© Suoseura — Finnish Peatland Society
Helsinki 1997

ISSN 0039-5471
*Suo 48(4): 115–126*

# 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

Mika Nieminen

*Mika Nieminen, The Finnish Forest Research Institute, Vantaa Research Centre, P.O. Box 18, FIN-01301 Vantaa, Finland (email: mika.nieminen@metla.fi)*

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 developing 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 & Mokwunye 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 phosphogypsym, 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, Dahanayake et al. 1995). This should both increase economical 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-

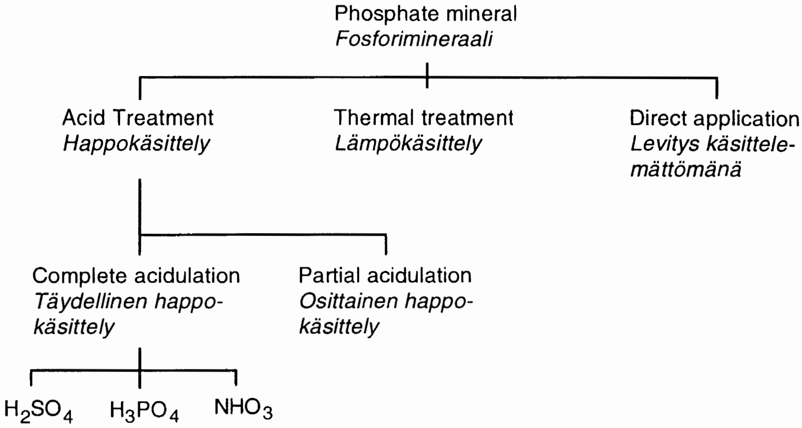


Fig. 1. Phosphate mineral is the primary source of phosphorus fertilizers. Reproduced from Bolan et al. (1993).

*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 manufacture 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.

## FERTLIZER 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 raakafosfaattien kokonaisfosforipitoisuus ja 2% sitruunahappoon liukeneva fosfori. Lähde: Bolan ym. (1993).*

| Phosphate rock<br>*Raakafosfaattilaji* | Origin<br>*Alkuperä* | Total P (%)<br>*Kokonais-P* | Citric P (% of total P)<br>*Sitruunahappoliukoinen P (% kokonais-P:stä)* |
|---|---|---|---|
| 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 |

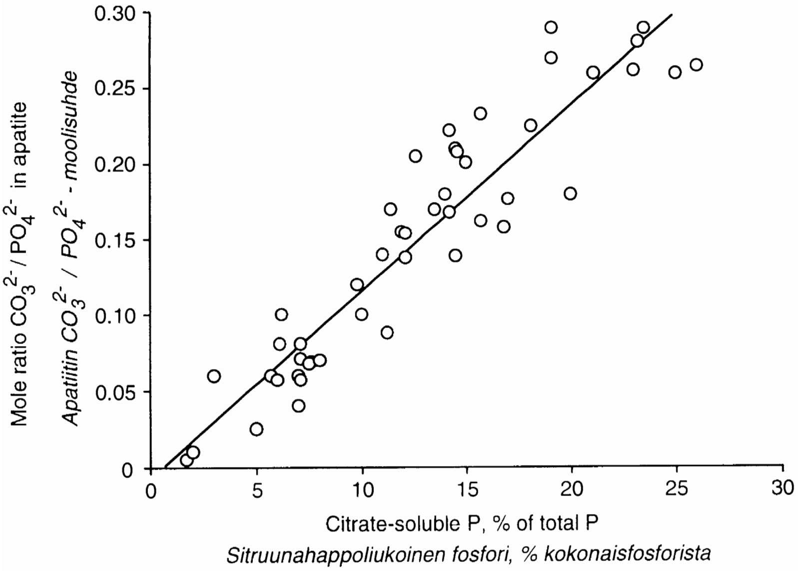


Fig. 2. Relationship between citrate solubility of apatite and its composition as indicated by the $CO_3/PO_4$ mole ratio. Source: Lehr and McClellan (1972).

*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 $CO_3^{2-}/PO_4^{2-}$ 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 peatland 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 adviseable, 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

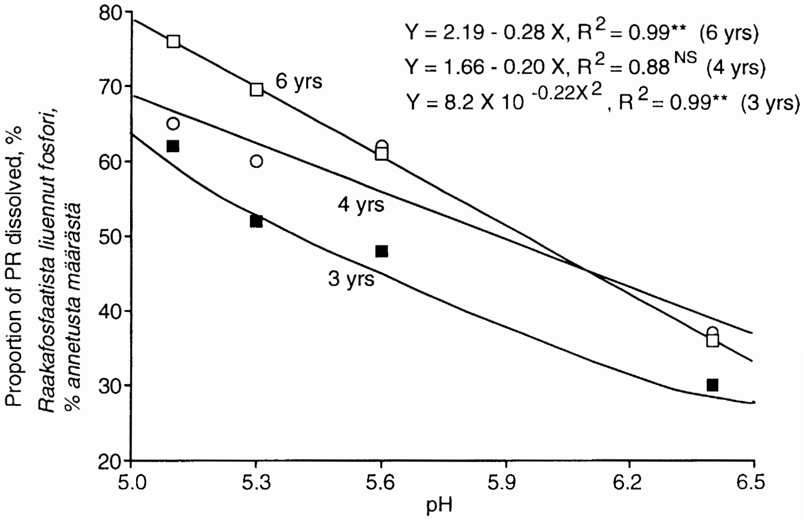


Fig. 3. Effect of soil pH on the proportion of added phosphate rock dissolved 3, 4 and 6 years after application. Source: Rajan et al. (1991).

*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:

$$Ca_{10}(PO_4)_6F_2 + 12H^+ \rightarrow 10Ca^{2+} + 6H_2PO_4^- + 2F^- \quad (1)$$

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 $H_2PO4^-$ 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 (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 (Pätilä & 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.

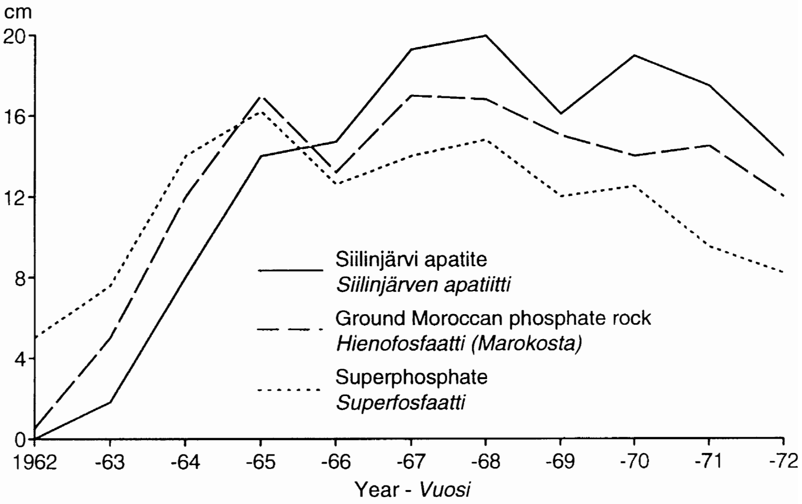
## PLANT RESPONSE TO SLOW-RELEASE P-FERTILIZERS

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 understorey 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 understorey 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, Almberger & 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 Almberger 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-

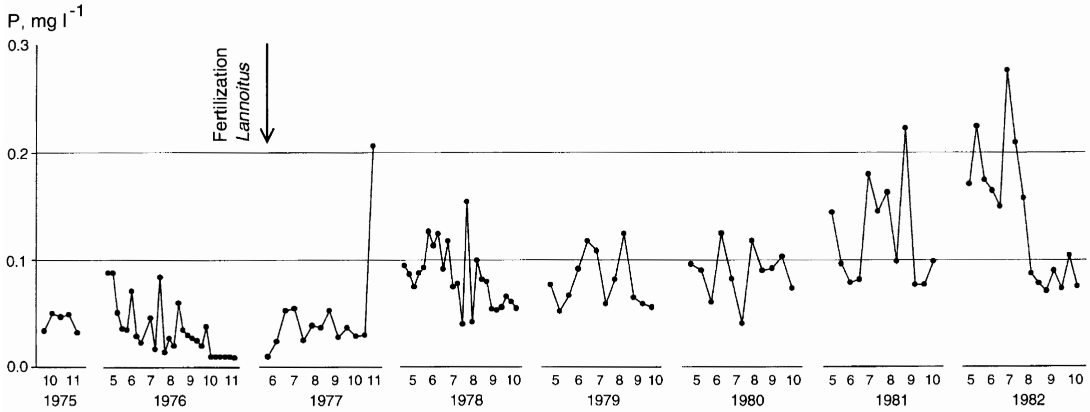


Fig. 5. Phosphorus concentrations of ditch water before (1975 and 1976) and after (1977–1982) fertilization with 500 kg ha$^{-1}$ of a commercial PK-fertilizer, including 8.3% of P as water-insoluble Moroccan phosphate rock. Only 10% of the area was fertilized. The values are the means of those presented 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 raakafosfaattia). 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 $CO_3^{2-}/PO_4^{2-}$ 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.

## ACKNOWLEDGEMENTS

I thank Prof. Seppo Kaunisto, Dr. Erkki Ahti and Dr. Leena Finér for valuable comments on the manuscript and Dr. Michael Starr for revising the English.

## REFERENCES

Ahti, E. 1983. Fertilizer-induced leaching of phosphorus and potassium from peatlands drained for forestry. Communicationes Instituti Forestalis Fenniae 111: 1–20.

Almberger, P. & Salomonsson, L-Å. 1979. Domänverkets gödlingsförsök på torvmarker. Mätningar av fosforutlakning efter gödsling med råfosfat. Sveriges Skogsvårdsförbunds Tidskrift 5–6: 1–7.

Bolan, N. S., Hedley, M. J. & Loganathan, P. 1993. Preparation, forms and properties of controlled-release phosphate fertilizers. Fertilizer Research 35: 13–24.

Bolland, M. D. A. & Gilkes, R. J. 1987. How effective are calciphos and phosphal. Fertilizer Research 12: 229–239.

Bolland, M. D. A. & Gilkes, R. J. 1991. Evaluation of two rock phosphates and a calcined rock phosphate as maintenance fertilizer for crop–pasture rotations in Western Australia. Fertilizer Research 28: 11–24.

Bolland, M. D. A. & Gilkes, R. J. 1995. Long-term residual value of North Carolina and Queensland rock phosphates compared with triple superphosphate. Fertilizer Research 41: 151–158.

Bolland, M. D. A., Clarke, M. F. & Yeates, J. S. 1995. Effectiveness of rock phosphate, coastal superphosphate and single superphosphate for pasture on deep sandy soils. Fertilizer Research 41: 129–143.

Chien, S. H. 1979. Dissolution of phosphate rocks in acid soils as influenced by nitrogen and potassium fertilizers. Soil Science 127: 371–376.

Chien, S. H. 1993. Solubility assessment for fertilizer containing phosphate rock. Fertilizer Research 35: 93–99.

Chien, S. H. & Menon, R. G. 1995. Factors affecting the agronomic effectiveness of phosphate rock for direct application. Fertilizer Reserach 41: 227–234.

Chien, S. H., Clayton, W. R. & McClellan, G. H. 1980. Kinetics of dissolution of phosphate rocks in soils. Soil Science Society of American Journal 44: 260–264.

Chien, S. H., Sale, P. W. G. & Hammond, L. L. 1990. Comparison of the effectiveness of phosphorus fertilizer products. In: Proc. Symposium on Phosphorus Requirements for Sustainable Agriculture in Asia and Oceania, pp. 143–156. International Rice Research Institute, Manila, Philippines.

Cuttle, S. P. 1983. Chemical properties of upland peats influencing the retention of phosphate and potassium ions. Journal of Soil Science 34: 75–82.

Dahanayake, K., Ratnayake, M. P. K. & Sunil, P. A. 1995. Potential of Eppawala Apatite as a directly applied low-cost fertilizer for rice production in Sri Lanka. Fertilizer Research 41: 145–150.

Flach, E. N., Quak, W. & Van Deist, A. 1987. A comparison of rock phosphate-mobilizing capacities of various crop species. Tropical Agriculture (Trinidad) 64: 347–352.

Garbouchev, I. P. 1981. The manufacture and agronomic efficiency of a partially acidulated phosphate rock fertilizer. Soil Science Society of American Journal 45: 970–974.

Gillion, I., Reinhorm, T., Semiat, R. & Hagin, J. 1979. Evaluation of granulated phosphate rock for direct application. In: Seminar on phosphate rock for direct application, pp. 387–394. International Fertilizer Development Centre, Muscle Shoals, Alabama.

Hagin, J. 1985. Partially acidulated phosphate rock – A review. Technion-Israel Institute of Technology, Haifa, Israel. pp. 14–56.

Hagin, J. & Harrison, R. 1993. Phosphate rocks and partially-acidulated phosphate rocks as controlled release P fertilizers. Fertilizer Research 35: 25–31.

Hammond, L. L. 1978. Agronomic measurements of phosphate rock effectiveness. In: Seminar on phosphate rock for direct application, pp. 147–173. International Fertilizer Development Centre, Muscle Shoals, Alabama.

Hammond, L. L., Chien, S. H. & Mokwunye, A. U. 1986. Agronomic value of unacidulated and partially acidulated phosphate rocks indigenous to tropics. Advances in Agronomy 40: 89–140.

Harriman, R. 1978. Nutrient leaching from fertilized forest watersheds in Scotland. Journal of Applied Ecology 15: 933–942.

Jarva, M., Kaunisto, S., Nieminen, M., Sallantaus, T. & Saura, M. 1995. Metsänlannoitteen huuhtoutuminen Liesinevan sarkaleveyskoekentältä – alustavia tuloksia. In: Saukkonen, S. & Kenttämies, K. (eds.). Metsätalouden vesistövaikutukset ja niiden torjunta. METVE-projektin loppuraportti, pp. 121–128. Suomen ympäristö 2 – ympäristönsuojelu. Helsinki.

Jones, U. S. 1948. Availability of phosphorus in rock phosphate as influenced by potassium and nitrogen salts, lime, and organic matter. Agron. J. 40: 765–770.

Karsisto, K. 1968. Eri fosforilajien soveltuvuus suometsien lannoitukseen (Summary: Using various phosphatic fertilizers in petland forests). Suo 19: 104–111.

Karsisto, K. 1970. Lannoituksessa annettujen ravinteiden huuhtoutumisesta turvemailta (Summary: On the washing of fertilizers from peaty soils). Suo 21: 60–66.

Karsisto, K. 1977. Kotimaisten fosforirikasteiden käyttökelpoisuus suometsien lannoituksessa (Summary: Possibilities of native phosphate concentrates in fertilizing peatland forests). Suo 28: 43–46.

Karsisto, K. & Ravela, H. 1971. Eri ajankohtina annettujen fosfori- ja kalilannoitteiden huuhtoutumisesta metsäojitusalueilta (Summary: Washing away of phosphorus and potassium from areas drained for forestry and topdressed at different times of the year). Suo 22: 39–46.

Kaunisto, S., Moilanen, M. & Issakainen, J. 1993. Apatiitti ja flogopiitti fosfori- ja kaliumlannoitteina suomänniköissä (Summary: Apatite and phlogopite as phosphorus and potassium fertilizers in peatland pine forests). Folia Forestalia 810: 1–30.

Kenttämies, K. 1981. The effects on water quality of forest drainage and fertilization in peatlands. Publications of Water Research Institute, National Board of Waters, Finland 43: 24–31.

Khasawneh, F. E. & Doll, E. C. 1978. The use of phosphate rock for direct application to soils. Advances in Agronomy 30: 159–206.

Mackay, A. D. & Syers, J. K. 1986. Effect of phosphate, calcium and pH on the dissolution of phosphate rock in soil. Fertilizer Research 10: 175–184.

Malcolm, D. C. & Cuttle, S. P. 1983. The application of fertilizers to drained peat. 1. Nutrient losses in drainage. Forestry 56: 155–174.

McClellan, G. H. & Gremillion, L. C. 1980. Evaluation of phosphatic raw materials. In: Khasawneh, F. E., Sample, E. C. & Kamprath, E. J. (eds). The role of phosphorus in agriculture, pp. 45–85. ASA-CSSA-SSA Madison, Wisconsin, USA.

McClellan, G. H. & Lehr, J. R. 1969. Crystal chemical investigation of natural apatites. The American Mineralogist 54: 1374–1391.

McKelvey, V. E. 1973. Abundance and distribution of phosphorus in the lithosphere. In: Griffith, E. J., Beeton, A., Spensor, J. M. & Mitchell, D. T. (eds). Environmental phosphorus handbook. John Wiley and Sons, New York. pp. 13–31.

McLean, E. O. & Logan, T. J. 1970. Sources of phosphorus for plants grown in soils with differing P fixation tendencies. Soil Science Society of American Proceedings 34: 907–911.

Moilanen, M. 1992. Suopuustojen ravinnetila Pohjois-Suomen vanhoilla ojitusalueilla. In: Valtanen, J., Murtovaara, I. & Moilanen, M. (eds.). Metsäntutkimuspäivä Taivalkoskella 1991. Metsäntutkimuslaitoksen tiedonantoja 419: 58–65.

Nieminen, M. & Ahti, E. 1993. Talvilannoituksen vaikutus ravinteiden huuhtoutumiseen karulta suolta (Summary: Leaching of nutrients from an ombrotrophic peatland area after fertilizer application on snow). Folia Forestalia 814: 1–22.

Nieminen, M. & Jarva, M. 1996. Phosphorus adsorption by peat from drained mires in southern Finland. Scandinavian Journal of Forest Research 11: 321–326.

Pätilä, A. & Nieminen, M. 1990. Effects of atmospheric deposition on the nutrient status of oligotrophic pine mires. In: Peat 90, Versatile peat. International conference on peat production and use. June 11.–15., 1990. Jyväskylä, Finland. Volume 2, posters. Association of Finnish Peat Industries, University of Jyväskylä, Continuing Education Centre. pp. 115–129.

Penttilä, T. & Moilanen, M. 1987. Fosforilannoitteet suometsien lannoituksessa Pohjois-Suomessa. In: Saarenmaa, H. & Poikajärvi, H. (eds.). Korkeiden maiden metsien uudistaminen. Ajankohtaista tutkimuksesta. Metsäntutkimuspäivät Rovaniemellä 1987. Metsäntutkimuslaitoksen tiedonantoja 278: 136–148.

Rajan, S. S. S. 1987. Partially acidulated phosphate rock as fertilizer and dissolution in soil of the residual rock phosphate. New Zealand Journal of Experimental Agriculture 15: 177–184.

Rajan, S. S. S. & Marwaha, B. C. 1993. Use of partially acidulated phosphate rocks as phosphate fertilizers. Fertilizer Research 35: 47–59.

Rajan, S. S. S. & Watkinson, J. H. 1992. Unacidulated and partially acidulated phosphate rock: Agronomic effectiveness and the rates of dissolution of phosphate rock. Fertilizer Research 33: 267–277.

Rajan, S. S. S., Fox, R. L. & Saunders, W. M. H. 1991. Influence of pH, time and rate of application on phosphate rock dissolution and availability to pastures. II. Soil chemical studies. Fertilizer Research 28: 95–101.

Rajan, S. S. S., O'Connor, M. B. & Sinclair, A. G. 1994. Partially acidulated phosphate rocks: Controlled release phosphorus fertilizers for more sustainable agriculture. Fertilizer Research 37: 69–78.

Sale, P. W. G. & Mokwunye, A. U. 1993. Use of phosphate rocks in the tropics. Fertilizer Research 35: 33–45.

Sanches, P. A. & Salinas, J. G. 1981. Low-input technology for managing Oxisols and Utisols in tropical America. Advances in Agronomy 34: 279–406.

Saura, M., Sallantaus, T., Bilaletdin, Ä. & Frisk, T. 1995. Metsälannoitteiden huuhtoutuminen Kalliojärven valuma-alueelta. In: Saukkonen, S. & Kenttämies, K. (eds.). Metsätalouden vesistövaikutukset ja niiden torjunta – METVE-projektin loppuraportti, pp. 87–104. Suomen ympäristö 2 – ympäristönsuojelu. Helsinki 1995.

Smyth, T. J. & & Sanches, P. A. 1982. Phosphate rock dissolution and availability in Cerrado soils as affected by phosphorus sorption capacity. Soil Science Society of American Journal 46: 339–345.

Stangel, P. J. 1979. The IFDC phosphate program. In: Seminar on phosphate rock for direct application, pp. 3–35. International Fertilizer Development Centre, Muscle Shoals, Alabama.

Syers, J. K. & Mackay, A. D. 1986. Reactions of Sechura phosphate rock and single superphosphate in soil. Soil Science Society of American Journal 50: 480–485.

Veijalainen, H. 1992. Neulasanalyysituloksia suometsistä talvella 1987–88 (Summary: Nutritional diagnosis of peatland forests by needle analysis in winter 1987–88). Metsäntutkimuslaitoksen tiedonantoja 408: 1–28.

Volk, G. W. 1944. Availability of rock and other phosphate fertilizers as influenced by lime and form of nitrogen fertilizer. Agron. J. 36: 46–56.

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 lannoitteiden 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 turvemailla.

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 kokonaismäärät 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 happokäsitellyt 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 $CO_3^{2-}/PO_4^{2-}$-moolisuhteen perusteella (Kuva 2). Fosfaatin korvautuminen karbonaatilla aiheuttaa kiderakenteessa muutoksia, jotka lisäävät fosforin liukoisuutta (Hammond ym. 1986).

Koska apatiitin kiderakenteen $CO_3^{2-}/PO_4^{2-}$-moolisuhteen mittaaminen on vaikeaa, veteenliukenemattoman fosforin liukoisuus määritetään yleensä neutraalilla ammonium nitraatilla, 2% sitruunahapolla tai 2% muurahaishapolla (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 lannoitteeseen lisätään 2–5% sitovia ainesosia (esim. mineraalihappoja) rakeiden fysikaalisten ominaisuuksien paranratamiseksi (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 typpeä.

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

Yhtälöstä voidaan päätellä, että kasvupaikan kyky tuotaa maaveteen vetyioneja ja toisaalta pidättää maavedestä kalsiumia ja fosforia ovat ratkaisevia tekijöitä hidasliukoisten fosforilannoitteiden liukenemisessa. Happamuuden voimakas vaikutus veteenliukenemattoman fosforin liukenemiseen näkyy Kuvasta 3. Ojitetuilla turvemailla maaveden vetyionipitoisuus (pH yleensä < 4–5) ei useinkaan rajoittane lannoitefosforin liukenemista. 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 liukenemista.

Muita lannoitefosforin liukenemiseen vaikuttavia kasvupaikkatekijöitä ovat kasvupaikan hydrologia ja maan lämpötila. Kuivuus ei rajoittane lannoitefosforin liukenemista suometsissä. Myöskään liiallinen kosteus ei estäne liukenemista, koska riisipelloilla tulvittamisen ei ole havaittu vähentävän hidasliukoisen fosforin liukenemista (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 hidasliukoisia 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 (seurantaa 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).

*Received 9.10.1997, accepted 18.11.1997*