1986). The samples were then extracted with 40 ml of 1 M NaOH to remove Al- and Fe-bound inorganic and organic P. The extraction times were 2 h and 16 h for the NaCl/TEA and NaOH extracts, respectively. Tambunan et al. (1993) used 0.5 M H_2SO_4 to subsequently extract the fertilizer-P residue. However, Siilinjärvi apatite has been shown not to completely dissolve in 0.5 M H_2SO_4 (Yli-Halla & Lumme 1987). Thus, a mixed acid digestion procedure was used in this study (Anon. 1990). This procedure, referred to as the HNO_3 -HCl- H_2SO_4 digestion, first involved the boiling dry of the residue remaining after the NaCl/TEA and NaOH extractions in a solution of concentrated HNO_3 (9 ml) and concentrated HCl (18 ml). After the sample had cooled, 20 ml of concentrated H_2SO_4 and 10 ml of concentrated HNO_3 were added, and the suspension was then boiled until it became clear (about 30 min). Distilled water (100 ml) was then added and the suspension boiled again for about 10 min. The suspension was then transferred to a 250 ml volumetric flask and made up to mark with distilled water.

Vacuum filtration was used to remove the solutions in the NaCl/TEA and NaOH extractions (Schleicher and Schuell Rundfilter 589²). Centrifugation could not be used, since peat being light did not settle tightly in the bottom of the centrifuge tube (see also Rannikko & Hartikainen 1980). The HNO_3 -HCl- H_2SO_4 -digestions were not filtered.

Phosphorus concentrations in all the solutions were determined by ICP/AES, ARL 3580.

The extent of fertilizer-P dissolution was calculated using the following equation:

$$\text{Percent dissolution (\%)} = \frac{((\text{HNO}_3\text{-HCl-H}_2\text{SO}_4\text{-P}_0 + \text{Fertilizer-P added}) - (\text{HNO}_3\text{-HCl-H}_2\text{SO}_4\text{-P}_t))}{\text{Fertilizer-P added}} \times 100 \quad (1)$$

The subscript 0 refers to the amount of P in the control quadrates, and t to that in the fertilized quadrates at the different times of sampling. To convert mg P kg⁻¹ soil to kg P ha⁻¹, bulk density values of the soil samples obtained at each sampling time were used.

In the P fractionation method used in this study, the following assumptions have been made: (1) the NaCl/TEA and NaOH extractions do not dissolve apatite; (2) the dissolution of apatite in acid Ca-poor *Sphagnum* peat is not expected to form any acid extractable Ca-P compounds (this is confirmed in the study made by Rannikko & Hartikainen (1980)), or the insoluble residual P fractions (Hedley et al. 1982); and (3) the fertilizer residues did not move outside the soil sampling zone. The assumptions made in this study somewhat differ from those of the earlier studies (Rajan 1983, 1987). This is because the HNO₃-HCl-H₂SO₄-digestion of the final residue is expected to dissolve not only apatite phosphate but also the chemically stable residual P compounds.

Recovery experiments were made to test the fractionation procedure. Siilinjärvi apatite and Moroccan phosphate rock, about 0.05 g each, were mixed with 1 g of unfertilized air-dried *Sphagnum* peat and analyzed using the above described P fractionation procedure. Both Siilinjärvi apatite and Moroccan phosphate rock contain insignificant amounts of water-soluble P (Table 2) and were dry-blended with the peat. The sequential extraction procedure was judged suitable if it recorded nil recovery during the extraction with NaCl/TEA and NaOH and 100 % recovery during digestion with HNO₃-HCl-H₂SO₄. Recovery of P from the fertilizers in different extracts was calculated using the following equation:

$$\text{Recovery (\%)} = \frac{\text{P (treated minus control)}}{\text{added P}} \times 100 \quad (2)$$

During the course of the field sample analysis it was realized that the milling of the samples with a mesh diameter of 2.0 mm did not give satisfactory results for all samples. Duplicate analysis was carried out for a few samples. The results showed very high variation in HNO₃-HCl-H₂SO₄-P concentrations for 4 samples with high amounts of residual fertilizer-P (> 3000 mg kg⁻¹). The coefficients of variation (CV) between duplicate analyses for HNO₃-HCl-H₂SO₄-P were > 25 %. The samples with high amounts (> 2000 mg kg⁻¹) of HNO₃-HCl-H₂SO₄-P (i.e. all the surface 0-5 cm peat samples containing undissolved residues of Siilinjärvi apatite, Moroccan phosphate rock, Mire-PK, and Forest-PK) were therefore re-milled to pass a mesh diameter of 0.2 mm and the P fractionations and the analyses of extracts repeated. The same previously mentioned four samples were then re-analysed in duplicate. The results showed that decreasing the diameter of the milled sample from about 2.0 mm to about

0.2 mm considerably decreased the within-sample variation. After re-milling, the CVs for $\text{HNO}_3\text{-HCl-H}_2\text{SO}_4\text{-P}$ were < 6 %.

The effect of different fertilizers on the concentrations of NaCl/TEA-P, NaOH-P, and $\text{HNO}_3\text{-HCl-H}_2\text{SO}_4\text{-P}$ in the soil was tested using analysis of variance for repeated-measures designs. The grouping factor was fertilizer treatment, with five levels, and the repeated or within factor was sampling time, also with five levels. To illustrate the trends in the dissolution of different P-fertilizers, the data were also analysed with regression analysis using sampling time as the independent variable and the percent fertilizer dissolution as the dependent variable. The statistical analyses were made using the BMDP (1990) software package.

RESULTS

Testing of the fractionation procedure

The NaCl/TEA extraction recovered about 0.5 % of the added Siilinjärvi apatite and Moroccan phosphate rock, and the NaOH extraction recovered a further 0.5 % (Table 4). The recovery of the added P in the $\text{HNO}_3\text{-HCl-H}_2\text{SO}_4$ digestion was 96 % for Siilinjärvi apatite, and about 94 % for Moroccan phosphate rock.

Sequential extraction of the field samples

Prior to the fertilizer application the values for $\text{HNO}_3\text{-HCl-H}_2\text{SO}_4\text{-P}$ ranged from 190 to 350 mg kg^{-1} in the surface 0-5 cm peat samples, and after application from 600 to $10\,237 \text{ mg kg}^{-1}$. In the 5-10 cm peat samples, the values prior to application ranged from 53 to 252 mg kg^{-1} and after application from 67 to 344 mg kg^{-1} . There were significant differences between fertilizer treatments ($p < 0.001$) and sampling times ($p < 0.001$) in the $\text{HNO}_3\text{-HCl-H}_2\text{SO}_4\text{-P}$ of surface 0-5 cm peat samples, and the interaction between fertilizer treatment and sampling time was also significant ($p < 0.001$). However, in the 5-10 cm peat samples there was no difference in $\text{HNO}_3\text{-HCl-H}_2\text{SO}_4\text{-P}$ among fertilizer treatments ($p = 0.431$) and the differences between the samples collected prior to the fertilizer application and after application were insignificant. These results indicate that there was negligible movement of fertilizer residues below 5 cm depth. The dissolution of different P-fertilizers was therefore calculated using only the values obtained from the surface (0-5 cm) peat samples.

The differences in NaCl/TEA-P between the fertilizer treatments ($p = 0.024$) and sampling times ($p < 0.001$) in the surface 0-5 cm peat samples were statistically significant. There was also a significant interaction between the fertilizer treatment and sampling time ($p < 0.001$). The concentrations of NaCl/TEA-P were higher for the plots fertilized with superphosphate and Mire-PK at the first sampling time after fertilization (Fig. 1). No substantial differences between the different fertilizer treatments were found at the later sampling times. The concentrations of NaOH-P in the surface peat samples at the first sampling occasion after fertilizer application were also higher for the plots fertilized with superphosphate and Mire-PK than for the other fertilizers (Fig. 2). The differences between fertilizer treatments ($p = 0.002$) and

sampling times ($p < 0.001$) were statistically significant, as was also the interaction between fertilizer treatment and sampling time ($p < 0.001$).

The rate of dissolution of superphosphate was particularly high during the first few months after fertilizer application compared with the other fertilizers (Fig. 3). Some of the added Mire-PK also dissolved immediately after fertilization, whereas the dissolution of Moroccan phosphate rock and Siilinjärvi apatite was only significant about three months after fertilizer application. About 93 % of the added superphosphate had dissolved after two years. For the other fertilizer treatments, the corresponding values were: Forest-PK and Moroccan phosphate rock 44 %, Mire-PK 58 %, and Siilinjärvi apatite 56 %.

DISCUSSION

Since the recovery of phosphate rock residue has been shown to be incomplete in acid soils using HCl (Tambunan et al. 1993) and Siilinjärvi apatite was not completely dissolved in H_2SO_4 (Yli-Halla & Lumme 1987), neither of these acids was judged suitable for extracting the fertilizer-P residue in our study. We therefore used a HNO_3 -HCl- H_2SO_4 mixture to digest the fertilizer-P residue. Near complete (94-96 %) recovery of added fertilizer-P was achieved in the HNO_3 -HCl- H_2SO_4 digestion, and given the uncertainties involved in P fractionation, the method was considered reliable. In practical peatland forest fertilization, the dissolution of fertilizer-P may be somewhat higher than that suggested by the results presented here however. This is because the application dose in the experiment (200 kg P ha^{-1}) was about five times higher than that used in practical peatland forestry ($35\text{-}45 \text{ kg P ha}^{-1}$), and the

proportion of phosphate rock that dissolves has been shown to decrease with increasing amounts of phosphate rock application (Rajan et al. 1991). In the dissolution experiments performed under field conditions, high additions of P fertilizer are usually used. This is because small additions make the P fractionation method inaccurate for soils with high levels of native P.

The rates and extents of dissolution of the fertilizers were related to their reactivity as measured using citric and formic acids (Table 2), except in the case of Siilinjärvi apatite. The unexpected high dissolution of Siilinjärvi apatite may be due to the small particle size of the fertilizer (Khasawneh & Doll 1978). In studies of fertilization and tree growth (Karsisto 1977, Kaunisto et al. 1993), the effectiveness of Siilinjärvi apatite has usually been less than that of Moroccan phosphate rock during the first few years after fertilization however. These results imply that Siilinjärvi apatite would dissolve more slowly than Moroccan phosphate rock.

Earlier studies have indicated rather small increases in tree growth during the first 1-2 years after the application of Moroccan phosphate rock and Siilinjärvi apatite (Karsisto 1977, Kaunisto et al. 1993), and also rather small changes in the leaching of P to water courses during the first few months after the application of Moroccan phosphate rock and Forest-PK (Karsisto 1970, Karsisto & Ravela 1971, AlMBERGER & Salomonsson 1979, Ahti 1983, Jarva et al. 1995). Applications of superphosphate have, in contrast, been shown to increase tree production significantly during the first year after application (Karsisto 1977), and fertilization with Mire-PK resulted in the leaching of P to water courses immediately after application (Nieminen & Ahti 1993).

These results can be explained by the differences in the rates of dissolution of the fertilizers as shown in this study. It is therefore concluded that information about the dissolution rates of P-fertilizers of different solubility is very important in understanding the behaviour of fertilizer-P on drained peatlands.

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Table 1. Some chemical properties of the surface peat layer (0-15 cm) at the study site.

Ash content ¹⁾ , %	1.39
pH ²⁾	3.5
P _{tot} ³⁾ , mg kg ⁻¹	524
K _{tot} ³⁾ , mg kg ⁻¹	388
Ca _{tot} ³⁾ , mg kg ⁻¹	1466
Mg _{tot} ³⁾ , mg kg ⁻¹	362
Al _{tot} ³⁾ , mg kg ⁻¹	451
Fe _{tot} ³⁾ , mg kg ⁻¹	805
P adsorption capacity ⁴⁾ , kg ha ⁻¹	3.0

Methods used:

¹⁾ Halonen et. al (1983)

²⁾ Soil: water (1 g:25 ml)

³⁾ Dry digestion in HCl (Halonen et. al 1983); ICP/AES

⁴⁾ Nieminen & Jarva (1996)

Table 2. Some chemical characteristics of the fertilizers used in the experiment.

Fertilizer	Total P ¹⁾ , %	% of Total P		
		Water-soluble ²⁾	2 % Citric acid soluble ³⁾	2 % Formic acid soluble ³⁾
Superphosphate	9.2	79.0	79.1	79.5
Mire-PK	9.1	15.8	46.0	40.6
Forest-PK	9.1	< 0.1	20.7	14.3
Moroccan phosphate rock	14.8	< 0.1	15.7	10.5
Siilinjärvi apatite	16.0	< 0.1	6.6	9.5

Methods used:

¹⁾ According to Anon. (1990).

²⁾ Analyzed by boiling (10 min) in deionized water using an initial fertilizer: solution ratio of 1:25.

³⁾ According to Chien (1993).

Table 3. Particle size distribution (weight fraction, %) of the fertilizers used in the experiment.

Fertilizer	Size range (mm)				
	< 0.045	0.045- 0.14	0.14- 0.4	0.4- 2.0	>2.0
Superphosphate	0	0	0	4	96
Mire-PK	0	0	1	21	78
Forest-PK	0	0	1	3	96
Moroccan phosphate rock	6	59	28	7	0
Siilinjärvi apatite	32	52	14	2	0

Table 4. Fertilizer-P recovered by sequential fractionation following an immediate addition of Siilinjärvi apatite (n=13) and Moroccan phosphate rock (n=15) to *Sphagnum* peat at a fertilizer: soil ratio of 1:20.

Fertilizer	Extract	Fertilizer-P recovery (%) \pm SD ¹⁾
Siilinjärvi apatite	NaCl / TEA	0.57 \pm 0.06
	NaOH	0.32 \pm 0.38
	HNO ₃ -HCl-H ₂ SO ₄	96.00 \pm 5.03
Moroccan phosphate rock	NaCl / TEA	0.50 \pm 0.27
	NaOH	0.65 \pm 0.36
	HNO ₃ -HCl- H ₂ SO ₄	93.74 \pm 4.18

¹⁾ SD = Standard deviation

Figure legends

Fig. 1. Changes in NaCl/TEA extractable P with time in the surface 0-5 cm peat samples. Values are standard deviations.

Fig. 2. Changes in NaOH extractable P with time in the surface 0-5 cm peat samples. Values are standard deviations.

Fig. 3. Rates of dissolution of the studied fertilizers. Fitted lines are the regression equations as shown in the figure.

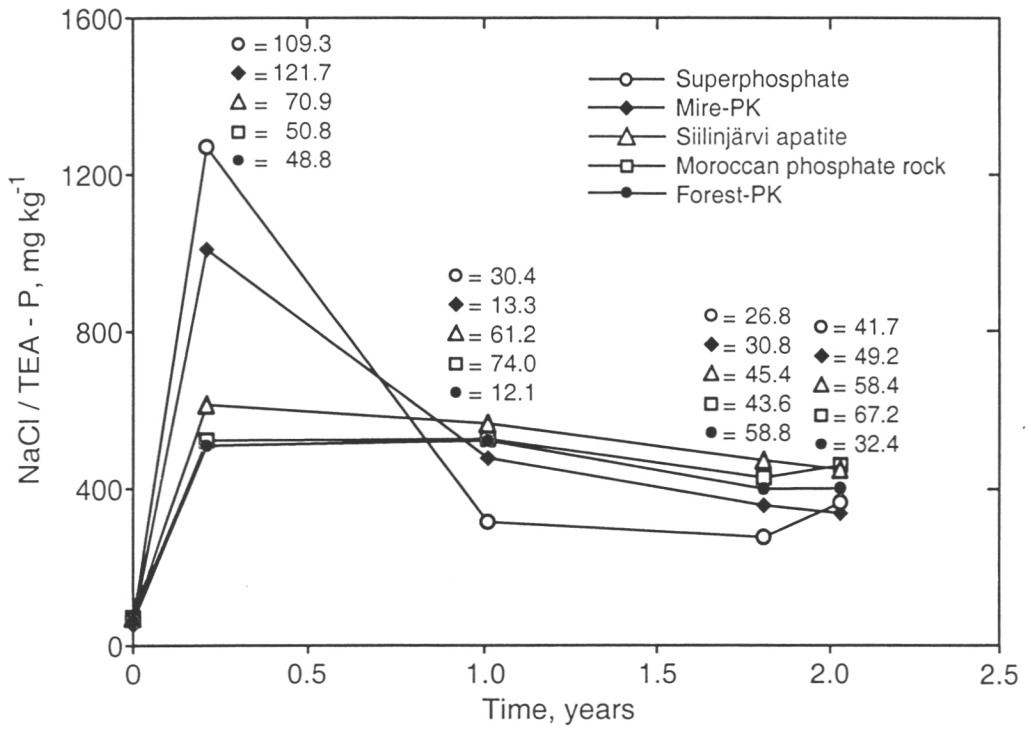


Fig. 1.

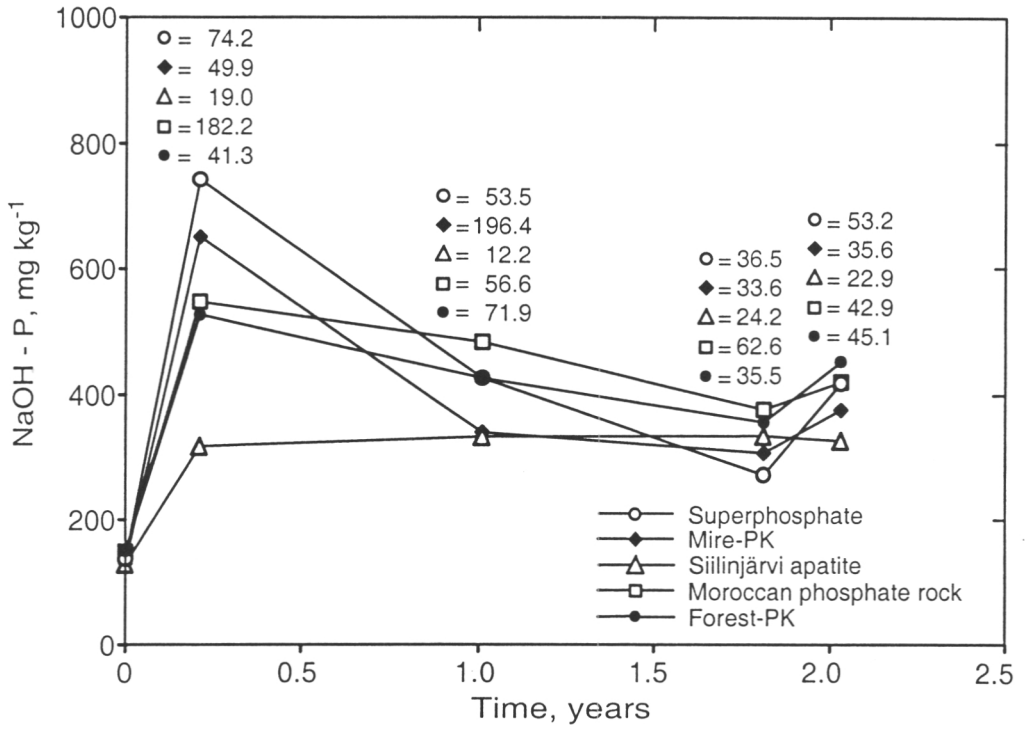


Fig. 2.

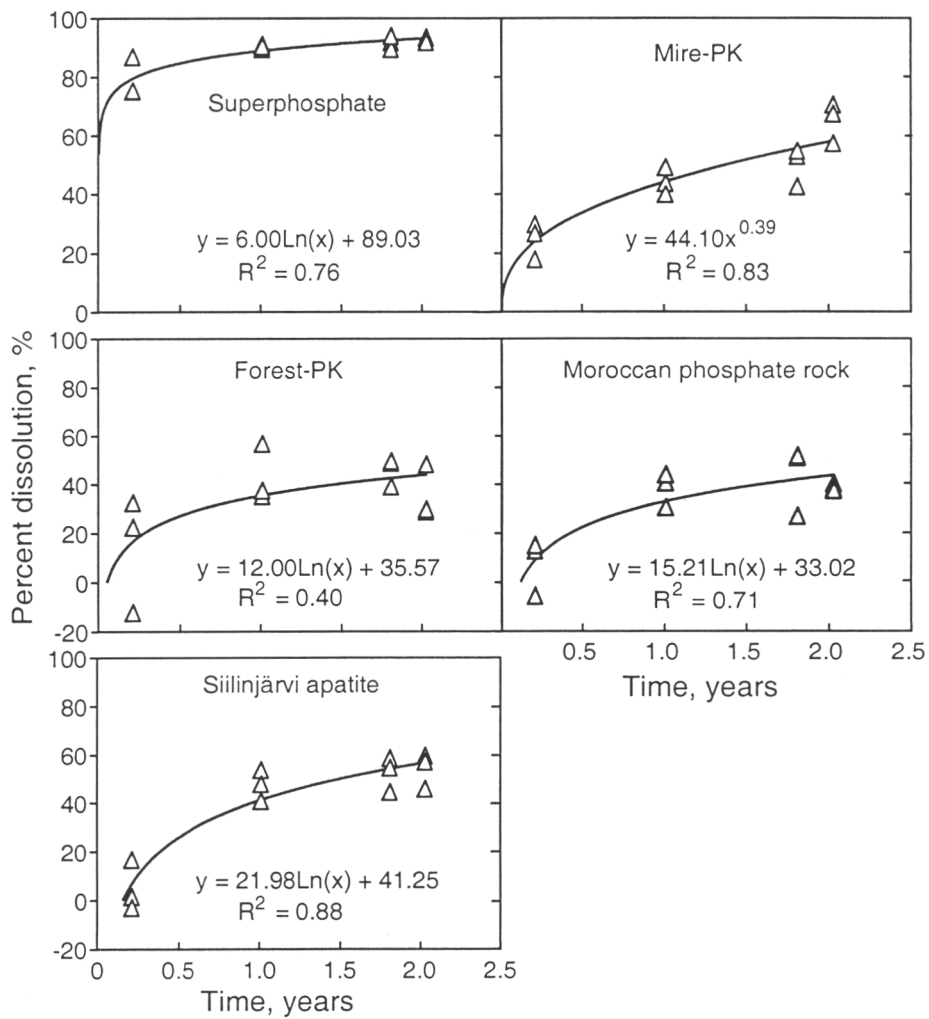


Fig. 3.

Dry Mass and the Amounts of Nutrients in Understorey Vegetation before and after Fertilization on a Drained Pine Bog

Leena Finér and Mika Nieminen

Finér, L. & Nieminen, M. 1997. Dry mass and the amounts of nutrients in understorey vegetation before and after fertilization on a drained pine bog. *Silva Fennica* 31(4): 391–400.

Dry mass and nutrient (N, P, K, Ca, Mg, B) contents of field layer vegetation and a combination of bottom layer vegetation and litter (referred to as bottom/litter layer in the text) were studied one year before and three years after fertilization (NPK and PK) on a drained low-shrub pine bog in eastern Finland. The results of an earlier study on the tree layer were combined with those of this study in order to estimate the changes caused by fertilization in the total plant biomass and litter. Before fertilization the average dry mass of the field and bottom/litter layers was 8400 kg ha⁻¹ and 7650 kg ha⁻¹, respectively. The above-ground parts accounted for 25 % of the total field layer biomass. The dry mass of the field and bottom/litter layers together was < 20 % of the dry mass accumulated in the total plant biomass and litter. The corresponding figures for N, P, K, Ca, Mg and B were 44 %, 38 %, 30 %, 38 %, 31 % and 17 %, respectively. Fertilization did not significantly affect the dry mass of either the field layer vegetation or the bottom/litter layer. 33 % of the applied P was accumulated in the total plant biomass and litter on the PK-fertilized plots, and 25 % on the NPK-fertilized plots. For the other elements, the proportions on the PK-fertilized plots were K 31 %, Ca 6 %, Mg 11 % and B 13 %. On the NPK-fertilized plots, the corresponding figures were N 62 %, K 32 %, Ca 6 %, Mg 9 % and B 13 %. Except for B and K, the accumulation of fertilizer nutrients in the understorey vegetation and litter was of the same magnitude or greater than the uptake by the tree layer.

Keywords biomass, litter, peatland, root systems, Scots pine

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1 Introduction

The understorey vegetation and litter layer account for a considerable proportion of the total nutrient storage in forested ombrotrophic peatlands (Haveraaen 1967, Paavilainen 1980, Brække 1988). Consequently, the processes which bind and/or release nutrients in these layers contribute significantly to the overall nutrient cycling in such ecosystems (Paavilainen 1980, Brække 1988). However, the proportion of nutrients bound by the understorey vegetation and litter layer varies according to the structure and density of the tree layer. When the tree layer reach a certain density, the shrub, field and moss layers are shaded out and the litter layer builds up (Reinikainen et al. 1984, Brække 1988). Thus, nutrient cycling becomes gradually more and more dominated by the tree layer growing on the site.

Scots pine stands usually respond to fertilization on drained ombrotrophic bogs (e. g. Meshechok 1968, Brække 1979, 1983, Paavilainen 1979). The composition of the understorey vegetation is also affected, i.e. some species suffer while others are better able to compete and expand due to the change in nutrient availability (Heikurainen and Laine 1976, Finér and Brække 1991). Increased total biomasses and nutrient concentrations of the above-ground parts of field layer species have been reported (Haveraaen 1967, Päivänen 1970, Vasander 1982), while the biomass of the moss layer decreases during the first years after fertilization (Vasander 1982, Jäppinen and Hotanen 1990, Vasander et al. 1993).

Several studies have been carried out on the dry mass and the amounts of nutrients in different vegetation layers on drained and fertilized peatlands (e.g. Haaveraen 1967, Paavilainen 1980, Brække 1988, Finér 1991a). However, only one study was found about the accumulation of fertilizer nutrients in the total plant biomass (including tree, field and bottom layers and root systems) (Vasander 1981). These results are important for achieving efficient and economical use of fertilizers, and for assessing the risk of nutrients leaching into water bodies. Information about the rates of accumulation can also be used for modelling purposes.

The aim of the study was to estimate the ef-

fects of PK and NPK fertilization on the dry mass and nutrient accumulation in 1) field layer vegetation, 2) bottom/litter layer, and 3) total plant biomass and litter on a drained ombrotrophic pine bog in eastern Finland. In order to determine the effects of fertilization on the total plant biomass and litter, the results of an earlier study (Finér 1991a) from the same site were used as an estimate of the fertilizer-induced changes in tree layer.

2 Material and Methods

2.1 Site Description and Experimental Design

The study site was located in eastern Finland (62°14'N; 29°50'E, 81 m a.s.l.). The peat layer was > 1 m thick and consisted of *Sphagnum* peat with remnants of wood and *Carex* species below the 20 cm surface peat layer. The chemical properties of the peat have been presented by Brække and Finér (1991). A naturally regenerated Scots pine (*Pinus sylvestris* L.) stand, with an average volume of 81 m³ ha⁻¹ in 1984, was growing on the site. According to the peatland site type classification used in Finland (Heikurainen and Pakarinen 1982), the site was a low-shrub pine bog. A detailed description of the vegetation is presented by Finér and Brække (1991). The site was drained in 1967 with a 50 m ditch spacing. The climatic data and fluctuation in the water table during 1984–1987 were reported by Finér (1991b).

A 3 × 3 Latin square design with a 1500 m² plot size was used. The treatments were: unfertilized (0), fertilized with PK(MgB), and with NPK(MgB). The amounts of the elements (kg ha⁻¹) applied were: N 150, Ca 135, P 53, K 100, Cl 95, Mg 25, S 28 and B 2.4. The fertilizers were applied in spring 1985 as ammonium nitrate, Moroccan phosphate rock, potassium chloride, magnesium sulphate, and sodium borate.

2.2 Field Work

Sampling was carried out twice: prior to fertili-

zation during 12.–27.9.1984 and after fertilization during 18.8.–3.9.1987. The above-ground parts of the understorey vegetation were harvested from 20 systematically located quadrates (0.25 m²) on each plot. The understorey vegetation was divided into bush, field and bottom/litter layers. Zero level for sampling of all layers was taken as the lower level of the living moss layer. The bush layer consisted of trees (*Pinus sylvestris* L., *Picea abies* (L.) Karsten, *Betula pubescens* Ehrh.) with height > 0.5 m and breast height diameter < 2.5 cm. However, the bush layer was very sparse and even missing from several of the plots. It was therefore excluded from the study. The sampled field layer consisted of the above-ground parts of dwarf shrubs, sedge-like species, juvenile trees (height < 0.5 m) and herbs. The coverage of the field layer was 42 % prior to fertilization in 1984 (Finér and Brække 1991). The bog dwarf shrubs (*Betula nana* L., *Ledum palustre* L., *Calluna vulgaris* L. Hull, *Chamaedaphne calyculata* L. Moench, *Vaccinium uliginosum* L.) and the forest dwarf shrubs (*Vaccinium myrtillus* L., *Vaccinium vitis-idaea* L.) both had a coverage of 19 %. *Eriophorum vaginatum* L. and *Carex globularis* L., the only sedge-like species, had a total coverage of 3 % in the field layer. The total coverage of the field layer was not affected by fertilization (Finér and Brække 1991). *Dryopteris* spp. and *Epilobium* spp. became established after fertilization, but occurred only sporadically.

The bottom layer consisted of bryophytes and lichens. Their total coverage before fertilization was 90 %, of which the coverage of *Sphagnum* species (*Sphagnum angustifolium* (Russow) C. Jens, *Sphagnum russowii* Warnst., *Sphagnum nemoreum* Scop.) was 31 % and that of *Pleurozium schreberi* (Brid.) Mitt. 52 % (Finér and Brække 1991). Fertilization did not affect the total coverage of the bottom layer. The *Sphagnum* species suffered from fertilization and were partly replaced by *Pleurozium schreberi*. A detailed description of the vegetation composition in the field and bottom layers before and after fertilization is presented by Finér and Brække (1991).

In the early stages of the field work it was evident that the accurate separation of the living bottom layer vegetation from the litter accumu-

lated on and between living bryophytes was technically very difficult. Thus, a composite sample including both the living bottom layer vegetation and all the litter (tree litter, field layer vegetation litter and bottom layer vegetation litter) that had accumulated in it was collected.

After collecting the above-ground parts of the understorey vegetation and the litter, a square peat core (24.7 cm²) was taken down to a depth of 40 cm in the middle of each vegetation harvesting quadrate. The living roots, rhizomes and buried stems (diameter ≤ 10 mm) of the field layer vegetation were extracted by hand from each subsample. The changes in the biomass of the field layer roots after fertilization have already been presented by Finér (1991b).

The changes in the dry mass and nutrient contents of the tree layer were presented by Finér (1991a). These results were combined with our data to calculate the changes in the total plant biomass and litter.

2.3 Laboratory Analyses and Calculations

All the samples were dried to constant mass at 60 °C. Subsamples were taken for dry mass determination at 105 °C. The samples were homogenized in a stainless steel mill (sieve mesh diameter 2 mm). Total N was determined by the Kjeldahl method, K, Ca and Mg by atomic absorption spectrophotometry after HCl digestion, P spectrophotometrically by the molybdate-hydrazine method, and B by the azomethine method (Halonen et al. 1983).

The change from 1984 to 1987 (i.e. the difference between three years after fertilization and prior to fertilization) was chosen as the parameter for determining the effect of fertilization on dry mass and nutrient accumulation in different vegetation compartments. Analysis of variance and Tukey's test were used to test whether the changes in dry mass and the amounts of nutrients from 1984 to 1987 differed between the treatments (0, PK, NPK). The statistical tests were done using the BMDP (1990) software package.

3 Results

3.1 Understorey Vegetation and Litter

Before fertilization the average above-ground dry mass of the field layer was 2100 kg ha⁻¹, and that of the bottom/litter layer 7650 kg ha⁻¹ (Tables 1 and 2). Neither the dry mass of the above-ground field layer nor the bottom/litter layer was affected by fertilization (Fig. 1).

Before fertilization the average amount of N in the above-ground field layer, field layer roots and bottom/litter layer was 16.8 kg ha⁻¹, 42.8 kg ha⁻¹ and 78.2 kg ha⁻¹, respectively (Tables 1, 2 and 3). Fertilization did not significantly affect the N contents of different layers (Fig. 2). Most of the understorey vegetation P was found in the bottom/litter layer, i.e. 6.4 kg ha⁻¹. The corresponding figure for the above-ground field layer was 1.6 kg ha⁻¹, and that for the field layer roots 2.6 kg ha⁻¹. Fertilization increased the amounts of P only in the bottom/litter layer on the PK-fertilized plots. The average amount of K prior to fertilization in the above-ground field layer, field layer root systems and bottom/litter layer was 5.0 kg ha⁻¹, 4.1 kg ha⁻¹ and 16.0 kg ha⁻¹, respectively. Fertilization did not increase the amounts of K in different layers.

The average amount of Ca in the above-ground field layer was 9.8 kg ha⁻¹ before fertilization. The corresponding figure for the field layer root systems was 9.2 kg ha⁻¹, and for the bottom/litter layer, 35.7 kg ha⁻¹. Fertilization increased the amounts of Ca only in the bottom/litter layer on the PK-

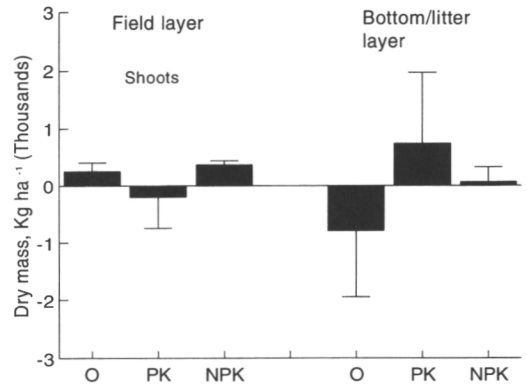


Fig. 1. Changes from 1984 to 1987 in the amount of dry mass stored in the above-ground field layer vegetation and the bottom/litter layer. The changes do not differ statistically significantly between treatments. Standard deviations are indicated by lines in the bars.

fertilized plots. The average amount of Mg in the above-ground field layer, field layer root systems and bottom/litter layer was 2.2 kg ha⁻¹, 2.2 kg ha⁻¹ and 5.7 kg ha⁻¹, respectively. There were no significant changes in the amounts of Mg after fertilization. The average amount of B in the above-ground field layer prior to fertilization was 0.021 kg ha⁻¹. The corresponding figure for the field layer root systems was 0.032 kg ha⁻¹, and for the bottom/litter layer 0.042 kg ha⁻¹. The bottom/litter layer B contents increased significantly after fertilization both on the PK- and NPK-fertilized plots.

Table 1. Dry mass and the amounts of nutrients stored in the above-ground field layer vegetation in the control (= 0) plots and the PK and NPK fertilized plots prior to fertilization in 1984. Standard deviations in parentheses.

	0	PK	NPK
Dry mass, kg ha ⁻¹	2291 (149)	2140 (222)	1874 (41)
N, kg ha ⁻¹	18.2 (0.8)	16.8 (1.4)	15.3 (0.9)
P, kg ha ⁻¹	1.7 (0.1)	1.5 (0.3)	1.5 (0.0)
K, kg ha ⁻¹	5.1 (0.3)	5.0 (0.9)	4.8 (0.4)
Ca, kg ha ⁻¹	10.3 (1.1)	9.4 (1.3)	9.8 (0.9)
Mg, kg ha ⁻¹	2.3 (0.1)	2.1 (0.3)	2.2 (0.2)
B, g ha ⁻¹	23.2 (1.1)	20.7 (4.4)	20.1 (4.1)

Table 2. Dry mass and the amounts of nutrients stored in the bottom/litter layer in the control (= 0) plots and PK and NPK fertilized plots prior to fertilization in 1984. Standard deviations in parentheses.

	0	PK	NPK
Dry mass, kg ha ⁻¹	7934 (700)	7805 (813)	7213 (1252)
N, kg ha ⁻¹	81.8 (9.5)	79.3 (9.1)	73.6 (13.2)
P, kg ha ⁻¹	6.8 (0.3)	6.3 (0.4)	6.1 (0.9)
K, kg ha ⁻¹	16.4 (0.9)	16.2 (1.9)	15.5 (3.0)
Ca, kg ha ⁻¹	38.9 (2.2)	34.0 (2.7)	34.1 (2.0)
Mg, kg ha ⁻¹	6.2 (0.6)	5.4 (0.5)	5.4 (0.5)
B, g ha ⁻¹	47.8 (5.7)	36.9 (1.2)	41.5 (5.7)

Table 3. Amounts of nutrients stored in the field layer roots in the control (= 0) plots and PK and NPK fertilized plots prior to fertilization in 1984. Standard deviations in parentheses.

	0	PK	NPK
N, kg ha ⁻¹	48.6 (6.4)	34.3 (4.6)	45.5 (3.2)
P, kg ha ⁻¹	2.7 (0.2)	2.2 (0.4)	2.9 (0.1)
K, kg ha ⁻¹	4.6 (0.2)	3.4 (0.7)	4.3 (0.1)
Ca, kg ha ⁻¹	9.7 (2.2)	7.2 (1.3)	10.8 (0.3)
Mg, kg ha ⁻¹	2.3 (0.5)	1.7 (0.6)	2.5 (0.4)
B, g ha ⁻¹	32.0 (7.1)	27.1 (3.3)	36.3 (8.2)

3.2 Total Plant Biomass

The field and the bottom/litter layers together accounted for < 20 % of the dry mass accumulated in the total plant biomass and litter (Fig. 3). The proportion of B (17 %) in the field and bottom/litter layers was also small, whereas the proportions of the other nutrients were greater. More than 40 % of N, 38 % of P, 30 % K, 38 % of Ca and 31 % of Mg was found in the field and bottom/litter layers.

Neither the dry mass of the tree layer nor the combination of the field and bottom/litter layers was significantly affected by fertilization (Table 4). Nitrogen accumulation in total plant biomass and litter increased by 46.2 kg ha⁻¹ on the PK-fertilized plots and by 93.7 kg ha⁻¹ on the NPK-fertilized plots. This increase was almost evenly distributed between the tree biomass and under-

storey vegetation and litter. The total fertilizer-induced increase in the amount of P was 17.3 kg ha⁻¹ on the PK-fertilized plots and 13.3 kg ha⁻¹ on the NPK-fertilized plots. Most of this increase (65 % on the PK fertilized plots and 59 % on the NPK fertilized plots) had occurred in the field and bottom/litter layers. The amount of K in the total plant biomass and litter increased by 32 kg ha⁻¹ on both the PK- and the NPK-fertilized plots after fertilization. A high proportion of the K (87 % on the PK-fertilized plots and 79 % on the NPK fertilized plots) had accumulated in the tree layer.

Fertilization decreased the amount of Ca in the tree layer. However, the amounts of Ca in the field and bottom/litter layers increased significantly and the change in the total Ca accumulation was thus positive on both the PK- (7.9 kg ha⁻¹) and NPK-fertilized (8.7 kg ha⁻¹) plots. Fer-

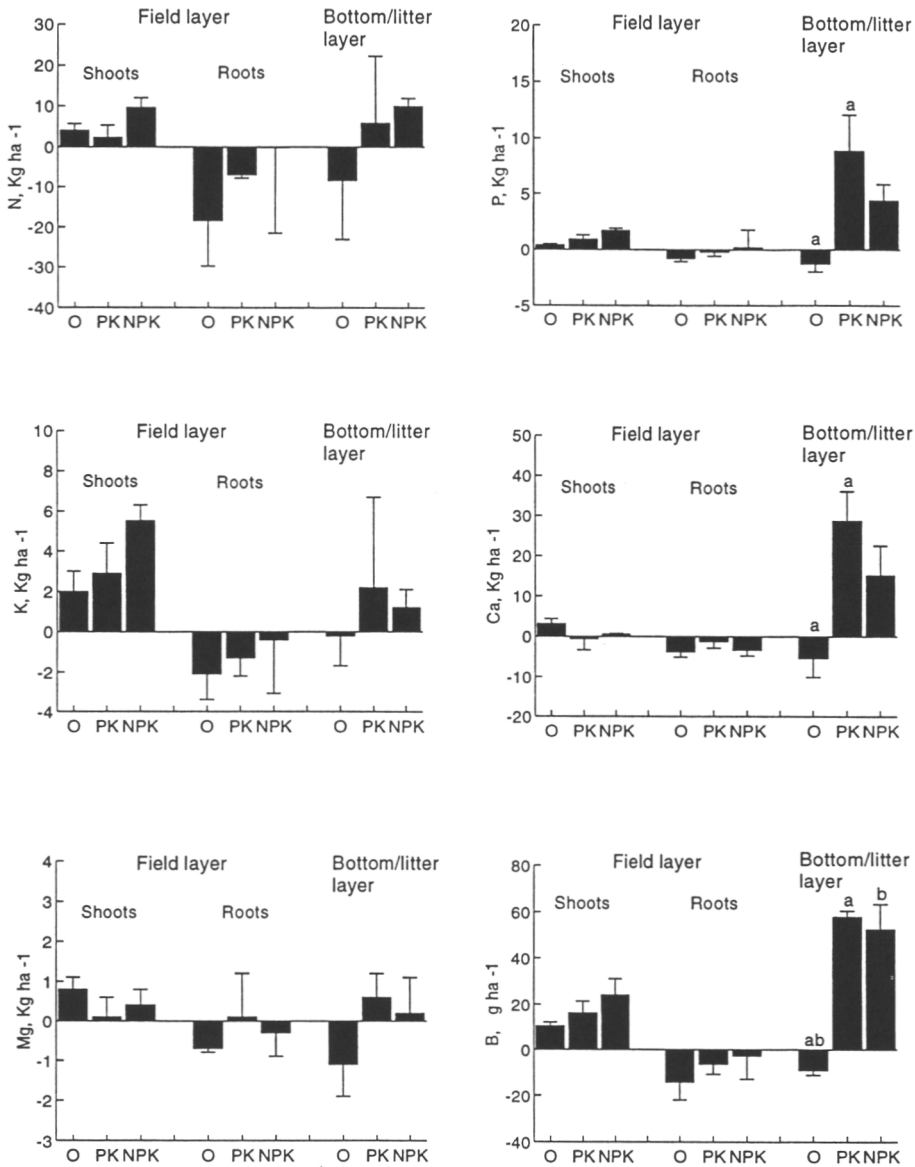


Fig. 2. Changes from 1984 to 1987 in the amounts of nutrients stored in the above-ground field layer vegetation, field layer roots and the bottom/litter layer. Standard deviations are indicated by lines in the bars. Values marked by the same letter differ statistically significantly ($p < 0.05$) from each other.

tilization did not significantly affect the amounts of Mg in either the tree layer or the field and bottom/litter layers. More B was accumulated in the tree layer than in the understorey vegetation and litter. More than 70 % of the total fertilized-

induced accumulation of B (0.30 kg ha^{-1} on the PK-fertilized plots, 0.32 kg ha^{-1} on the NPK-fertilized plots) occurred in the tree layer.

The total increase in the stores of P caused by fertilization (the change in the control plots is

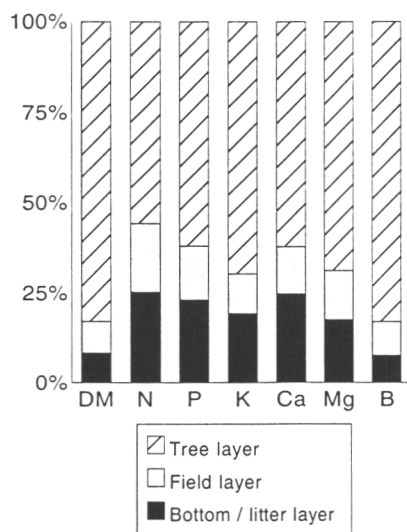


Fig. 3. Average percentual distribution of dry mass and nutrients in the tree, field and bottom/litter layers prior to fertilization in 1984.

accounted for as in Table 4) was 33 % of the applied P on the PK-fertilized plots. For the other elements, the percentages on the PK-fertilized plots were K 31, Ca 6, and B 13. On the NPK-fertilized plots, the corresponding figures were N 62 %, P 25 %, K 32 %, Ca 6 %, and B 13 %.

4 Discussion

4.1 Dry Mass

The dry mass of the above-ground field layer (2100 kg ha⁻¹) was within the range reported for drained mires in Fennoscandia (Tamm 1954, Paavilainen 1980, Vasander 1987, Brække 1988, Laiho 1996). The average root biomass of the field layer prior to fertilization was 6300 kg ha⁻¹ on our study site (Finér 1991b). This was greater than that reported by Paavilainen (1980) for a drained low-shrub pine bog and by Laiho and Finér (1996) for tall-sedge pine fens in Finland, but almost similar to that presented by Håland and Brække (1989) for a pristine bog in Norway. Only 25 % of the total field layer biomass was in the above-ground parts. Our results are thus in

Table 4. Fertilizer-induced change in dry mass and nutrient content (kg ha⁻¹) of the combined field layer vegetation and bottom/litter layer and tree layer during the study period (from 1984 to 1987). Fertilizer-induced changes have been calculated by either adding the decrease on the control plots from 1984 to 1987 to the change on the fertilized plots or subtracting the increase on the control plots from the change on the fertilized plots. Fertilizer-induced changes in the field and bottom/litter layers are based on this study and those in the tree layer on Finér's (1991b) study at the same site. The tree layer includes the following compartments: cones, needles, living branches, dead branches, stembark, stemwood, stump and coarse roots, and small and fine (Ø 10 mm) roots. NS indicates that the change from 1984 to 1987 does not differ statistically significantly ($p > 0.05$) between treatments (0, PK, NPK) according to the analysis of variance.

		Trees	Field and bottom/litter layers
Dry mass	PK	+711	+1923
	NPK	+1377	+1859
	NS	NS	NS
N	PK	+22.7	+23.5
	NPK	+51.9	+41.8
P	PK	+6.0	+11.3
	NPK	+5.4	+7.9
K	PK	+27.3	+4.1
	NPK	+25.1	+6.7
			NS
Ca	PK	-18.9	+26.8
	NPK	-9.7	+18.4
Mg	PK	+0.82	+1.83
	NPK	+0.86	+1.32
	NS	NS	NS
B	PK	+0.22	+0.08
	NPK	+0.23	+0.09

accordance with previous ones showing that most of the dry mass of the field layer vegetation is located in the root systems on drained bogs (Paavilainen 1980, Wallén 1986).

The dry mass of the bottom/litter layer was

only half of that on an old drained oligotrophic pine bog studied by Brække (1988) in southern Norway. However, Jäppinen and Hotanen (1990) reported a lower biomass for the bottom layer vegetation on a drained herb-rich pine mire and spruce mire, as well as Vasander (1982) for a drained ombrotrophic bog and Laiho (1996) for drained tall-sedge pine fens. These differences probably result from differences in sampling. On Brække's (1988) site the living mosses had almost disappeared due to shading by the trees, and mainly tree litter that had accumulated on the soil surface was sampled. Jäppinen and Hotanen (1990), Vasander (1982) and Laiho (1996) sampled only living mosses, not litter.

The dry mass of the above-ground field layer did not respond to fertilization. These results are contradictory to those from poorly stocked raised bogs, where NPK-fertilization increased the above-ground dry mass of the field layer (Vasander 1982, Vasander et al. 1993). Tamm (1954) and Päivänen (1970) also reported a positive field layer response to fertilization on open mires. This positive response of field layer vegetation to fertilization is, however, probably a short-term phenomenon, since the field layer species are eventually shaded out due to the increased growth and consequent shading of the tree layer (Brække 1988, Laine et al. 1995).

The root biomass of the field layer decreased from 1984 to 1987 in all treatments (Finér 1991b). Finér (1991b) attributed this to the exceptionally cold winter in 1986–1987, which had probably damaged the living roots. Compared with the control plots, the decrease in root biomass was lower on the fertilized plots. This was interpreted to indicate a positive effect of fertilization on the root biomass (Finér 1991b).

The dry mass of the bottom/litter layer was not affected by fertilization. This may at first seem to be contradictory to the observations indicating that bryophytes suffer from direct contact with high doses of nutrients, especially those comprising readily soluble nitrogen and potassium (Jäppinen and Hotanen 1990, Finér and Brække 1991, Dirkse and Martakis 1992, Vasander et al. 1993). However, *Pleurozium schreberi* was the most common bryophyte on our site and it is known that fertilization has a more destructive effect on peat mosses than on forest

mosses (Heikurainen and Laine 1976, Jäppinen and Hotanen 1990, Finér and Brække 1991, Vasander et al. 1993). Because the bottom layer vegetation and litter were included in the same sample, the dry mass of the bottom layer vegetation may have decreased as in the previously mentioned studies, if the dry mass of the litter had increased. However, this was probably not the case, since the dry mass of the tree litterfall was not affected by fertilization on our study site (Finér 1991a).

4.2 Nutrient Content

The amounts of nutrients in the above- and below-ground parts of the field layer vegetation were inside the range reported for ombrotrophic pine bogs by Paavilainen (1980), Vasander (1981), Håland and Brække (1989) and Brække and Håland (1990). However, they were substantially higher than those presented by Brække (1988) for a drained and fertilized oligotrophic pine bog, but of the same magnitude or lower than those reported by Brække for only a drained bog. The distribution of nutrients between the root systems and the above-ground parts of the field layer differed from that of the biomass. While almost 70 % of the total field layer dry mass was in the root systems, only N was clearly more abundant in the roots than in the above-ground parts. These results indicate that the below-ground parts of field layer species accumulate relatively more carbon than nutrients. The amounts of nutrients in the bottom/litter layer were generally lower in our study than those reported by Brække (1988).

Päivänen (1970) studied the changes in the nutrient contents of the above-ground parts of the field layer during the first three years after fertilization of an open low-sedge bog. He found that 36 kg ha⁻¹ more N (36 % of applied N), 3.1 kg ha⁻¹ more P (7 % of applied P) and 16 kg ha⁻¹ more K (19 % of applied K) were fixed in the field layer on the fertilized plots. Haveraaen (1967) studied nutrient amounts in the above-ground field layer biomass of an afforested soligenous mire four years after fertilization. He found that fixation by the field layer accounted for 13 % of the applied 145 kg K ha⁻¹ and 13 %

of the applied 50 kg P ha⁻¹. The corresponding percentages for 72.5 kg K ha⁻¹ and 25 kg P ha⁻¹ were 11 and 14. These figures are high compared to those found in this study. Because of the dense tree layer, light was probably more of a limiting growth factor for the field layer species than the deficiency of nutrients on our site.

According to Finér (1991a), the amounts of nutrients in needle or other tree litter were not significantly influenced by fertilization on our study site. Thus, the fertilizer-induced changes in the nutrient contents of the bottom/litter layer are probably mainly due to changes in the nutrient contents of bryophytes and lichens, and not to changes in the litter.

The high increase in the Ca contents of bottom/litter layer was opposite to that found in the tree and field layers, where Ca accumulation decreased after fertilization. There were also no changes in the Ca contents of needle or other tree litter after fertilization (Finér 1991a). The dissolution rate of Ca in Moroccan rock phosphate is probably slow. Thus, the bottom/litter layer samples probably still contained residual unreactive rock phosphate at the time of sampling. The solubility of phosphorus in rock phosphate is also slow (Yli-Halla and Lumme 1987). The high increase in P amounts in the bottom/litter layer after fertilization could thus partly result from the same reason.

The nitrogen amounts in the understorey vegetation and litter did not increase only on the NPK-fertilized plots, but also on the PK-fertilized plots after fertilization (Table 4). This indicates that the PK treatment had a priming effect on peat N mineralization and vegetation N uptake.

Except for B and K, the accumulation of fertilizer nutrients in understorey vegetation and litter was of the same magnitude or greater than the uptake by tree layer. The field and bottom/litter layers are thus of great importance in the biogeochemical nutrient cycle of ombrotrophic pine bogs.

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IV

Phosphorus Adsorption by Peat from Drained Mires in Southern Finland

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The phosphorus adsorption capacity of 20 peat soils and those soil properties likely to influence it (Al, Fe, Ca, Mg, pH, ash content) were studied. Phosphorus adsorption was correlated only weakly to the site type classification of peatlands. However, the P adsorption was strongly correlated with the concentration of Fe in the peat. Thus, soil chemical analysis should be used to support site type classification in order to assess the effectiveness of peatlands to adsorb P. When expressed on a volume basis, the P adsorption capacity varied from 7 kg ha⁻¹ to 673 kg ha⁻¹ in the 0–30 cm layer. Compared with the amounts of P used in practical peatland forest fertilization in Finland (40–45 kg ha⁻¹), the P adsorption capacity of several peat soils studied was substantially lower. It was thus concluded that slowly soluble P fertilizers or applications <40–45 kg ha⁻¹ should be used where the P adsorption capacity is low. *Key words:* Adsorption capacity, adsorption isotherm, fertilization, iron, phosphorus.

INTRODUCTION

The area of peatlands in Finland totals about 10 million ha, which corresponds to one-third of the total land area. About 50% of the peatland area has been drained for forestry purposes. For satisfactory tree production, one or more fertilizer applications with P during the rotation is often needed. Several studies on the leaching of applied P from drained peatlands have been done (Karsisto 1970, Särkkä 1970, Karsisto & Ravela 1971, Kenttämies 1981, Nieminen & Ahti 1993). The risk for high leaching rates of applied P is substantial, at least in the most nutrient-poor, acid *Sphagnum* peats. This is related directly to their low Fe and Al content and consequent low P adsorption (Kaila 1959, Rannikko & Hartikainen 1980, Cuttle 1983). Owing to a lack of information about P adsorption capacities, as well as Al and Fe contents, of different kinds of peaty soils in Finland, the actual risk areas cannot be differentiated from those exhibiting high adsorption capacities.

An understanding of the retention of P by peat is important both for assessing the risk for eutrophication of water bodies resulting from the leaching of phosphate from fertilized areas and for achieving efficient and economical use of different P fertilizers on drained peatland forests. Information about the P adsorption capacities of peat soils can also be used for assessing the effectiveness of peatlands to act as P-saturated waste-water filtration systems (Richardson 1985).

In this paper, the adsorption of P by peat from a range of drained peatlands is reported. The peatlands differ from each other with respect to peat chemical and physical properties, as well as with respect to peatland site type. The mechanisms controlling P adsorption were also studied.

MATERIAL AND METHODS

Study sites

Samples from 20 sites were collected from different parts of southern Finland (between latitudes 60°N and 62°N) in the summer of 1994. The basic principle in the selection of individual peatlands was to obtain material representing the most common types of drained peatland sites in Finland (Table 1). Most samples were collected from permanent sample plots established on drained peatlands by the Finnish Forest Research Institute or by the University of Helsinki.

Collection of peat samples

At each site vertical volumetric peat samples (0–15 and 15–30 cm) were taken using a square-section corer (section area 25 cm²) at 5, 10 and 15 m distance from the nearest ditch and combined by layers. Two adjacent samples were taken from each position: the first set for the chemical analyses to be made from moist samples, the second for the bulk density determinations and for chemical analyses from dried sam-

Table 1. Peatland site type, drainage status and site quality index of the sampling areas

Sample	Peatland site type ¹⁾ ^a	Drainage status ^b	Site quality index ^c
1	Eutrophic pine fen	OPF	8.0
2	Herb-rich hardwood-spruce swamp	OPF	10.0
3	Herb-rich sedge birch-pine swamp	OPF	7.0
4	Herb-rich sedge hardwood-spruce swamp	TDP	9.0
5	Herb-rich tall-sedge fen	TDP	6.5
6	Herb-rich sedge hardwood-spruce swamp	RDP	9.0
7	<i>Vaccinium myrtillus</i> spruce swamp	OPF	7.5
8	<i>Vaccinium myrtillus</i> spruce swamp	TDP	7.5
9	Tall-sedge pine swamp	OPF	5.0
10	Tall-sedge pine swamp	TDP	5.0
11	Tall-sedge fen	TDP	5.0
12	<i>Carex globularis</i> pine swamp	OPF	4.5
13	Spruce-pine swamp	TDP	3.5
14	Low-shrub pine bog	OPF	3.0
15	Low-shrub pine bog	TDP	3.0
16	Cottongrass pine bog	TDP	2.5
17	Cottongrass pine bog	TDP	2.5
18	Small-sedge <i>Sphagnum papillosum</i> pine bog	RDP	3.0
19	Ombrotrophic small-sedge bog	TDP	3.0
20	<i>Sphagnum fuscum</i> pine bog-Cottongrass pine bog	TDP	2.5

^a According to Heikurainen & Pakarinen (1982).

^b According to Heikurainen & Pakarinen (1982): "Recently drained peatlands (RDP) are characterized by a vegetation which has changed only slightly from the original virgin phase...No clear response to drainage can be observed in the growth of trees and, as is the case with treeless sites, afforestation is often incomplete."

"Transitional drained peatlands (TDP) exhibit more advanced changes in their ground vegetation. In this instance the tree stand shows a clear response to drainage...Cover of *Sphagnum* mosses usually decreases significantly at this phase, while certain shrubs (e.g.) *Betula nana* increase in abundance..."

"Old peatland forests (OPF) are characterized by a rather stable ground vegetation which clearly differs from that of virgin peatlands, resembling more the vegetation associated with mineral soil forests. The tree stand can be likened to that of ordinary upland forests, showing clearly the effects of silvicultural treatments where performed."

^c Site quality index has been developed to depict the potential post-drainage tree growth afforded by sites of varying soil fertility, pre-drainage tree stand and location with respect to south-north direction in Finland (e.g. Heikurainen 1982). An arbitrary scale of 1-10 has been devised so that the most fertile sites, having a well-developed tree stand prior to drainage, is equal to 10 in southernmost Finland. The values presented here are for southernmost Finland.

ples. Peat samples were taken from a level surface, not from hollows or hummocks. If there was a raw humus layer on the peat surface (Kaunisto & Paavilainen 1988), it was removed prior to sampling. All the samples were stored in a freezer (-18°C).

Laboratory analysis

The analyses were carried out in the Central Laboratory of the Finnish Forest Research Institute. The moist samples were used for determining P adsorption isotherms (Bache & Williams 1971, Richardson 1985; see also Fig. 1). When increasing amounts of P are added to a series of soil suspensions, the P

adsorbed (mg g⁻¹ soil) can be plotted against the equilibrium P concentration. The resulting curve is called a P adsorption isotherm. In this study the adsorption isotherms were determined as described below.

After thawing at room temperature, the peat samples were coarsely shredded and thoroughly mixed. Larger roots (>2 mm in diameter) were removed at the same time. A subsample was then weighed and dried at 105°C to determine the water content. A further subsample of moist peat (equivalent to 1 g dry weight) was added to bottles containing solutions (60 ml) with 0, 0.1, 0.3, 0.5, 0.7, 1, 2, 3, 5, 7, 9, 12, 15,

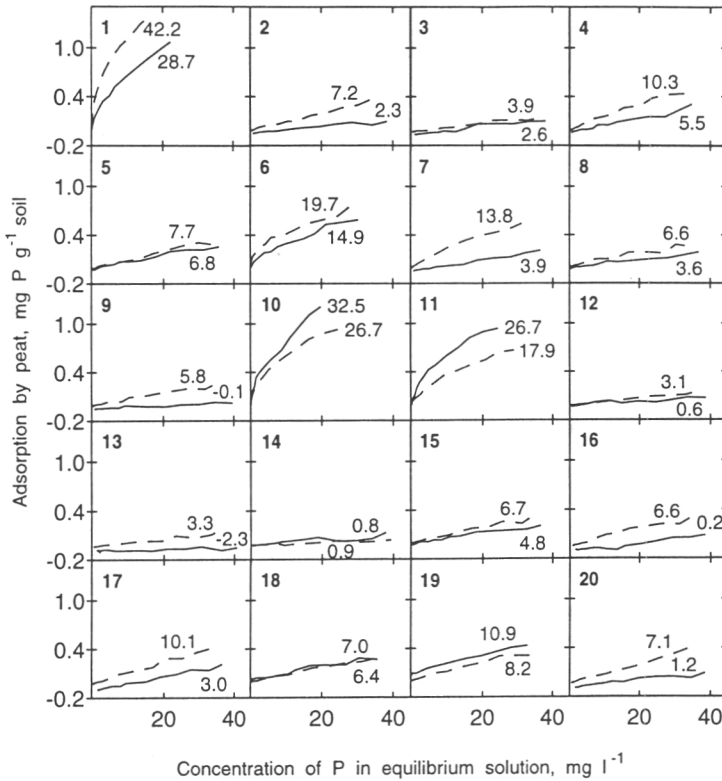


Fig. 1. Phosphorus adsorption isotherms for the 0–15 cm (solid line) and 15–30 cm (broken line) sampling depths. The sample number (see Table 1) is given in the upper left corner of each subfigure. Values for PSI (see text) are also given for each curve.

20, 25, 30, 35 or 40 mg l⁻¹ of P. The bottles were shaken vigorously on a reciprocating shaker for 1 h. The suspensions were then left to stand for 23 h, after which they were shaken again for 10 min. The suspensions were then centrifuged at 4000 r.p.m. for 10 min, passed first through a glass fibre paper and then through a membrane filter. The concentration of P remaining in the filtrate was determined immediately after equilibration by inductively coupled plasma emission spectrometry (ICP/AES, ARL 3580). The amount of P adsorbed was calculated from the difference between the initial amount of P in the solution and that of the filtrate after treatment.

A preliminary study had established that there were no significant differences in adsorption curves made when using the ascorbic acid, the molybdate-hydrazine, the stannous-chloride and the ICP/AES methods to determine phosphorus. For example, the interdependence between the ascorbic acid method and the ICP/AES method in two different data sets was as follows:

$$P_{\text{ascorbic acid}} = 0.9398 \cdot P_{\text{ICP}} + 0.015$$

$$r^2 = 0.999 \quad n = 126$$

$$P_{\text{ascorbic acid}} = 0.9998 \cdot P_{\text{ICP}} + 0.167$$

$$r^2 = 0.998 \quad n = 36$$

The remainder of the moist samples was used for the determination of oxalate soluble Al (Al_{ox}) and Fe (Fe_{ox}). 28.5 ml of 0.05 M oxalic acid was added to 31.5 ml of 0.05 M ammonium oxalate. Moist peat (8 g) was added to a bottle containing 60 ml of this solution. The suspension was then shaken for 2 h, centrifuged at 4000 r.p.m. for 10 min and passed first through a Whatman GF/G filter paper and then through a Schleicher and Schuell Rundfilter (589³). Al_{ox} and Fe_{ox} were determined by ICP/AES, ARL 3580.

The second set of the samples were dried at 70°C and used for total analyses and bulk density determinations. For total analyses, the samples were dry combusted and the ash taken up in HCl acid according to the standard methods used in the Finnish

Forest Research Institute (Halonen et al. 1983). The samples were analysed for Fe (Fe_{tot}), Al (Al_{tot}), Ca (Ca_{tot}) and Mg (Mg_{tot}) by ICP/AES, ARL 3580. Soil pH was measured in deionized water (1:25). Ash content was determined by thermogravimetry at 500°C.

Calculation of P adsorption index (PSI) and P adsorption capacity (PAC)

There is no suitable method for determining maximum adsorption directly (Bache & Williams 1971). For example, when determining P adsorption isotherms, adsorption usually continues to increase with increasing P additions, and a well-defined maximum is not obtained. However, the adsorption data can be treated with a number of adsorption equations and adsorption indices from which adsorption can be calculated. The P adsorption index (PSI), which has frequently been used as an indicator of P adsorption (e.g. Bache & Williams 1971, Cuttle 1983, Richardson 1985, Mozaffari & Sims 1994), was used in this study. The PSI was calculated as: $X/\log C$, where X is the quantity of P adsorbed by the sample ($mg\ P\ (100\ g)^{-1}$ dry weight of peat) and C is the concentration of P in equilibrium solution.

The total P adsorption capacity (PAC) was calculated by multiplying the PSI value by the bulk density of the sample, and by expressing the adsorption as kg P sorbed ha^{-1} .

Table 2. Correlation coefficients between phosphorus adsorption index (PSI) values and site quality index (see Table 1) and some peat properties for the 0–15 cm and 15–30 cm peat layers ($n = 20$)

Significance level: * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$

	PSI	
	0–15 cm	15–30 cm
Site quality index	0.216	0.363
pH	0.486*	0.561**
Ash content	0.413	0.292
Fe_{tot}	0.859***	0.935***
Fe_{ox}	0.901***	0.901***
Al_{tot}	0.197	0.297
Al_{ox}	0.233	0.193
Ca_{tot}	-0.117	0.009
Mg_{tot}	-0.211	-0.049

Simple Pearson correlation analysis was used to examine the dependence of P adsorption on the site quality index and peat chemical properties. In analysis of regression, logarithmic transformations were used to normalize the distribution of variables. The statistical tests were made using the BMDP (1990) software package.

RESULTS

Phosphorus adsorption isotherms and adsorption indices (PSI)

The only eutrophic peatland site included in the study (sample 1) exhibited the highest P adsorption (Fig. 1). The highest PSI value in the upper peat layer was 32.5 (sample 10) and 42.2 in the lower layer (sample 1). The lowest values for the upper and lower layers were -2.3 (sample 13) and 0.9 (sample 14), respectively. High-fertility or intermediate-fertility sites frequently exhibited high adsorption, whereas many low-fertility sites had low adsorption. However, there was no clear relationship between the site quality index and P adsorption (Table 2). It should be noted that several of the samples had very low adsorption values (samples 3, 9, 12, 13 and 14). Even with the highest additions of P, the amounts adsorbed by the peat samples remained negligible.

Peat properties controlling adsorption

In the upper peat layer, Al_{ox} contents varied from 194 to 4017 $mg\ kg^{-1}$, Al_{tot} contents from 315 to 5782 $mg\ kg^{-1}$, Fe_{ox} contents from 424 to 24 696 $mg\ kg^{-1}$, Fe_{tot} contents from 533 to 33 780 $mg\ kg^{-1}$, Ca_{tot} contents from 908 to 11 208 $mg\ kg^{-1}$, Mg_{tot} contents from 143 to 1311 $mg\ kg^{-1}$, ash contents from 0.9 to 32.7%, and pH values from 3.3 to 4.5. In the lower peat layer, the ranges were: Al_{ox} 171–5577 $mg\ kg^{-1}$; Al_{tot} 263–13 573 $mg\ kg^{-1}$; Fe_{ox} 297–28 135 $mg\ kg^{-1}$; Fe_{tot} 315–33 751 $mg\ kg^{-1}$; Ca_{tot} 689–18 870 $mg\ kg^{-1}$; Mg_{tot} 60–1 510 $mg\ kg^{-1}$; ash content 0.8–77.8% and pH 3.6–5.0.

Correlations between PSI and selected chemical properties of the peat likely to influence P adsorption showed that PSI was correlated most strongly to Fe contents (Table 2). Except for Fe and pH, no other statistically significant correlations could be observed.

Total phosphorus adsorption capacity (PAC)

The highest PAC value in the upper peat layer was 200 $kg\ ha^{-1}$ and 569 $kg\ ha^{-1}$ in the lower layer

Table 3. Phosphorus adsorption capacity (PAC) values

Sample ^a	PAC, (kg ha ⁻¹)		
	0–15 cm	15–30 cm	0–30 cm
1	184	263	447
2	15	42	57
3	17	27	44
4	29	81	110
5	43	39	82
6	104	569	673
7	21	99	120
8	16	38	54
9	0	25	25
10	200	173	373
11	161	76	237
12	2	14	16
13	0	25	25
14	3	4	7
15	27	48	75
16	1	31	32
17	8	25	33
18	24	23	47
19	32	23	55
20	3	18	21

^a see Table 1.

(Table 3). The lowest values for the same layers were 0 kg ha⁻¹ and 4 kg ha⁻¹, respectively. The total adsorption capacity of the 0–30 cm peat layer was highest for sample 6 (673 kg ha⁻¹) and lowest for sample 14 (7 kg ha⁻¹).

The large range in PAC values and the dependence of PAC upon the amount of iron in the peat, but not site quality index, are depicted in Figure 2.

DISCUSSION

“Adsorption isotherms or adsorption indices are indicative of phosphorus retention but most probably overestimate the actual maximum adsorption in the field. This is because water movement occurs mainly in the large pores and channels, thus reducing contact with a large portion of the soil matrix” (Richardson 1985). Input–output data from fertilized basin areas is the only method to determine the actual retention of P. However, adsorption isotherms and especially adsorption indices offer a simple, yet adequate, method to study the dependence of P adsorption on the chemical and physical properties of the soil.

Only the P adsorption of the uppermost 0–30 cm peat layer was determined. If the deeper peat layers

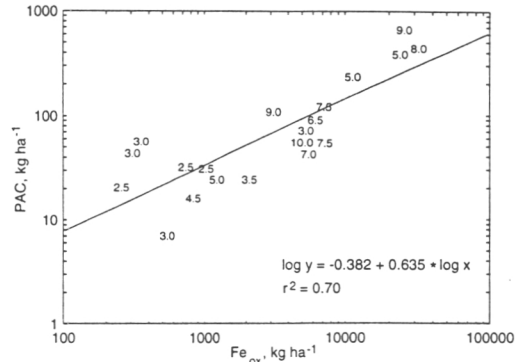


Fig. 2. The relationship between PAC (see text) and the amount of Fe_{ox} in the 0–30 cm peat layer. The samples are identified by their values for the site quality index (Table 2). Logarithmic scales.

exhibit significant P adsorption, the total P adsorption capacity for the site would be underestimated accordingly. However, deeper peat layers are unlikely to exhibit P adsorption because conditions are anaerobic for most of the year. Anaerobiosis inhibits P adsorption due to the reduction and redistribution of Fe (Armstrong 1975).

It was not possible to assess the relationship between PSI or PAC values and actual P adsorption in the field. However, the results of a fertilization experiment (Nieminen & Ahti 1993) performed in one of the sampling areas used in this study (sample 20), which has both low PSI and PAC values (Fig. 1, Table 3), indicated high leaching rates of applied P.

The PSI values in this study ranged from –2.3 to 42.2. Similar values have been reported by both Cuttle (1983) (values ranging from –0.4 to 43.7) and by Lopez-Hernandez & Burnham (1974) (values ranging from 0 to 58.7) for organic soils in Britain. Substantially higher values were reported for freshwater wetlands (including both organic soils and mineral soil wetlands) in North America, where the PSI values ranged from 8 to 163 (Richardson 1985).

There was no clear relationship between the site quality index and P adsorption. Thus, the P retention capacity cannot be evaluated by simply classifying soils on the basis of their vegetation cover. Soil analysis, particularly for Fe, should also be used.

Compared with the amounts of P fertilizer applied to Finnish peatland forests in practice (40–45 kg ha⁻¹), the PAC values (Table 3) for several of the peatlands studied must be regarded as substantially low. As previously mentioned, P adsorption indices

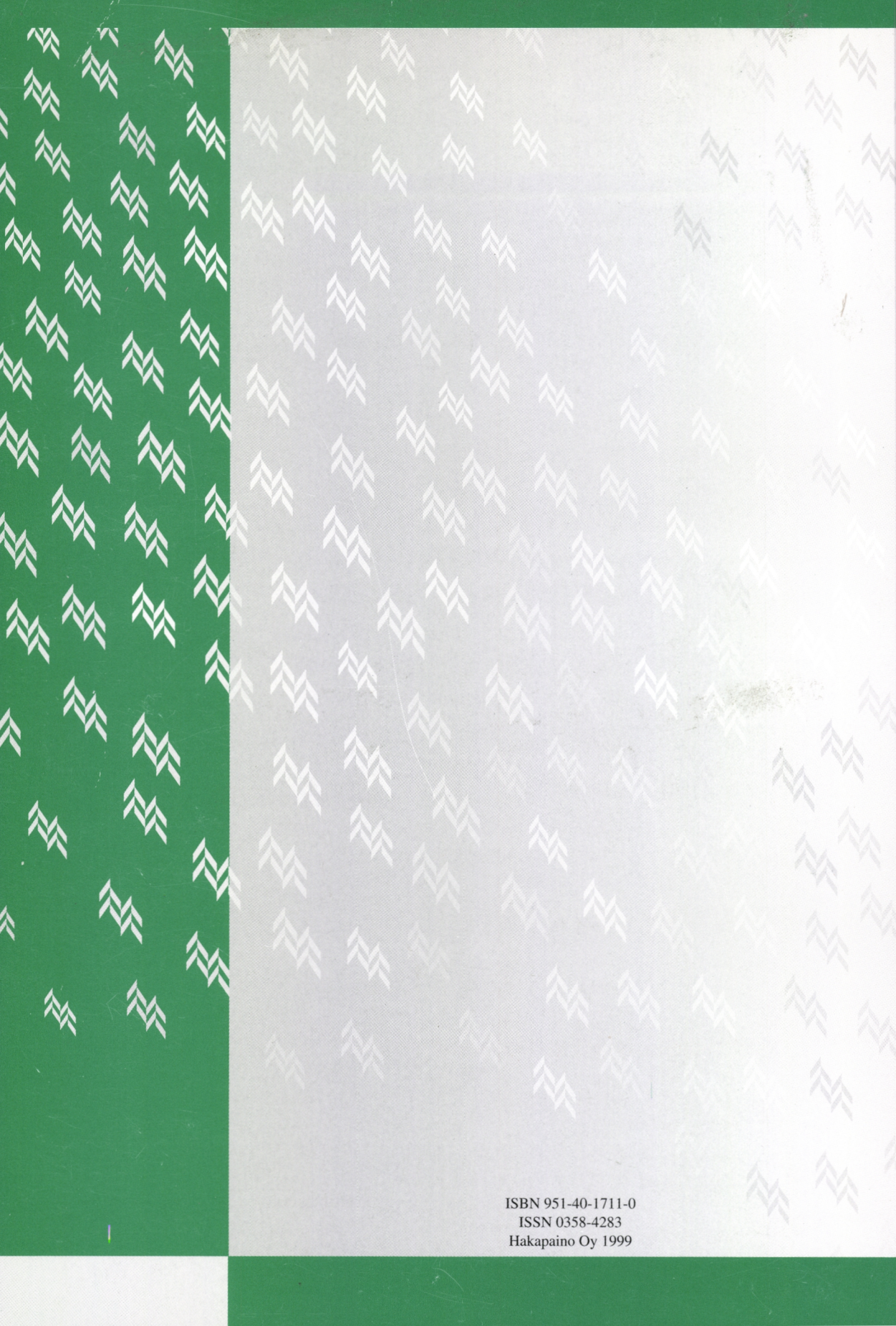
probably overestimate the actual P retention. Thus, those peats exhibiting a PAC value of $\leq 40\text{--}45$ kg ha⁻¹ probably have very little ability to retain dissolved phosphate against leaching. According to Finér (1989), the annual uptake of P from peat varies from 2.5 to 3.4 kg ha⁻¹ in well-developed tree stands on drained peatlands, indicating that uptake by the tree stand is of minor importance in restricting leaching losses. Consequently, where the P adsorption capacity is low, very slowly soluble P fertilizers or applications of less than 40–45 kg ha⁻¹ ought to be used.

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