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PETRI EKHOLM

Algal-available phosphorus originating from
agriculture and municipalities

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Petri Ekholm

**Algal-available phosphorus originating from agriculture
and municipalities**

Yhteenveto: Maatalous ja yhdyskunnat leville käyttökelpoisen fosforin
lähteinä

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Contents

Summarised publications and the author's contribution	5
List of commonly used abbreviations	6
1 Introduction	8
1.1 Background	8
1.2 Forms, analysis and reactions of phosphorus	9
1.2.1 Forms	9
1.2.2 Analysis	9
1.2.3 Sorption-desorption reactions	10
1.3 Different phosphorus forms as nutrient sources for planktonic algae	11
1.4 Measurement of potentially algal-available phosphorus	12
1.4.1 Algal assays	12
1.4.2 Chemical methods	14
1.5 Actual availability of phosphorus	15
1.6 Loss of phosphorus from agricultural land	15
1.7 Objectives of this study	16
2 Materials and methods	16
2.1 Analysis of phosphorus	16
2.2 Determination of algal-available phosphorus	17
2.2.1 Samples	17
2.2.2 Dual culture assays	21
2.2.3 Batch assays	22
2.2.4 Determination of reversibly adsorbed phosphorus	22
2.3 Sorption-desorption experiments	23
2.4 Lake phosphorus balance	23
2.5 Modelling of the concentration of dissolved reactive phosphorus in field surface runoff	25
3 Results and discussion	27
3.1 Determination of potentially algal-available phosphorus	27
3.1.1 Effect of direct contact between algae and particles on phosphorus release	28
3.1.2 Applicability of dual culture assays to the estimation of potentially algal-available phosphorus	29
3.1.3 Comparison between the dual culture assay and a chemical determination	32
3.2 Potential availability of the phosphorus fractions	33
3.2.1 Dissolved phosphorus	33
3.2.2 Particulate phosphorus	35
3.3 Agriculture vs. municipalities as sources of available phosphorus	35
3.4 Actual availability of phosphorus: effects of pH and ambient phosphorus concentration	39
3.5 Cycling of phosphorus in an agriculturally loaded lake	40
3.5.1 Phosphorus balance	40
3.5.2 External vs. internal loading of algal-available phosphorus	41
3.6 Assessment of the loss of available phosphorus from agricultural land	42
3.6.1 Origin of dissolved reactive phosphorus in surface runoff	42
3.6.2 Modelling the concentration of dissolved reactive phosphorus in surface runoff	43

4 Concluding remarks	46
5 Summary	47
6 Yhteenveto	49
Acknowledgements	51
References	53

Summarised publications and the author's contribution

This thesis is a synthesis of the following papers referred to in the text by their Roman numerals I–VII. In addition, some previously unpublished results are presented.

I Ekholm P. 1994. Bioavailability of phosphorus in agriculturally loaded rivers in southern Finland. *Hydrobiologia* 287: 179–194.

II Ekholm P. & Yli-Halla M. 1992. Reversibly adsorbed phosphorus in agriculturally loaded rivers in southern Finland. *Aqua Fenn.* 22: 35–41.

III Krogerus K. & Ekholm P. 1998. Availability of soil phosphorus to the green alga *Selenastrum capricornutum*. In: Berthelin J., Huang P.-M., Bollag J.-M. & Andreux F. (eds.), *Effect of mineral-organic-microorganism interactions on soil and freshwater environments*, Plenum Publishing Corporation, New York (in press).

IV Rekolainen S., Ekholm P., Ulén B. & Gustafson A. 1997. Phosphorus losses from agriculture to surface waters in the Nordic countries. In: Tunney H., Carton O.T., Brookes P.C. & Johnston A.E. (eds.), *Phosphorus loss from soil to water*, CAB International, Wallingford, UK, pp. 77–93.

V Ekholm P. & Krogerus K. 1998. Bioavailability of phosphorus in purified municipal wastewaters. *Wat. Res.* 32: 343–351.

VI Ekholm P., Malve O. & Kirkkala T. 1997. Internal and external loading as regulators of nutrient concentrations in the agriculturally loaded Lake Pyhäjärvi (southwest Finland). *Hydrobiologia* 345: 3–14.

VII Ekholm P., Kallio K., Turtola E., Rekolainen S. & Puustinen M. An empirical equation overestimates dissolved phosphorus in runoff from Finnish clayey soils. Submitted to *Agric. Ecosyst. & Environ.* in February 1998.

- Petri Ekholm was fully responsible for paper I and for the examination of previously unpublished data (algal-availability of P in rivers discharging into lake Pyhäjärvi and in municipal wastewaters of St Petersburg).
- In paper II, the experiments were planned by Markku Yli-Halla and P. Ekholm and conducted by M. Yli-Halla. Both participated in data processing, interpretation of results and writing, P. Ekholm having the main responsibility.
- Kirsti Krogerus initiated the study described in paper III, whereas both authors (K. Krogerus and P. Ekholm) participated in the planning of the experiments, data processing, interpretation of results and writing.
- Arne Gustafson initiated the study described in paper IV. Seppo Rekolainen had the main responsibility for writing the paper, except the section 'Bioavailability of agricultural phosphorus loss', which was written by P. Ekholm. P. Ekholm also participated in the compilation of other sections. Barbro Ulén and A. Gustafson provided data for the paper and commented on the manuscript.
- In paper V, both authors (K. Krogerus and P. Ekholm) participated in the planning of the experiments, data processing, interpretation of results and writing, P. Ekholm having the main responsibility.
- In paper VI, all authors (P. Ekholm, Olli Malve and Teija Kirkkala) took part in the planning of the experiments, data processing and interpretation of results. P. Ekholm wrote the paper and O. Malve and T. Kirkkala commented on the manuscript.
- P. Ekholm had the main responsibility for the modelling exercises, interpretation of results and writing of paper VII. Eila Turtola and Markku Puustinen provided the data from the experimental fields. Kari Kallio and S. Rekolainen participated in the model development. All authors commented on the manuscript.

List of commonly used abbreviations

DP	=	Dissolved Phosphorus
DRP	=	Dissolved Reactive Phosphorus
DUP	=	Dissolved Unreactive Phosphorus
P	=	Phosphorus
PP	=	Particulate Phosphorus
RP	=	Reactive Phosphorus
TP	=	Total Phosphorus
TSS	=	Total Suspended Solids

Algal-available phosphorus originating from agriculture and municipalities

Petri Ekholm

Finnish Environment Institute, P.O. Box 140, FIN-00251 Helsinki, Finland

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Eutrophication of surface waters is attributed to an excess supply of nutrients, particularly phosphorus (P). Due to water pollution control measures, the P load from municipalities has drastically decreased in Finland, but no corresponding decrease in the load from agriculture has occurred. Both municipal and agricultural emissions contain several different P forms. Some of the P forms do not enhance the growth of algae and thus do not contribute to eutrophication. Therefore, when implementing further P-reduction measures, the focus should be on algal-available P rather than on total P. The aim of this study was to estimate what portion, and which forms of the P originating from agriculture and municipalities can be transformed into forms which planktonic algae are able to utilise in freshwater systems. In addition, efforts were made to estimate the sources of available P in agricultural emissions, to model its loss in surface runoff and to assess its fate in a lake. A comparison of two algal assay techniques showed that the potentially available P can be most reliably estimated with a dual culture assay, whereas a commonly used batch assay tends to underestimate potentially available P. The algal assays are labourious, but for the time being cannot be replaced by the simple chemical method tested in the study (determination of reversibly adsorbed P). According to the dual culture assays, total P was a poor absolute or relative indicator of the algal-available P, whereas the determination of dissolved reactive P appeared to offer a reliable measure of the minimum amount of algal-available P. The available P from agriculture primarily consisted of dissolved reactive P, whereas available P in purified municipal wastewaters was composed of dissolved unreactive P and particulate P in addition to dissolved reactive P. Surface soil of agricultural land was richer in algal-available P than eroded soil particles in agriculturally loaded rivers. This observation suggests that dissolved reactive P is not only desorbed from the soil remaining in the field but also from eroded soil particles during the erosion process. The modelling efforts suggested that the factors controlling the loss of dissolved reactive P from cultivated soil are still partly unknown; the empirical Sharpley equation applied in this study produced unrealistic values for dissolved reactive P in the surface runoff from two clayey soils. The observations on the P balance of an agriculturally loaded lake supported the results from the algal assays that dissolved reactive P is readily utilised by algae. Although the lake efficiently retained incoming P, a substantial amount of available P was supplied from the bottom of the lake. The mechanism of P release remained unidentified; however, resuspension of inorganic matter did not appear to contribute to this release.

Key words: Eutrophication, phosphorus, agriculture, municipal wastewaters, algal availability, algal assays, surface runoff, lakes

1 Introduction

1.1 Background

Eutrophication of surface waters, *i.e.* elevated aquatic primary productivity, is a severe environmental problem in Europe (Kauppi 1990, Boers and van der Molen 1993). Eutrophic literally means well-nourished, and indeed increased aquatic productivity is attributed to the excess supply of nutrients. Of these, phosphorus (P) has the lowest reserves compared with the requirements of algae in most northern temperate lakes. Enrichment of P increases production in these waters, and together with nitrogen, also increases production in many marine areas and estuaries (*e.g.* Fisher *et al.* 1995). As phytoplankton typically contains approximately 0.2% P by weight, one gram of P can theoretically produce 500 grams of algal biomass.

In pristine conditions, the mobilisation of P from terrestrial to aquatic systems is slow and ultimately controlled by the weathering of primary minerals, mainly apatite. However, human activities have substantially accelerated P mobilisation; the current P input into the oceans of the world has been estimated to be up to threefold the input during the pre-agricultural period (Howarth *et al.* 1995). On the other hand, in many European countries the P emissions from *point sources* have recently been reduced due to pollution control measures (*e.g.* van der Molen *et al.* 1998, Kronvang *et al.* 1995). In Finland, the current total P load discharged into surface waters from municipalities and industry is only 1/5 of the load in the beginning of the 1970s (Rosenström *et al.* 1996). The investments in municipal wastewater treatment have been particularly efficient. Most wastewaters are currently purified by an activated sludge process with simultaneous P precipitation, which removes more than 90% of P in raw sewage. However, there has been no similar decrease in the emissions from *diffuse sources*, particularly from agriculture (Kauppi 1984, Rekolainen 1989a, Rekolainen *et al.* 1995). Although only 7% of the total land area in Finland is agricultural land, approximately 60% of the anthropogenic P loading originates today from agriculture; the corresponding proportion for municipalities is only 5% (Ministry of the Environment 1998). The national goal is to further reduce the point source emissions (*ibid.*), but large investments will be needed for an

appreciable reduction (*cf.* Boers and van der Molen 1993). Therefore, the focus of P-control plans has been shifted from point sources to agricultural runoff in Finland as well as in several other European countries (*e.g.* Kronvang *et al.* 1995, van der Molen *et al.* 1998).

Water protection programmes in Finland are largely based on reduction of the *total phosphorus* (TP) load (Ministry of the Environment 1998). However, industrial and municipal effluents as well as agricultural runoff contain several different P forms. In the receiving waters, algae readily use part of the P, whereas some P forms may become available only slowly or may be entirely inert (*e.g.* Boström *et al.* 1988a). In order to efficiently abate eutrophication, the measures to reduce P load should target algal-available P rather than TP. This requires knowledge on the availability and origin of different P forms. Potential availability of P in various sources has been estimated by algal assays and chemical methods in numerous laboratory experiments (*e.g.* Lee *et al.* 1980, Sonzogni *et al.* 1982, Hegemann *et al.* 1983, Hegemann and Keenan 1985, Boström *et al.* 1988a). However, the non-uniformity of the methods and the site specificity of the studies (Hegemann *et al.* 1983) decrease the applicability of the results to Finnish conditions. In addition, the estimates obtained for P availability under laboratory conditions may not be valid for natural conditions.

The problems related to the assessment and reduction of available P can be well exemplified by considering agricultural emissions. First, P in agricultural runoff consists of two major fractions: P in eroded soil particles and P in dissolved form (Rekolainen 1989b, Pietiläinen and Rekolainen 1991, Puustinen 1994). Is the reduction of one P fraction more important than that of the other? How should the reduction be effected? The factors regulating erosion are well known (Rekolainen 1993), but those affecting the loss of dissolved P are more uncertain. Some agricultural management practices implemented to reduce TP load may effectively decrease particulate P but have a negligible, or even an increasing effect on dissolved P (Logan 1982). Furthermore, agricultural loading enters waters mainly outside the productive period (Rekolainen *et al.* 1991, Pitkänen 1994), and a substantial proportion of P in eroded soil particles has already settled on the bottom of a lake before the onset of algal production. On the other hand, most Finnish agricultural lakes are

shallow, and thus P release from bottom sediments, *i.e.* *internal loading*, may substantially increase the algal-available P pool and consequently the biomass of algae (Knuutila *et al.* 1994).

What forms of P are likely to exist in surface waters? How can they be analysed and how do they react? How can the potentially algal-available P be best determined? Which factors affect the actual release of potentially available P in the receiving waters? What are the sources of P in agricultural surface runoff? These questions will be discussed in the following.

1.2 Forms, analysis and reactions of phosphorus

1.2.1 Forms

In nature, P exists predominantly as phosphate with an oxidation state of +5 (Stevens 1980, Frossard *et al.* 1995). Some natural compounds containing P–C and P–N bonds exist, but these are considered quantitatively insignificant compared with phosphates (Emsley 1980, Stevens 1980). Orthophosphate refers to the tetrahedral PO_4 group. The reactions of orthophosphate that control the different forms of P likely to exist in natural waters are (modified from Stevens 1980):

- condensation resulting in *e.g.* chain (pyro- and polyphosphates) and cyclic structures (poly-metaphosphates) with P–O–P bonds,
- esterification resulting in compounds with P–O–C bonds,
- precipitation forming low-solubility compounds,
- sorption by hydrous metal oxides and clay minerals and
- soluble complex formation with transition and alkaline earth metals.

More complex P compounds may also be involved in the above reactions. For example, in addition to orthophosphate, organically bound P may be sorbed by metal oxides and clay minerals. The anions of orthophosphoric acid (H_3PO_4) are here referred to as *dissolved orthophosphate*. The proportion of the anions of different charge (PO_4^{3-} , HPO_4^{2-} , H_2PO_4^-) depends on pH: within the typi-

cal aquatic pH range of 5–9, the dominant species are HPO_4^{2-} and H_2PO_4^- .

1.2.2 Analysis

Natural phosphates seldom occur as well-defined chemical compounds. Therefore, in limnological studies P forms are usually grouped on the basis of physical and chemical criteria. The most common procedure of P analysis (see Broberg and Persson 1988, Fig. 1) begins with a physical separation by filtration, and proceeds with a chemical characterisation based on the reactivity with molybdate and ease of hydrolysis (or digestion). By this scheme, total P is divided into *particulate P* (PP) and [total] *dissolved P* (DP), and the latter is further partitioned into *dissolved reactive P* (DRP) and *dissolved unreactive P* (DUP). Sometimes [total] *reactive P* (RP) is also determined. Alternative and more specific methods exist, such as enzymatic, radiobiological and chromatographic techniques, but are considered premature for routine application (Broberg and Persson 1988).

The cut-off value between 'particulate' and 'dissolved' matter is commonly set at approximately 0.5 μm , which means that, in addition to truly dissolved P forms, inorganic and organic P in small particles and colloids may also pass the filter (Broberg and Persson 1988). On the other hand, colloids can also be sorbed onto filters, and due to clogging of the filter, the effective pore size can be lower than the nominal pore size (see Tarapchak *et al.* 1982, Broberg and Persson 1988, Turtola 1996). Incorrect results are also obtained if organisms or detritus particles are damaged during filtration (see Tarapchak *et al.* 1982) or if the filters contain holes larger than the nominal pore size (Stockner *et al.* 1990).

The P determination is based on the following reactions (Murphy and Riley 1962, Fig. 1): in acid solution, orthophosphate forms with ammonium molybdate a yellow phosphomolybdate complex that is reduced by ascorbic acid to a blue complex (molybdenum blue). Phosphorus analysed from an undigested filtrate by this *molybdenum blue method*, *i.e.* DRP, tends to overestimate the true concentration of dissolved orthophosphate, sometimes even by one to two orders of magnitude (Stainton 1980). The acidic conditions may (i) hydrolyse labile esters and polyphosphates, (ii) disintegrate metal-orthophosphate complexes, (iii) dis-

solve P containing colloidal and particulate hydrous metal oxides and (iv) hydrolyse organic colloidal P (Stevens 1979, 1980, Stainton 1980). In addition, the molybdenum blue method is not specific for P, the most important potential interferences being the complexes formed between molybdate and silicate or arsenic ions (Broberg and Petterson 1988). Furthermore, due to the use of ascorbic acid some reductant-sensitive P forms may also be released (see Hartikainen 1979). Due to an obvious difference between the true dissolved orthophosphate and P analysed by the molybdenum blue method, the latter should be referred to as [molybdate] reactive P rather than orthophosphate (Broberg and Persson 1988, Broberg and Petterson 1988, Haygarth *et al.* 1995). Dissolved reactive P has often been called soluble reactive P. The word soluble refers to a substance 'capable of being dissolved, esp. easily dissolved in some solvent, usually water' (HarperCollins Publishers 1995). As the aim is, despite all potential artefacts, to analyse substances already dissolved, the term dissolved P should be preferred to soluble P.

As regards the analysis of TP, the results obtained depend on the method of digestion. The widely used peroxodisulphate digestion tends to underestimate P particularly in samples rich in soil matter (O'Connor and Syers 1975, Logan *et al.* 1979, Turtola 1996). For example, P occluded in Fe oxides may remain unattached (O'Connor and Syers 1975).

1.2.3 Sorption-desorption reactions

Starting from its initial mobilisation from the terrestrial to the aquatic environment and continuing to its eventual long-term loss from the aquatic productive system by burial in deep sediments, the fate of P is largely controlled by exchange reactions between dissolved and solid phases. In this section, abiotic P exchange will be discussed in the light of the *sorption-desorption* theory. This theory probably describes the exchange reactions of P more accurately than the traditional solubility considerations of different well-defined P compounds. However, it should be noted that P exchange probably occurs as a continuum between the sorption-desorption and precipitation-dissolution processes, not as pure sorption-desorption reactions (Bohn *et al.* 1985, Frossard *et*

al. 1995). Adsorption is defined as the accumulation of matter at the solid-solution interface, and absorption as retention in the interior structure of the solid phase. The differentiation of these two reactions is beyond the scope of this study, and thus the general term sorption, which includes both retention reactions, is used here. Desorption refers to the transfer of sorbed P to the dissolved phase.

Sorption of P can be divided into physical and chemical sorption based on the type and strength of the P binding mechanism. Phosphorus is initially sorbed by a rapid reaction. It includes a physical anion exchange on positively charged surfaces (rare in Finnish soils) and a chemical ligand exchange, which also occurs on negatively charged surfaces (White 1980). In the ligand exchange, phosphate anions form a phosphated surface complex with the functional surface groups, usually those of metal oxyhydroxides, whereas hydroxyl or water molecules are released from the surface. The rapid reaction is followed by a slow diffusion-controlled process towards the interior of the solid phase, which may continue for at least several months (Barrow 1985, Portielje and Lijklema 1993). Not all of the P sorbed is readily desorbed (Peaslee and Phillips 1981): the slow step of sorption is important in fixing P to unavailable form both in soils and in benthic sediments. Boers *et al.* (1993) emphasized the importance of understanding the slow reaction in the assessment of the future behaviour of sedimentary P after changes in external loading.

The direction of the sorption-desorption reaction depends on (i) the quality and quantity of sorptive components, (ii) their degree of saturation and (iii) the ambient conditions. In Finnish soils and lake sediments, poorly crystallised hydrous oxides of Al and Fe are the most important sorptive components (Hartikainen 1979). In addition, clay minerals sorb P, although less than oxides, as do complexes of humic compounds containing Fe and Al. Desorption of P is favoured when the amount of sorptive components is low or when they are largely occupied (Frossard *et al.* 1995); when the amount of sorbed anions increases, the number of available sorption sites decreases and the negative charge of the surface increases. For example, Jensen *et al.* (1992) found that freshwater sediments with high molar Fe:P ratios were capable of retaining P in the oxidized surface layer, whereas P was released when the ratio was low.

The P concentration in solution crucially affects sorption reactions. The P concentration at which no net desorption from or sorption to the solid phase occurs is called the equilibrium phosphate concentration (EPC). It expresses the maximum level to which the dissolved orthophosphate in the receiving water can be increased by the particles; no net desorption is possible above this concentration (Taylor and Kunishi 1971, Hartikainen 1982a). An increase in pH usually enhances desorption in non-calcareous environments; first, hydroxyl ions compete more effectively with dissolved orthophosphate of sorption sites than water molecules, and second, the negative charge of the sorbing oxides increases with increasing pH (Hartikainen 1981, Hartikainen and Yli-Halla 1996). Desorption is also promoted by increase in the amount of other compounds competing with P for sorption sites, such as organic anions and sulphate (Hartikainen 1979, Hartikainen and Yli-Halla 1982, Caraco *et al.* 1989, Hartikainen and Yli-Halla 1996). On the other hand, increase in ionic strength suppresses desorption (Hartikainen and Yli-Halla 1982). Divalent cations are more effective in reducing P desorption than are monovalent cations (Hartikainen 1989). Desorption of P usually increases with increasing water-soil ratios (Sharpley *et al.* 1981a, b, Yli-Halla *et al.* 1995, Yli-Halla and Hartikainen 1996). This is a net effect of the more dilute environment. The constancy of dissolved orthophosphate levels (approximately 30–60 $\mu\text{g l}^{-1}$) observed in many estuaries has been attributed to desorption of P from suspended solids during the mixing of river and sea waters (*e.g.* Carritt and Goodgal 1954, Froelich 1988). This release is primarily a result of competition for sorption sites with other anions, since ionic strength alone would be expected to increase rather than decrease P sorption (Froelich 1988). Although high temperature increases the rate of both sorption and desorption, desorption seems to be more favoured (Yli-Halla and Hartikainen 1996).

1.3 Different phosphorus forms as nutrient sources for planktonic algae

Microalgae take up P mostly in the form of dissolved orthophosphate (Cembella *et al.* 1984, Boström *et al.* 1988a). In some cases inorganic pyrophosphate and low molecular weight organic

P have probably been directly taken up by algae as alternative sources of P (Cembella *et al.* 1984). Furthermore, facultative phagotrophic phytoplankton species, such as dinoflagellates, are thought to be able to assimilate P by intracellularly degrading ingested particles or macromolecules which are not truly dissolved (*ibid.*). In general, however, dissolved orthophosphate can be considered as the only *directly available* P form; the availability of other P forms depends on the rate and extent to which they are transformed into dissolved orthophosphate. For example, condensed inorganic P and esterified P from plant tissue and animal wastes are considered to be rapidly hydrolysed to dissolved orthophosphate (Sonzogni *et al.* 1982). Alternatively, a substantial part of soil P is relatively stable, the most refractory forms being apatite and P incorporated into high molecular weight compounds during humification (Frossard *et al.* 1995).

As discussed by Boström *et al.* (1988a), studies on lake water have often focused on determination of the P pool which is *immediately available* to algae. This pool refers to dissolved orthophosphate and P forms with similar uptake kinetics during a short-term assay, usually lasting less than 4 hours (*ibid.*). Information on the immediately available P is crucial to understanding P dynamics in waters. However, as the immediately available P does not include P forms which would become available in the long run, it is less valuable from the standpoint of eutrophication management (*ibid.*). Therefore, a number of studies dealing with P from point as well as diffuse sources have aimed at the determination of *potentially available P*, *i.e.* an upper limit of the algal-available P (Sonzogni *et al.* 1982, see also Williams *et al.* 1980).

Potentially available P can be considered as the sum of directly available P and the P that can be transformed into an available form by naturally occurring physical, chemical and biological processes (*cf.* Boström *et al.* 1988a). As discussed by Boström *et al.* (1988a) this definition is problematic, in particular, with regard to the time perspective. Should it equal the hydraulic residence time of P in the water column determined by flushing and eventually sedimentation, or should it also include the time when benthic P may be translocated to the water phase, *i.e.* the time before the permanent burial, which may well exceed 10 years (see Sonzogni *et al.* 1982). The issue of time is closely connected with the release rate of available P (see

e.g. Verhoff and Heffner 1979). Generally, the rate is initially rapid but decreases substantially with time (DePinto *et al.* 1981, I, III, V). With respect to eutrophication, an extremely slow release of algal-available P from sediments may be insignificant compared with other sources of available P, especially in eutrophic waters receiving substantial external P loading. In this case, potentially available P would not include all *geochemically active P*. The opposite applies if slowly released P accumulates for example as Fe-compounds, which may be suddenly activated by reduced redox-potential.

Other components of aquatic biota may be able to utilise a wider variety of P forms than planktonic algae. To highlight this possibility, the term algal-available P is used here instead of bioavailable P. Nevertheless, dissolved orthophosphate is probably also the primary P form taken up by bacteria, which form another crucial component of the pelagic nutrient cycle (Jansson 1988, Tamminen 1990). In fact, bacteria and algae have been proposed to compete for available P (*ibid.*). Recently, a technique to estimate available P was introduced, analogous to batch assays (see section 1.4.1) but having a natural mixture of heterotrophic bacteria as test organism (deJonge *et al.* 1993). Bacteria were chosen instead of algae because 'the natural bacterial population may contain many specialists so that the figures for bioavailability of phosphorus may be maximum values' (*ibid.*). However, the amounts of P utilised by the bacteria were 10 to 20% of TP in marine bottom sediments (*ibid.*), which covers the lower range of that utilised by algae in freshwater sediments (Golterman *et al.* 1969, Fitzgerald 1970a, b, Grobler and Davies 1979, 1981, Williams *et al.* 1980, Hosomi *et al.* 1981, Klapwijk *et al.* 1982, Bruning and Klapwijk 1984, Premazzi and Zanon 1984, Young *et al.* 1985, Engle and Sarnelle 1990, Fabre *et al.* 1996, Dorioz *et al.* 1998).

1.4 Measurement of potentially algal-available phosphorus

1.4.1 Algal assays

The potential availability of P has usually been assessed by laboratory scale algal assays (see reviews by Lee *et al.* (1980), Sonzogni *et al.* (1982), Hegemann *et al.* (1983), Hegemann and Keenan

(1985) and Boström *et al.* (1988a)). As regards aquatic P, the first study on potential availability was performed by Golterman *et al.* (1969) on lake sediments. However, the basics of the approach were applied and discussed already by Tchan (1959), who studied the availability of soil P. Most algal assays have been performed with particulate matter as the P source, but some studies have also considered the dissolved fraction or whole water samples.

In a typical algal assay, the conditions are 'optimal' for algal growth, except for P, which is supplied only from the sample being investigated. However, the conditions are also made favourable for several mechanisms of P release. For example, the use of P-starved algae in a P-limited environment maintains a steep concentration gradient, which enhances the desorption of P and also induces phosphatase formation (phosphatases are enzymes which hydrolyse organic P forms). In addition, photosynthesis increases the pH, which may further increase P desorption. Furthermore, the tests are usually performed at a temperature favourable for P desorption and mineralisation of organic matter (approximately 20 °C).

Despite these conditions, the true potentially available P is probably underestimated by algal assays. First, most assays last only a few weeks and thus do not determine the ultimately available P (Lee *et al.* 1980, Hegemann *et al.* 1983). However, this problem may be mitigated if the release rate of available P is determined and the ultimately available P is mathematically extrapolated (e.g. DePinto *et al.* 1981). Second, the conditions prevailing in assays do not allow all mechanisms that effect P mobilisation to occur, such as release due to anoxia (Boström *et al.* 1988a). Finally, assays are usually conducted using only one algal species, either *Selenastrum capricornutum* and *Scenedesmus* spp., all of which are chlorophyceans. As variable utilisation of different P compounds has been observed among different algal species (Cembella *et al.* 1984), the results from uni-algal tests may not be valid for the entire planktonic algal community. This problem has sometimes been alleviated by performing replicate assays with different algal species (Smith *et al.* 1978, Persson 1990, Sharpley 1993b) and by using a mixed laboratory algal culture (Grobbelaar 1983) or a natural community of algae (Porcella *et al.* 1970, Smith *et al.* 1977, Verhoff and Heffner 1979, Løvstad and Wold 1984, Blakar and Løvstad 1990, Krogstad

and Løvstad 1991) as test organisms.

The two major techniques applied in the algal-availability testing are *batch assays* and *dual culture assays*; the fundamental difference being that the former allows direct contact between algae and particles, whereas the latter technique separates algae and particles. Batch assays have been recommended, for example, by Boström *et al.* (1988a) mainly on the basis of the assumption that direct access of algae to P-carrying particles allows surface-bound enzymes to influence the mobilisation of P (see also Hegemann and Keenan 1985). However, when the P source and the P sink are mixed, measurement of the P exchange is problematic (Hegemann *et al.* 1983). In some batch approaches, the algal-available P has been estimated by monitoring the increase in algal P content (Williams *et al.* 1980) or the depletion in sample P (Sagher *et al.* 1975, Sagher 1976, Dorich *et al.* 1980, 1984a, b, 1985, Ellis and Stanford 1988) by chemical P fractionations. As the fractionations tend to be unspecific (see section 1.4.2), these approaches may give biased results.

Most often the available P is determined indirectly in the batch approach by comparing the algal yield in actual tests either with that obtained in a set of standard cultures using various amounts of dissolved orthophosphate or with experimentally determined fixed coefficients of algal P content. The comparison should reveal what proportion of the P in the sample was utilised by algae. The algal yield has been determined by counting algal cells at the stationary growth phase (Golterman *et al.* 1969, Wildung and Schmidt 1973, Chiou and Boyd 1974, Cowen and Lee 1976, Cowen *et al.* 1978, Smith *et al.* 1978, Klapwijk *et al.* 1982, Kauppi and Niemi 1984, Løvstad and Wold 1984, Ellis and Stanford 1988, Blakar and Løvstad 1990, Engle and Sarnelle 1990, Källqvist and Berge 1990, Persson 1990, Krogstad and Løvstad 1991, Sharpley *et al.* 1991, Sharpley 1993a, b, III), and by measuring optical density (Fitzgerald 1970a, Wildung and Schmidt 1973, Dobolyi and Ördög 1979, Hanna and Dauta 1983, Bradford and Peters 1987, Butkus *et al.* 1988, Priha 1994, Fabre *et al.* 1996, Qotbi *et al.* 1996), chlorophyll-a content (Viner 1988, Dorioz *et al.* 1998) and the organic or total carbon of the assay suspension (Grobler and Davies 1979, 1981, Grobbelaar 1983) or by derivative spectroscopy (Bruning and Klapwijk 1984). However, even in carefully performed experiments, the yield may not depend solely on al-

gal-available P. According to Bradford and Peters (1987), one gram of P may produce 430 to 805 grams (dry weight) of *Selenastrum capricornutum* in laboratory cultures. Young *et al.* (1982) observed that P from wastewater samples was taken up by algae even when the algal biomass was decreasing. The relationship between P concentration and cell yield has also been shown to depend on the P-concentration range (Chiou and Boyd 1974, Källqvist and Berge 1990). Possibly due to inaccurate P determination, availabilities exceeding 100% have been recorded in batch assays (Kauppi and Niemi 1984, Källqvist and Berge 1990, Persson 1990).

In the dual culture assays, algae and P carrying samples are separated from each other by a dialysis bag (Fitzgerald 1970a, b, Hanna 1989, Priha 1994) or a membrane filter (Fitzgerald 1970b, Wildung and Schmidt 1973, DePinto *et al.* 1981, Hosomi *et al.* 1981, Young *et al.* 1982, 1985, Premazzi and Zanon 1984, Marengo and Premazzi 1985, Zlinszky and Herodek 1990, Dorioz *et al.* 1998, I, III, V). This approach makes it possible to directly determine the increase in algal P, as well as the corresponding decrease in the sample P. In addition, the algal culture can be replaced during the assays to ensure maintenance of the P gradient and to estimate the release rate of algal-available P (DePinto *et al.* 1981, DePinto 1982, Young *et al.* 1982, 1985, III, V). On the other hand, the investigation of surface-bound enzymes in P mobilization is not possible with these assays (Boström *et al.* 1988a). According to Golterman (1984), pH might also increase more in the closed systems applied in most dual culture assays than in batch assays. The pH has been controlled in some approaches by bubbling with a mixture of carbon dioxide and air (Marengo and Premazzi 1985) or by buffering the test suspensions (I, III, V). Other types of algal assays include incubation of algae on agar, in which P-carrying particles are mixed (Golterman 1977) and various mesocosm techniques (Porcella *et al.* 1970, Smith *et al.* 1977, Verhoff and Heffner 1979). To my knowledge, no comparisons between batch assays and dual culture assays have been made using the same material, except in III (see also Dorioz *et al.* 1998).

Various sample pretreatments have often been performed prior to assays. These include the separation of particulate and dissolved fractions, fractionation of particles into size classes and the drying, sieving, freezing, autoclaving and sterilisa-

tion of the samples. Sterilisation is performed in some batch assays to eliminate the growth of indigenous algae. Most sample pretreatments are liable to affect the P status of the samples (Twinch 1987, Klotz 1988, Berge and Källqvist 1990, Grobbelaar and House 1995).

1.4.2 Chemical methods

Algal assays have generally been considered the most reliable method of assessing algal-available P (e.g. Hegemann *et al.* 1983, Hegemann and Keenan 1985, Bradford and Peters 1987, Boström *et al.* 1988a, Golterman 1988). However, assays are time-consuming, costly and, as the test organisms are sensitive to changes in the environment, subject to experimental errors. For example, if the sample contains toxic substances, the assays yield incorrect results (Williams *et al.* 1980, Källqvist and Berge 1990). Furthermore, the range of environmental conditions that can be studied using algal assays is limited. Therefore, a chemical surrogate for algal assays was already investigated by Golterman *et al.* (1969) and in a number of studies that followed (e.g. Porcella *et al.* 1970, Sagher *et al.* 1975, Dorich *et al.* 1980, 1984a, b, 1985, Williams *et al.* 1980, Golterman 1982, Young *et al.* 1982, 1985, Sharpley *et al.* 1991). In general, the chemical methods applied have been based on one of two alternative assumptions: (i) available P is composed of some fractions of P which can be characterised, or (ii) the available P equals the desorbable P.

The P fractionations were originally developed for agricultural purposes after realisation that only a part of the soil P is available for plant growth and that the TP content of soil is a poor predictor of plant-available P (Williams *et al.* 1971a, 1980). In principle, the fractionation techniques are based on a sequence of extractions of particulate matter in an increasing order of extraction rigour that yields P fractions in a sequence of decreasing availability. The extractants used include neutral salts or water, reducing agents, strong acids and bases and chelating substances (Williams *et al.* 1971a, b, 1976, Hartikainen 1979, Hieltjes and Lijklema 1980, Golterman 1982, Psenner *et al.* 1985). As regards aquatic particles, the correlations between algal-available P and chemical P fractions, or alternatively, the changes in the fractions during the algal assays, have suggested that a substantial por-

tion of non-apatite inorganic P is often available to algae, whereas allochthonous organic P and apatite P are only sparingly, if at all, available (e.g. Porcella *et al.* 1970, Sagher *et al.* 1975, Williams *et al.* 1980, Dorich *et al.* 1980, 1984a, b, 1985, Young *et al.* 1982, 1985, Sharpley *et al.* 1991). In noncalcareous environments, nonapatite inorganic P mainly corresponds to P bound by Al and Fe.

Golterman (1984) stated that 'one of the most frustrating problems of sediment phosphate chemistry is that we have no good way of separating the different phosphate compounds'. Indeed, the problem with fractionations using more or less vigorous reagents is that they do not extract homogeneous pools of P (Golterman *et al.* 1969, Golterman 1984, Frossard *et al.* 1995). In addition, they do not yield information on the saturation of sorptive components and they ignore the kinetics of P release (Hartikainen 1979, Frossard *et al.* 1995). The good correlations between algal-available P and one or a combination of the P fractions found in individual studies have been shown to be site-specific and to depend on the characteristics of the investigated material (Grobler and Davies 1981, Boström *et al.* 1988a). For example, apatite P may also be utilised by algae, particularly when its crystal size is small (Golterman 1977, Smith *et al.* 1977, 1978, Premazzi and Zanon 1984), whereas nonapatite inorganic P does not predict the availability of P in wastewater (Young *et al.* 1982). Furthermore, Golterman *et al.* (1969), Grobler and Davies (1979, 1981), Klapwijk *et al.* (1982) and Grobbelaar (1983) found that no single chemical fraction represented potentially algal-available P satisfactorily. However, even if the fractionations do not give accurate information on the availability of P, they provide useful information on the potential mobility of P under different conditions.

In the methods quantifying desorption, a P gradient similar to that in the algal assays has been created by introducing a chemical P sink in a sample. For example, in the determination of reversibly adsorbed P, the P sink is provided by iron oxide coated filter papers (van der Zee *et al.* 1987). Reversibly adsorbed P is closely correlated with the P uptake of plants in pot experiments performed on Finnish mineral soils (Yli-Halla 1989, 1990, 1991) and with the number of cells of four common freshwater algal species produced in batch assays on agricultural runoff (Sharpley 1993a, b). The determination was proposed by Sharpley (1993a, b) as a convenient and interfer-

ence-free method to routinely estimate algal available P. Anion-exchange resins have also been widely used as P sinks (Amer *et al.* 1955, Wildung and Schmidt 1973, Cowen and Lee 1976, Cowen *et al.* 1978, Hanna 1989, Fabre *et al.* 1996), but the results obtained using resins have been suspected to underestimate desorption, possibly because the concentration of dissolved P maintained by the resin is not low enough (Sonzogni *et al.* 1982). On the other hand, Huettl *et al.* (1979) found a strong correlation between P retained by hydroxy-Al affixed to a cation exchange resin and available P determined by algal assays. Desorbable P has also been assessed by various techniques of isotopic exchange but the results obtained have not been compared with those from algal assays. It should be noted that the chemical methods with a short incubation time do not account for the release of available P by mineralisation.

1.5 Actual availability of phosphorus

Several investigators (Cowen and Lee 1976, Lee *et al.* 1980, Williams *et al.* 1980) have considered it unlikely that the conditions in receiving waters would be as favourable for P release as those in the algal assays. According to this view, the *actual availability* of P is lower than the potential availability determined by algal assays. However, as the true potentially algal-available P tends to be underestimated by the assays (see section 1.4.1), the opposite may also apply.

The conditions in receiving waters are usually most advantageous for the release of P during periods of high production. Provided that turbidity caused by suspended solids does not inhibit light penetration into the water column, the conditions at this time usually resemble those in the algal-assays: the concentration of dissolved orthophosphate is low, the water is slightly alkaline, temperature is relatively high and enzymes may enhance P release. However, the opposite is true for the seasons when most loading, particularly agricultural loading, enters surface waters. Therefore, a crucial factor controlling the release of available P from particulate matter is the residence time of particles in the photic zone (*e.g.* Lee *et al.* 1980, Williams *et al.* 1980, Kauppi and Niemi 1984). Although silt and clay particles, rich in P, settle slowly (Sonzogni *et al.* 1982), most particles that entered the lakes and coastal water during low pro-

ductive seasons may have settled out of the photic zone before the onset of algal production. However, sedimentation does not represent a permanent loss of P from the aquatic system. First, the matter settled on the bottom may be resuspended to the photic zone by wind-induced currents in shallow waters (Williams *et al.* 1980, Søndergaard *et al.* 1992). Second, P is also translocated in dissolved form from the bottom sediment to the aqueous phase.

Internal P loading is a complex function of physical, chemical and biological processes (Boström *et al.* 1982, 1988b). Mineralisation of organic P is the first and driving step in the benthic P cycling and sediment-water exchange processes (Boers *et al.* 1993). Under aerobic conditions, temperature, turbulence and bioturbation, NO_3^- , SO_4^{2-} , pH and organic matter are all important factors in P exchange (*e.g.* Andersen 1975, 1982, Lee *et al.* 1977, Lijklema 1977, Boström *et al.* 1982, 1988b, Caraco *et al.* 1989, Jensen and Andersen 1992). The exchange of P across the sediment-water interface usually increases when the surface sediment becomes anoxic (Boström *et al.* 1982, Knuutila *et al.* 1994). Anoxic conditions may induce (i) the reduction of Fe^{3+} to Fe^{2+} and a subsequent release of Fe-bound P (Einsle 1936, 1938, Mortimer 1941, 1942) or (ii) the release of P, stored as polyphosphates during the preceding aerobic conditions, by facultative anaerobic bacteria (Gächter *et al.* 1988). On the other hand, if Al is the main P-sorbing compound (Portielje and Lijklema 1993), the direct effect of reduced redox conditions is low. Aluminium may offer permanent storage of P in sediments (Portielje and Lijklema 1993).

1.6 Loss of phosphorus from agricultural land

Cultivated soils of Finland tend to be naturally poor in plant-available P (Hartikainen 1979). To improve their P-status, the use of chemical P fertilisers became common after World War II. However, not all of the P added has been utilised by plants; a substantial amount has also accumulated in the soil mainly as Al- and Fe-bound P (Hartikainen 1991). Accordingly, the P content of the surface soil has increased by approximately 30% from the period before intensive fertilisation (Saarela 1991, ref. Rekolainen 1993).

The loss of P from agricultural land is initiated by contact between rain or snowmelt water and the surface soil (see *e.g.* Logan 1982). This contact, and the subsequent transport of water over the surface of the field (*surface runoff*), detaches soil particles which are carried to a variable distance from the place of detachment. This process of *erosion* removes, in particular, the smallest particles and organic matter, which both tend to have a higher P content than the bulk of soil. Moreover, the contact between P enriched top soil and dilute water induces desorption of soil P. In addition, P from plant residues and sometimes from fertilizer granules may also be released (Schreiber and McDowell 1985, Turtola and Jaakkola 1995). The exchange of P between soil particles and water is largely governed by sorption-desorption reactions (*e.g.* Yli-Halla *et al.* 1995, Yli-Halla and Hartikainen 1996). Desorption of soil P is promoted by increase in the labile P content of soil and in the water-soil ratio (Sharpley *et al.* 1981a, b, Yli-Halla *et al.* 1995, Yli-Halla and Hartikainen 1996). Furthermore, the amount of desorbed P increases with the increase in the amount of contacting soil, *i.e.* as the depth of the interactive soil layer becomes deeper. This depth has been reported to depend on the slope of the field, soil aggregation, soil cover and rainfall intensity (Sharpley 1985). During the transport from field via ditches and rivers to larger bodies of water, the widening of the water-soil ratio favours further desorption of P from eroded soil particles. However, most P in agricultural rivers consists of P bound to eroded soil particles (*e.g.* Ekholm and Kallio 1996).

In addition to surface runoff, water as well as P is transported in the upper more permeable soil layer ('interflow') and by subsurface drainage. However, due to the low water conductivity of the clayey soils of southern Finland, surface runoff is a major transport mechanism in these soils (Seuna and Kauppi 1981, Bengtsson *et al.* 1992, Turtola and Paajanen 1995).

The DRP transport by surface runoff has been estimated using various models. Many of these are based on the empirical equation of Sharpley *et al.* (1981a, b, 1985). The equation predicts the DRP concentration in surface runoff from labile P and from other soil characteristics and from the effective depth of interaction, water-soil ratio and runoff volume of each runoff event. The Sharpley equation was developed for conditions in the southeastern USA, and has been tested only to a limited ex-

tent outside the USA. Thus, its applicability under the climatic and edaphic conditions of intensively cultivated regions of southern Finland is unclear.

1.7 Objectives of this study

The major objectives of this study were to improve the understanding of the algal utilisation of P originating from agriculture and municipalities, and to determine the sources of algal available P. Understanding algal utilisation of P and the sources of this P will contribute directly to the control of eutrophication. More specifically, the aims were to answer the following questions:

- By which experimental techniques can the potentially algal-available P be reliably determined?
- Is it possible to approximate the potentially algal-available P by simple routine P analyses?
- What proportion of P in agricultural runoff and purified municipal wastewaters is potentially available to algae?
- What are the origins of algal-available P in agricultural runoff and can the P loss be estimated by a simple model?
- To what extent is potentially available P actually released in receiving waters?

2 Materials and methods

2.1 Analysis of phosphorus

In the analysis of TP, various inorganic and organic P forms were first digested by potassium peroxodisulphate in a solution made acid with sulphuric acid (Fig. 1). After digestion, P was analysed spectrophotometrically by a modification of the molybdenum blue method (Murphy and Riley 1962). Reactive P (III) was analysed similarly to TP but without digestion (see Krogstad and Løvstad 1989). Dissolved P and dissolved reactive P were analysed from a filtered sample; in DP analysis the sample was digested before the staining, whereas DRP was determined without the digestion. Particulate P was obtained as TP minus DP and DUP as DP minus DRP. All suspensions used in the algal assays (except I) were diluted 1:4 to 1:20 with distilled water prior to TP analysis (see Turtola 1996). Detection limits for P were 2

$\mu\text{g l}^{-1}$ (I, II, VI, VII) or $1 \mu\text{g l}^{-1}$ (III, V). The procedure above has been used in Finland since 1986, is detailed by the Finnish Standards Association SFS (1986a, b) and is essentially the same as the European standard EN 1189 (European Committee for Standardization 1996). The TP data examined in VI also covered six earlier years when a method with approximately 50% lower concentration of sulphuric acid was used. According to the Finnish Standards Association SFS (1986b), both methods give similar results for TP. This must be considered cautiously as Turtola (1996) found that the TP values for waters with appreciable soil increased when a still higher concentration of acid was used as proposed by the current method. The TP content of soil samples (III) was analysed by means of digestion with salicylic acid, sulphuric acid and sodium thiosulphate, followed by P analysis using the molybdenum blue method (Ahl and Lindeval 1974).

Most samples were turbid. As turbidity distorts absorbance readings, a blank consisting of the

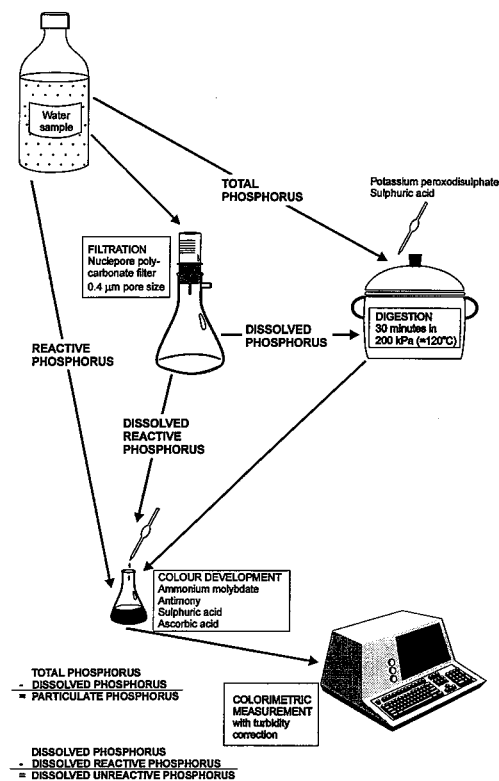


Fig. 1. Diagram of the analysis of P in water samples.

sample and modified reagent was included in all P analyses. In the modified reagent, distilled water replaced ammonium molybdate and antimony and so no colour development occurred. The absorbance of the blank was subtracted from the absorbance of a sample treated with full colour reagent.

In I, II, III, V and VI, total suspended solids (TSS) were determined gravimetrically according to Finnish Standards Association SFS (1996), except for the filters used (see below). In addition, no effort was made to keep the filtration time below 1 min, and usually the time exceeded 1 min. In VII, total suspended solids were analysed as evaporation residue. The P content of suspended solids was calculated by dividing PP by TSS.

In this work, Nuclepore polycarbonate filters with $0.4 \mu\text{m}$ pore size were predominantly used in filtrations. These filters are P-free and they efficiently retain suspended solids from a variety of natural waters (Hirvikallio *et al.* 1979, Pietiläinen and Rekolainen 1991, Turtola 1996). In addition, as the filters are light and stable and do not include soluble matter, they are advantageous for TSS analysis (Hirvikallio *et al.* 1979). Dissolved reactive P in the runoff from the Jokioinen (Kotkanoja) field was analysed by Nuclepore filters of $0.2 \mu\text{m}$ pore size. In addition, in the determination of reversibly adsorbed P, Sartorius nitrocellulose filters of $0.2 \mu\text{m}$ pore size were used for concentrated river water samples.

2.2 Determination of algal-available phosphorus

2.2.1 Samples

Algal-available P was determined from (Table 1):

- A total of 22 water samples from 8 rivers situated in southern Finland (Table 2). All the rivers drain areas with high proportions of agricultural land (22–43%) on fine textured soils (mainly clay or silt). The loads originating from point sources were small in all the rivers. The samples tested in papers I and II were taken during October–May in 1988–1990. The samples from the three rivers discharging into lake Pyhäjärvi (R. Luhtoja, R. Pyhäjoki, R. Yläneenjoki) were taken in May–September 1992. Some of the river water samples were also used in the sorption-desorption studies.

Table 1. Samples tested for algal-available P using dual culture assays (DCA), batch assays (BA) or determination of reversibly adsorbed P (P_{REV}).

Sample type	Number of samples	Pretreatment	Test method	Reference
River waters				
R. Haltiajoki	3	None	DCA, P_{REV}	I, II
R. Lanskinjoki	2	None	DCA, P_{REV}	I, II
R. Lirinoja	1	Concentration ¹	DCA, P_{REV}	I, II
R. Litinjoki	2	None	DCA, P_{REV}	I, II
R. Luhtoja	1	None	DCA	This study
R. Paimionjoki	8 ²	Concentration ¹ /None	DCA, P_{REV}	I, II
R. Pyhäjoki	2	None	DCA	This study
R. Yläneenjoki	3	None	DCA	This study
Total	22			
Lacustrine particles				
L. Lappajärvi	1	None	DCA	I
L. Villikkalanjärvi	1	None	DCA	I
Total	2			
Surface soils				
Aurajoki field	4	Drying, remoisturing	DCA, BA	III
Jokioinen field	3	None	DCA, BA	III
Total	7			
Municipal wastewaters				
Hämeenlinna	1	None	DCA	V
Lavia	4	None	DCA	V
Luopioinen	5	None	DCA	V
Pälkäne	5	None	DCA	V
Tampere	5	None	DCA	V
St Petersburg	10	None	DCA	This study
Total	30			
Grand total	61			

1 = By centrifuging, microfiltration or ultrafiltration.

2 = Of which 7 were tested with dual culture assays and 6 using P_{REV} -determination. One sample was included in the P_{REV} -determination but not in the algal assays.

- Two samples of lacustrine particles from agriculturally loaded lakes (I). Surface sediments were cored in lake Lappajärvi (central Finland) from a bottom area sensitive to resuspension in May 1991. Settling matter, which represented mainly resuspended bottom sediments, was collected by sedimentation traps from lake Villikkalanjärvi (southeastern Finland) in October 1990.
- Seven surface soil samples (0–10 cm) from two experimental fields situated in southern Finland (Table 3, III). Four samples were taken from plots under different cultivation practices at the Aurajoki field in June–August 1993, and one sample was taken from a field under cultivation and two from an agricultural buffer strip at the Jokioinen (Lintupaju) field in June 1995.
- A total of 20 one-day composite samples taken in proportion to flow from the final effluent streams of five Finnish municipal wastewater treatment plants in 1993–1995 (Table 4, V). All the plants had an activated sludge system and simultaneous P precipitation with $FeSO_4$. Two of the plants also had a post precipitation unit based on Al or combined Al–Fe chemicals. The other plants had wastewater nitrification.

Table 2. Characteristics of the rivers examined (I, Malve *et al.* 1994, Kähäri *et al.* 1987).

River	Mean discharge $\text{m}^3 \text{ s}^{-1}$	Drainage basin		
		Area km^2	Agricultural land	
			Proportion %	Soil type
R. Haltiajoki	1.2	125	27	Sandy clay, silt
R. Lanskinjoki	2.2	232	37	Sandy clay, silt
R. Lirinoja	–	6	22	Sandy clay, silt
R. Litinjoki	0.3	36	39	Sandy clay, silt
R. Luhtoja ¹	–	8	23	Silty clay
R. Paimionjoki	9.9	1088	43	Gyttja clay, sandy clay
R. Pyhäjoki	0.8	78	23	Silt, sand
R. Yläneenjoki	2.5	234	27	Silt, gyttja clay, sandy clay

1 = Figures refer to the area above the sampling point, which was situated in the lower reaches of the river.

Table 3. Characteristics and treatments of the experimental fields examined. The Aurajoki field was detailed by Puustinen (1994), the Jokioinen, Lintupaju field by Uusi-Kämpö and Ylänta (1996) and the Jokioinen, Kotkanoja field by Turtola and Paajanen (1995).

Field	Surface soil	Plots included in this study
Aurajoki ¹ 60°29'N, 22°22'E	Clay loam	A6: Ploughed in autumn, harrowed and sown (wheat) in spring A3: Ploughed, harrowed and sown (wheat) in autumn A7: Tillage with spring tooth harrow in autumn and spring, sown (wheat) in spring A4: No tillage in autumn, tillage with spring tooth harrow and sown (wheat) in spring
Jokioinen, Lintupaju 60°48'N, 23°28'E	Silty clay	J1: Grass buffer strip J2: Barley, normal ploughing + fertilisation J3: Vegetated buffer strip
Jokioinen, Kotkanoja ¹ 60°48'N, 23°29'E	Silty clay	1, 9: Ploughed in autumn after 2-year grass, sown with barley next spring, ploughed in the following autumn 5, 13: Grass killed with glyphosate, sown with barley next spring, no tillage in the following autumn

1 = All plots fertilised.

- Finally, ten one-day composite samples from two large municipal wastewater treatment plants in St Petersburg (Russian Federation) were tested. These plants (northern and central wastewater treatment plant) perform only biological purification. The samples were taken in 1996–1997. The results concerning the Russian plants are examined only in section 3.3. Table 5 shows the concentrations of the P fractions in the above samples.

Pretreatments

River waters were stored in the dark at 4 °C for 0.5 to 15 months until they were concentrated or used in the tests. Suspended solids were concentrated from 8 samples (7 from the river Paimionjoki and 1 from the river Lirinoja) by centrifugation, microfiltration or ultrafiltration (Table 1, I). All techniques allowed the concentration of the suspended solids in their original solution without drying. The concentrates were stored 8 to 13 months in the dark at 4 °C until used in the tests.

Table 4. Characteristics of the treatment plants examined.

Plant	Population equivalents ¹	Purification process	Reduction during purification	
			Total P %	Total N %
Hämeenlinna	62 000	Simultaneous precipitation with FeSO ₄ , nitrification	93	42
Lavia	1 300	Simultaneous precipitation with FeSO ₄ , post-precipitation with Al ₂ (SO ₄) ₃	87	35
Luopioinen	500	Simultaneous precipitation with FeSO ₄ , nitrification	98	34
Pälkäne	1 900	Simultaneous precipitation with FeSO ₄ , post-precipitation with FeSO ₄ + Al ₂ (SO ₄) ₃	94	27
Tampere	166 000	Simultaneous precipitation with FeSO ₄ , nitrification during summer	95	36

1 = Based on total P in effluent.

Table 5. Characteristics of the samples tested for algal-available P. PP = particulate P, DRP = dissolved reactive P, DUP = dissolved unreactive P, TSS = total suspended solids.

Sample type	PP	DRP μg l ⁻¹	DUP	P content of TSS mg g ⁻¹
River waters	35–360	12–69	0–14	0.9–3.9
Municipal wastewaters				
Finnish plants ¹	69–510	1–90	18–54	4.9–21
Russian plants	55–2600	140–1400	0–620	–
Lacustrine particles	.	.	.	1.3–2.2
Soil samples	.	.	.	1–1.8

1 = Subsets of undiluted samples were analysed for P fractions.

The concentration step was later omitted because of possible artefacts (I). The sample of settling matter was tested after 7 months of storage, whereas the sample of bottom sediments was tested three days after the sampling.

The Aurajoki soils were air-dried, homogenised, rewetted to a moisture content of 20% and stored at 5 °C for almost 2 years before the algal assays. The Jokioinen soils were ground but other-

wise untreated before being used in the assays one week after the sampling. The effluent samples from the Finnish municipal treatment plants were transported to the laboratory within a few hours after the sampling. They were stored in the dark at 4 °C for no more than two days before testing. The samples from St Petersburg were transported within three days to the laboratory and were tested within two weeks after the sampling.

2.2.2 Dual culture assays

Potentially algal-available P (papers I, III, and V) was determined with a technique originally designed for quantification of the gross rates of pollutant transfer between particles and water (DePinto *et al.* 1981, DePinto 1982). In the technique, outlined in Fig. 2, a P-starved unaxenic culture of *Selenastrum capricornutum* Printz and a P-carrying sample were incubated in a two-chambered vessel (Fig. 3), separated by a Nuclepore polycarbonate membrane (0.4 μm pore size). The vessels were incubated on a shaking table (20 ± 1 °C, 4200 ± 200 lux) for 2 to 4 weeks. After each week (in paper I also after the first 3 days) the algal culture was replaced by a fresh P-starved culture. The fresh and harvested cultures were analysed for P. After the experiments, the darkened sample chambers were also emptied and the contents were analysed. Control vessels were treated as the other vessels, but instead of a sample, K_2HPO_4 and P-free nutrient medium were added into the sample chamber. The modifications of the original method applied in this study were (see I): (i) aeration of the assay chamber to prevent CO_2 deficiency, and (ii) buffering of the system at pH 7 or 8 by Tris (tris(hydroxymethyl)-aminomethane). Tris in the applied concentration (2 mmol l^{-1}) did not interfere with P determination or markedly inhibit algal growth (I). The assays, except the controls, were mostly performed in duplicate.

The concentrated river waters, lacustrine particles, soils and most wastewater samples were suspended in/diluted with P-free nutrient medium to decrease the P concentration to an appropriate level (often approximately $200 \mu\text{g l}^{-1}$). The possible toxicity of concentrated river waters was ruled out by testing them with a Microtox method (Ribo and Kaiser 1987). The toxicity of other samples was not tested but no indications of toxicity were observed.

Potentially algal-available TP was assumed to equal the cumulative amount of P taken up by the algae during the assay. The P uptake was determined from the increase in PP in the algal suspension during each harvest. The availability of DRP and DUP was approximated from the changes in the concentration of these P fractions in the vessels. If the amount of P taken up by the algae exceeded the amount of algal-available DRP and DUP, the rest of the algal-available P was assumed to have originated from the PP pool.

1. PREPARATION OF A P-STARVED ALGAL CULTURE

a. Inoculation with algal culture



Nutrient medium with $20 \mu\text{g l}^{-1}$ P

b. Incubation



4200 ± 200 lux
 20 ± 1 °C

c. Dilution 1:2 with P-free nutrient medium



2. INCUBATION for 2 - 4 weeks, with weekly harvests



4200 ± 200 lux
 20 ± 1 °C
pH 7 or 8

3. HARVESTS Analysis of fresh and harvested algal culture



4. TERMINATION Analysis of the contents of the sample chamber



5. CALCULATION OF RESULTS

The total amount of P utilised by algae equals the cumulative increase in particulate P in the assay chamber

$$\frac{\text{TP} - \text{DP}}{\text{PP}}$$

Fig. 2. Procedure employed in the dual culture assays.

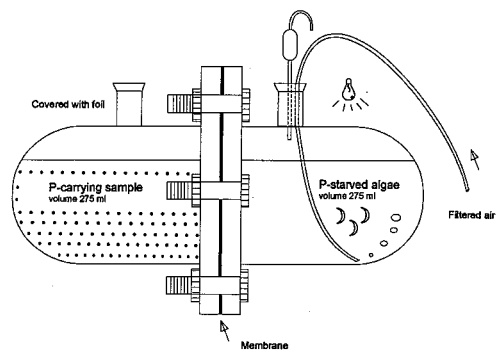


Fig. 3. Two-chambered vessel used in the dual culture assays.

The use of at least two algal cultures in each test enabled the approximation of the kinetics of P release (III, V). The long-term availability of P was estimated by assuming that ultimately available P (P_0) was converted into available form according to the first-order kinetics (DePinto 1982, Young *et al.* 1982):

$$P_a(t) = P_0(1 - e^{-kt}) \quad (1)$$

where P_a is the amount of P taken up by the algae during t days and k the rate at which P becomes available. The values of P_0 and k were determined by the method of least squares of regression. Prior to the actual tests, the P exchange and algal P uptake in the vessel were studied by diffusion experiments (see DePinto 1982).

In paper V, the differences in available P between the treatment plants were tested by one-way analysis of variance (ANOVA). When ANOVA showed a difference between the means, Duncan and Waller-Duncan multiple comparison tests were used for grouping the plants. A significance level of $P = 0.05$ was used in all comparisons.

2.2.3 Batch assays

From the soil samples, algal-available P was also estimated using batch assays (III, Fig. 4). The batch assays were started by pipetting 7-day algal culture of *Selenastrum capricornutum* Printz into Erlenmeyer flasks containing soil suspension or nutrient medium with K_2HPO_4 (the controls). The flasks were incubated for 2 to 3 weeks under conditions similar to those used in the dual culture assays (3 replicates). After each week, the number of algal cells was counted (no growth of indigenous algae was observed). Algal-available P was calculated from a regression equation determined earlier between algal cell number and P in a set of solutions containing 0 to $100 \mu g l^{-1}$ P as K_2HPO_4 (Fig. 5). The difference between the results given by batch assays and dual culture assays were tested by ANOVA. The nutrient medium used in the batch and dual culture assays was 5% Z8 (Kotai 1972).

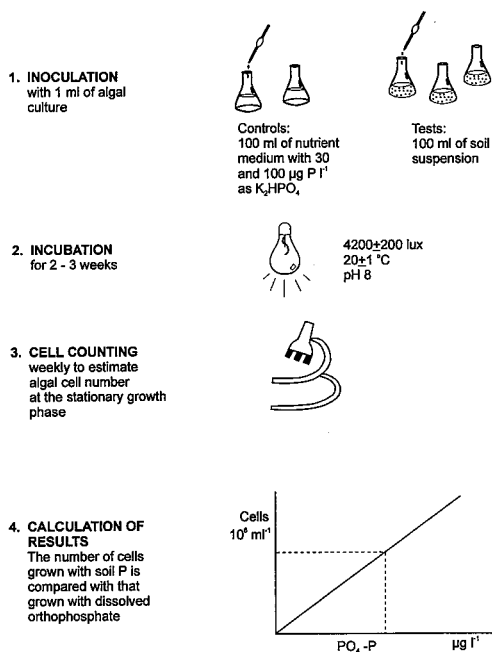


Fig. 4. Procedure employed in the batch assays.

2.2.4 Determination of reversibly adsorbed phosphorus

Reversibly adsorbed P was determined according to the principles described by van der Zee *et al.* (1987) from 14 river water samples, of which 13 were also tested with dual culture assays (II). In the determination, the samples were incubated with filter paper strips impregnated with freshly precipitated ferric hydroxide. When testing nine unconcentrated samples, 160 ml of a sample was incubated both with one and with two filter paper strips (2 replicates), whereas in the tests of five concentrated samples, a sample volume of 40 ml and three strips were used (3 replicates). The samples with strips were shaken for one hour and allowed to stand overnight. After further shaking (10 min), the filter papers were removed, washed with distilled water to remove attached particles and extracted for one hour with 40 ml of 0.1 M sulphuric acid, which dissolved the Fe-hydroxide coatings. Extracts were filtered and analysed for DP. The Sartorius filters, used in the filtering of concentrated samples, were found to be a potential source of P. In each separate test series, two

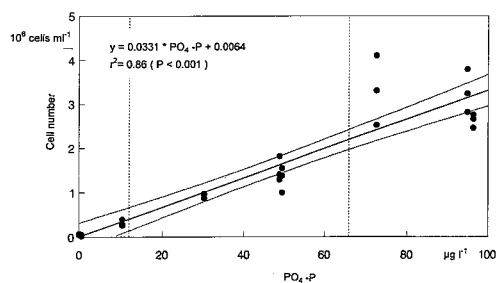


Fig. 5. Algal cell number as a function of the concentration of dissolved orthophosphate. The broken lines show the calculated range of P released by the tested soil samples.

control samples containing distilled water were also shaken with filter paper strips. The DP of the control samples was subtracted from the DP of the test samples. Thus, the errors caused by the potential P release from the Sartorius filters were at least partly corrected. The determinations of reversibly adsorbed P were performed within 6 months of the algal assays. The results of the tests performed using one filter paper strip were omitted, as it was suspected that one strip did not have sufficient capacity to sorb P (see II).

2.3 Sorption-desorption experiments

The actual release of the potentially algal-available P was assessed by P retention experiments conducted on 6 concentrated river waters. The waters were diluted with cold (4 °C) autoclaved P-free nutrient medium buffered either to pH 7 or to pH 9 with Tris. The suspensions were transferred into Erlenmeyer flasks and standard KH_2PO_4 solution was added to obtain initial P concentrations of 0, 10, (20), 30, 50, (100) and 150 $\mu\text{g l}^{-1}$. The suspensions were left standing in the dark at 4 °C (to minimize biological P uptake) for 1 and 24 hours. Before the end of the incubation the suspensions were shaken for 10 minutes, after which they were filtered for DRP determination. Two control flasks with nutrient medium and 30 and 150 $\mu\text{g l}^{-1}$ of P were treated similarly. Net sorption or desorption was calculated from the changes in the DRP concentration occurring during incubation. The P exchange by samples was expressed as a Freundlich adsorption isotherm as modified by Fitter and Sutton (1975):

$$Y = aX^b - c \quad (2)$$

where Y is sorbed or desorbed P (mg kg^{-1}), X the concentration of DRP ($\mu\text{g l}^{-1}$) in suspension after incubation and a , b and c the constants fitted by the method of least squares of regression. The intersecting point of the sorption-desorption graph on the x-axis ($Y = 0$) represents the zero point of P exchange, *i.e.* the EPC.

2.4 Lake phosphorus balance

The actual availability of P was also assessed by examining the P balances of lake Pyhäjärvi (Fig. 6), an agriculturally loaded shallow lake in south-western Finland (VI). The mean summer algal biomass of lake Pyhäjärvi is 0.88 mg l^{-1} (Table 6), which indicates incipient eutrophy (Heinonen 1980). Sediment studies have shown that the lake became more productive in the late 1950s, probably in response to increased nutrient supply from agriculture (Räsänen *et al.* 1992). Currently, field cultivation and animal husbandry comprise 55% of the external P load to lake Pyhäjärvi. The rest of the load originates from atmospheric deposition to the lake (20% of the P load), forestry practices, the sparse population and summer cottages. Internal load is an important P source in lake Pyhäjärvi.

Table 6. Characteristics of lake Pyhäjärvi and its drainage basin. Data from Malve *et al.* (1994) and Sarvala *et al.* (1994).

Lake Pyhäjärvi	
Surface area (km^2)	154
Mean depth (m)	5.4
Maximum depth (m)	26
Water residence time (a)	3
Mean external load ($\text{g m}^{-2} \text{a}^{-1}$)	0.14 P, 3.4 N
Secchi depth (m)	2–5
Mean algal biomass (mg l^{-1})	0.88
Mean concentration of chlorophyll a ($\mu\text{g l}^{-1}$)	5.5
Fish catch (kg ha^{-1})	34
Drainage basin area (km^2)	
Total (including the lake)	615
R. Yläneenjoki	234
R. Pyhäjoki	77.5
Unmonitored area	149.5

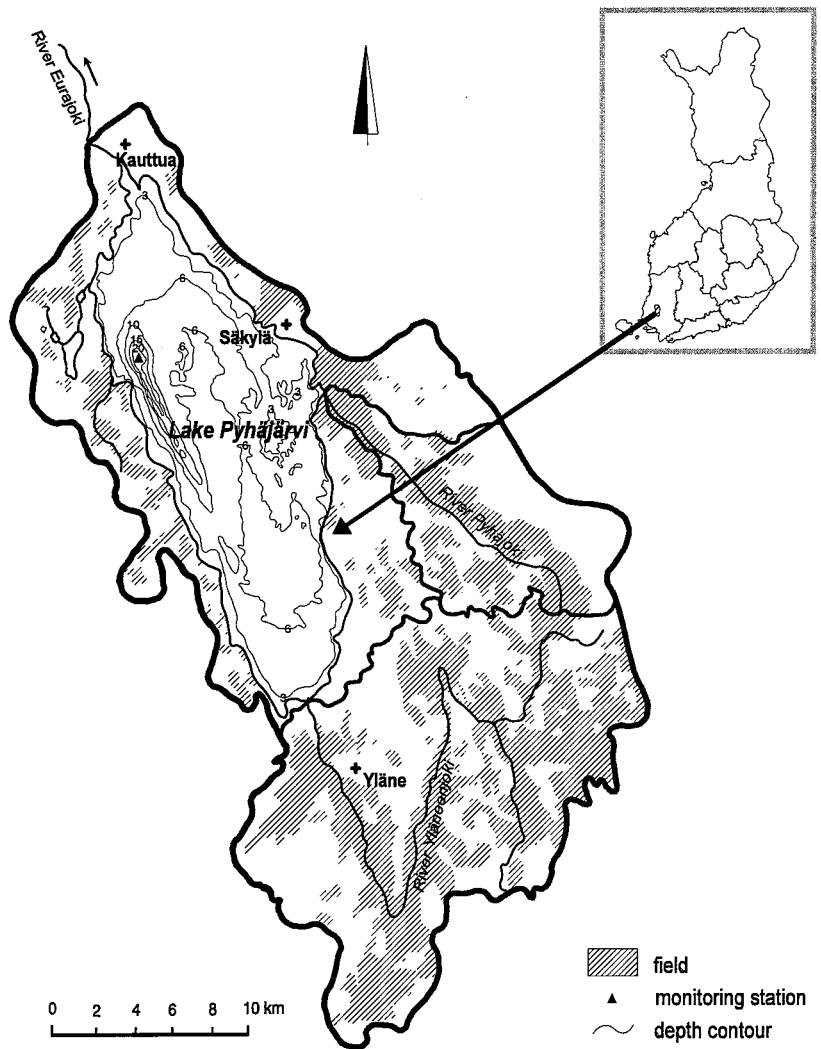


Fig. 6. Lake Pyhäjärvi and its drainage basin.

The lake is open and shallow and is thus sensitive to wind-induced resuspension during the ice-free period. Furthermore, the deepest part of the lake becomes anoxic in winter.

Two P balances for the lake were estimated: a long-term balance of TP for the years 1980 to 1992, and a more detailed balance, which included the P fractions, for 1992. The long-term balance was based on river fluxes, atmospheric deposition, outflow, nutrient removal in the fish catch and

storage changes in the lake (VI). In addition to these factors, the detailed balance was based on sedimentation measurements (Huttula 1994, Krogerus, unpublished data) and algal assays (Krogerus and Ekholm, unpublished data). The water quality data was based on monitoring of the lake and the incoming and outflowing rivers, carried out by the Southwest Finland Regional Environment Centre and the Water Protection Association of Southwestern Finland. The rivers Ylä-

neenjoki and Pyhäjoki (Table 2), which cover 68% of the drainage basin, were monitored at least once a month with additional samples taken during the spring and autumn floods (13–54 samples annually). The outlet, the river Eurajoki, was sampled 10 to 50 times a year. Composite or grab water samples were taken from the central deep of Pyhäjärvi 1 to 4 times a month during the ice-free period and once during the ice-covered period (in March). The water quality at the central deep represents rather well the general quality of water in lake Pyhäjärvi (Malve *et al.* 1994).

The river fluxes were calculated as the sum of the product of mean monthly flow and mean monthly flow-weighted concentration (see *e.g.* Ekholm *et al.* 1995). From all the rivers, daily discharges were taken from the hydrological data base of the Finnish Environment Institute (FEI). The load from the unmonitored area, which comprised 32% of the drainage area (Table 6), was approximated from the specific nutrient loss in the Pyhäjoki basin (see Sarvala and Jumppanen 1988). Atmospheric deposition onto the lake surface was estimated from the bulk deposition measurements made at three stations adjacent to the lake: Oripää, Jokioinen and Peipohja (data from the deposition data base of the FEI). The amount of P removed from the lake with the fish catch (consisting mainly of vendace and whitefish) was estimated by multiplying the nutrient contents of the main fish species (Jumppanen 1983) by the estimated mean catch.

In the detailed balance, the mean internal load (*IL*) of TP and TSS for the ice-free period was estimated as follows:

$$IL = O + GS + dM/dt - I \quad (3)$$

where *O* is outflow, *GS* is gross sedimentation, *dM/dt* is the storage change and *I* is input. The mean gross sedimentation was estimated from the sedimentation measurements and the mean P content of the settling matter.

2.5 Modelling of the concentration of dissolved reactive phosphorus in field surface runoff

The concentration of DRP in surface runoff was assessed using the Sharpley equation (VII). The equation was applied to two clay-textured experi-

mental fields (Aurajoki and Jokioinen, Kotkan-oja) located in an intensively cultivated region of southwestern Finland. The soils of both fields contained high proportions of clay, showed the presence of a udic moisture regime (Soil Survey Staff 1996) and were classified as Vertic Cambisols (Food and Agriculture Organization 1988) or very fine, mixed Typic Cryaquepts (Soil Survey Staff 1996). However, the soils differed in their labile P content (Table 7). From the Aurajoki site (see Puustinen 1994) four plots were chosen, which had the following cropping-tillage conditions: one spring wheat and one winter wheat plot under conventional tillage, one spring wheat plot under reduced tillage and one untilled spring wheat plot (Table 3). The data used here were for the years 1990 to 1993. The Jokioinen site (see Turtola and Jaakkola 1995, Turtola and Paajanen 1995) consisted of four plots, which had been under grass for two years prior to the

Table 7. Labile P in the soils of the experimental fields included in the modelling efforts.

Field plot	Bray I extraction ¹	Water extraction ²		
		0–10 cm mg kg ⁻¹	0–10 cm 10–25 cm mg kg ⁻¹	
Aurajoki				
A6	66	17	16	16
A3	55	15	14	14
A7	66	23	16	19
A4	69	21	14	17
Jokioinen				
1	23	4.3	2.7	3.3
9	29	2.7	2.8	2.7
5	21	4.7	1.8	3.0
13	27	3.0	1.9	2.3

1 = Determined by shaking 2 g dry soil with 14 ml of 0.03 M NH₄F and 0.025 M HCl for 1 min followed by filtration (Schleicher&Schuell blue ribbon or Whatman 42 filters) and DRP analysis (Bray and Kurtz 1945).

2 = Determined by shaking moist soil (corresponding to 1 g of soil dry matter) with 50 ml of deionized water for 1 hour, after which the suspension was allowed to stand for 17 hours and finally shaken for a further 10 min followed by filtration (using 0.2-µm Nuclepore polycarbonate filters) and DRP analysis (Hartikainen 1982b).

experiments. During the first experiment (from autumn 1993 to spring 1994), two of the plots were ploughed and compared with two plots left untilled after the grass had been killed with glyphosate. During the second experiment (from spring 1994 to early summer 1995), all four plots were sown with spring barley, after which two of the plots were ploughed the following autumn and two were left untilled (Table 3). These two experiments are referred to hereafter as the grass and barley experiments.

Most of the soil data used in the modelling was that detailed by Yli-Halla *et al.* (1995) and consisted of various determinations performed on samples taken from the 0–10 and 10–25 cm (or 10–20 cm) soil layers in May–August 1993. Samples were air-dried and homogenised, and an aliquot was rewetted to a moisture content of 20% and stored at 5 °C.

The runoff data were taken from experiments measuring the effects of various cultivation practices on nutrient losses (Puustinen 1994, Turtola and Puustinen 1998). At Aurajoki, water from 0–10 and 10–30 cm soil layers was collected separately with a dual-level collector, designed for obtaining the 'plough' layer runoff from the plots. The collectors were placed in a trench dug at the lower edge of each experimental plot. The two soil layers were separated by steel dividers pushed to a depth of 6 cm in the untreated soil. The water from the plots were lead through the collectors into an observation cabin for runoff volume measurement and sampling. For the volume of 'surface runoff' at Aurajoki, the sum of water collected from both layers was used. Correspondingly, the flow-weighted mean concentration of DRP in these two layers was used in the modelling calculations. At Aurajoki, surface runoff accounted for $\geq 75\%$ of the total runoff volume (Puustinen, unpublished data). At Jokioinen, surface runoff was collected in an open ditch at the lower edge of the plot and lead to an observation cabin. Surface runoff accounted for 26 to 81% of the total runoff volume and for a somewhat higher percentage of the total DRP loss (Turtola, unpublished data). The volume of runoff at both sites was measured with tipping buckets. At periods of appreciable runoff, the cumulative runoff volume was recorded several times a week. A portion of the total discharge was collected in plastic containers in proportion to the flow. Samples were stored prior to transfer to the laboratory (< 10 °C) for no longer than 4 d. In the

laboratory, samples were stored at 4 °C for no more than 7 d before the analysis. The number of cumulative water samples was 15 to 20 per winter period at Aurajoki, 30 to 32 in the grass experiment, and 50 to 53 in the barley experiment at Jokioinen. In the modelling calculations, the mean concentrations of DRP and TSS are mean flow-weighted concentrations during the observation period.

The equation of Sharpley *et al.* (1985) predicts the concentration of DRP (mg l^{-1}) in surface runoff as follows:

$$\text{DRP} = \frac{K_B P_D (\text{EDI}) D_b t^\alpha W^\beta}{V} \quad (4)$$

where P_D is desorbable P in soil (mg kg^{-1}), EDI is the depth of the interactive soil layer (mm), D_b is bulk density (g cm^{-3}), t is duration of the runoff event (min), W is water-soil ratio ($\text{cm}^3 \text{g}^{-1}$), V is surface runoff volume (mm) and K_B , α and β are constants for each soil. In this study, the equation was applied according to the approach of Sharpley and Smith (1989). In their approach, t was set to 30 min, EDI was calculated from soil aggregation (SA) and from erosion (E , kg ha^{-1}) by an equation presented by Sharpley (1985):

$$\ln \text{EDI} = -3.13 + 0.071 SA + 0.5761 \ln E \quad (5)$$

and W was derived from the ratio between runoff volume and erosion:

$$W = \frac{V 10^4}{E} \quad (6)$$

Note that W is the reciprocal of TSS concentration, *i.e.* $W = 10^6/\text{TSS}$, when TSS is given in mg l^{-1} . Furthermore, the coefficients K_B , α and β were calculated from the ratios of clay and organic C in soil using the equations given by Sharpley (1983):

$$K_B = 0.630 \left(\frac{\text{clay \%}}{\text{org. C \%}} \right)^{-0.698} \quad (7)$$

$$\alpha = 0.815 \left(\frac{\text{clay \%}}{\text{org. C \%}} \right)^{-0.540} \quad (8)$$

$$\beta = 0.141 \left(\frac{\text{clay \%}}{\text{org. C \%}} \right)^{0.429} \quad (9)$$

Table 8. Values of some input variables for the Sharpley equation.

Field plot	Clay ¹ %	Org. C ^{1,2} %	Bulk density ^{1,3} g cm ⁻³	Aggregation ^{1,4}	Runoff ⁵ mm	Erosion ⁵ kg ha ⁻¹
Aurajoki						
A6	42	3.4	1.1	14	200	2600
A3	35	3.4	1.1	–	190	1300
A7	46	3.8	1.1	–	210	1800
A4	38	3.4	1.1	–	120	360
Jokioinen						
1	66	2.8	1.2	–	88	520
9	61	2.8	1.2	–	77	390
5	59	2.5	1.2	14	140	200
13	53	2.4	1.2	–	160	270

1 = Layer 0–25 cm at Aurajoki and 0–20 cm at Jokioinen.

2 = Assuming that the carbon content of organic matter is 58%.

3 = Estimated from the soil type (Ervö 1970) at Aurajoki, measured at Jokioinen.

4 = Determined as the ratio of the proportion of clay-sized matter (< 2 µm) in dispersed and undispersed samples (Sharpley *et al.* 1985). Analysed only for one plot in each field and assumed to be the same in other plots.

5 = Mean of the three winter periods at Aurajoki, and of the grass and barley experiments at Jokioinen.

Finally, P_D was estimated by Bray extraction. Table 8 shows the values of some input variables of the Sharpley equation. In this study, a series of modifications was also made to the equation. In these, P_D was assessed by water extraction.

To facilitate the analysis of the Sharpley equation, it was reduced and re-organised as follows (VII):

$$\text{DRP} = A \times B \quad (10)$$

$$A = K_B P_D D_b t^\alpha 10^{6\beta-1.152} e^{-3.13+0.071SA} \quad (11)$$

$$B = \text{TSS}^{0.576-\beta} V^{-0.424} \quad (12)$$

where A denotes the term constant for each soil and B the term related to each runoff event. The term t^α is included in A , because t was set to 30 min.

The main interest was to assess whether the Sharpley equation can correctly predict the mean concentration of DRP in surface runoff from treatments under different management practices. Thus, for each treatment the flow-weighted mean of the simulated concentrations was calculated and

compared with the corresponding observed mean concentration. In the evaluation of model fit, and in all other statistical evaluations, a level of $P = 0.05$ was used as a minimum level for significant correlation.

3 Results and discussion

3.1 Determination of potentially algal-available phosphorus

The experimental setup strongly affects the results obtained in studies dealing with the available forms of nutrients such as P (Lee *et al.* 1980, Hegemann *et al.* 1983). In this section, the methodological factors related to the measurement of potentially algal-available P are discussed. First, the choice between batch and dual culture assays is examined. Second, the degree to which true potentially algal-available P can be estimated from algal assays is discussed. Finally, the possibility of using the determination of reversibly adsorbed P as a surrogate for the algal assays is assessed.

3.1.1 Effect of direct contact between algae and particles on phosphorus release

For 5 out of 7 soil samples tested with both techniques, the dual culture assays gave higher values for the potentially algal-available P than the batch assays (Fig. 7, III). Only for one sample did the batch assay give a clearly higher result. Although the variation in the replicates was high in both assays, the difference between the results obtained by the two techniques was statistically significant ($P < 0.05$). The comparison indicates that direct contact between algae and particles does not enhance the release of available soil P, at least not to such an extent that it would override the effects of other experimental factors (III).

To my knowledge, the hypothesis that algae could utilise P more efficiently when in direct contact with particles has never been explicitly demonstrated. Grobler and Davies (1979) proposed restriction of physical contact between particles and algae as a possible reason why their batch assays (which allowed full contact) gave higher values for algal-available P in bottom sediments than the assays performed by Golterman (1977) in which sediments were mixed in agar. Furthermore, the statement of Williams *et al.* (1980) that 'algae can utilise some of the P present in geological materials [sedimentary matter in the Laurentian Great Lakes] provided that the cell population has direct access to the source of P' was inferred from the difference between the results of batch assays performed by the authors themselves and many others and those of Fitzgerald (1970b), who separated algae from lake muds by a dialysis membrane and obtained poor or no algal growth. Furthermore, Hegemann and Keenan (1985) also concluded in their review article on watershed P, that 'maximum values of algal-available P are achieved in assays where soil samples are in direct contact with algae'. The conclusion was also drawn from the observation that the batch assays tend to give higher values than assays in which soils have been enclosed within dialysis tubing or mixed within agar.

Whether or not direct contact regulates P availability depends on the mechanisms by which available P is released from particles. The proposed mechanisms include desorption and dissolution reactions and degradation of organic matter. Desorption and dissolution are induced primarily

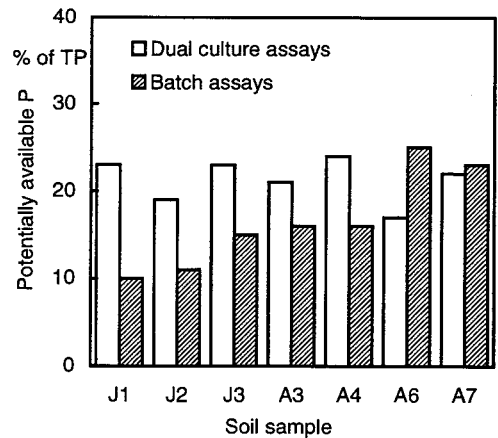


Fig. 7. Potentially algal-available P in soil as estimated by dual culture assays and batch assays.

by physical and chemical reactions, but algae indirectly affect them by modifying the environment. For example, algal growth maintains the concentration gradient between solid and dissolved phases and affects the solution pH. In addition, algae may secrete organic substances which may promote release of sorbed P (Grobbehaar 1983). Furthermore, Ellis and Stanford (1988) suggested the mobilisation of P to be mediated by a redox gradient created by heterotrophic bacteria attached to the particle surfaces. According to this hypothesis, mobilised P is initially incorporated in bacterial cells but eventually released into solution as bacterial metabolites. As all these effects are mediated via the solution phase, they should occur in batch as well as in dual culture assays. On the other hand, when examining the availability of P in natural apatites to several freshwater planktonic algae, Smith *et al.* (1978) observed that all species grew on the surfaces of apatite crystals. Apatite supported limited growth of the algae, which was attributed to the partial dissolution of apatite crystals in a medium with pH 7.8. However, no explanation of the attachment of algae to apatite crystals was given. Finally, the results of Kuwabara *et al.* (1986) on the algal utilisation of P sorbed by TiO_2 particles indicated that algae were able to utilise P on titania particles but that the algal exudate production did not appreciably induce P desorption. The tendency of cells to clump around titania particles indicated a mechanism by which 'close physical association of algal cells and inorganic particles may aid in nutrient transport' (Kuwabara *et al.*

1986). A possible mechanism affecting the P release, mentioned by Kuwabara *et al.* (1986), was based on high pH in the microenvironment around photosynthesising algae. On the other hand, the tendency of algae to be associated with particles may reflect mere physical flocculation rather than a nutrient uptake strategy (see Avnimelech *et al.* 1982).

According to Cowen and Lee (1976), physical and chemical processes are more important than microbial mineralisation in regulating the release of P from particles in urban runoff. However, as regards other sources of P loading, mineralisation may play a significant role. Replicate assays have been performed with sterilised and unsterilised aliquots of samples in some studies on riverine particles and lake bottom matter. Golterman *et al.* (1969) and Dorich *et al.* (1980) obtained similar results for both subsets of samples, whereas Marengo and Premazzi (1985) found a higher amount of available P in unsterilised samples. However, it is difficult to infer the effect of biological mineralisation on P availability from these results, because sterilisation may have directly affected the P release (Berge and Källqvist 1990, Grobbelaar and House 1995).

Whether or not microalgae can utilise organic P as a nutrient source depends generally on the ability of the cells to enzymatically hydrolyse the ester linkage joining the P group to the organic moiety (Cembella *et al.* 1984). In most species this hydrolysis is achieved by the activity of broad-spectrum phosphatases at the cell surface (*ibid.*). However, the phosphatase activity is usually associated with the hydrolysis of dissolved organic compounds, especially in the low molecular weight fraction, rather than with particulate allochthonous organic P (see *e.g.* Broberg 1985, Hino 1988). Even if phosphatases were to enhance P release from particulate organic matter, this mechanism is not necessarily more efficient in the batch assays than in the dual culture assays, because phosphatases are also released into solution (Cembella *et al.* 1984). Furthermore, assuming that the activity of algal phosphatases were restricted to the cell wall, some of the organic P might eventually become available to algae via bacterial degradation (*ibid.*). In fact, bacterial action has been considered to be the principal route for the degradation of organic P forms to an algal-available form (Hegemann *et al.* 1983). Finally, Grobbelaar (1983) found that alkaline phosphatase was not respon-

sible for rendering P in riverine suspended solids to a form available to algae. The discussion above indicates that direct contact between algae and particles may not be necessary in the mineralisation of organic matter. However, the validity of this hypothesis should be tested with samples with a high proportion of organic P.

3.1.2 Applicability of dual culture assays to the estimation of potentially algal-available phosphorus

When evaluating the results obtained for potentially available P by any assay technique, three major factors must be considered: (i) the discrepancy between the assay conditions and those most favourable for the transformation of unavailable P forms to available forms likely to occur in the receiving waters, (ii) the rate of this transformation, and (iii) the method-specific factors which may cause bias in the results. These factors are examined in this section. It can be concluded that the results obtained by the dual culture assays to some extent underestimate the true potentially available P.

Conditions in the assays vs. receiving waters

In algal assays, the pH may rise to 10–11 (IV, Klapwijk *et al.* 1982, Bruning and Klapwijk 1984), whereas in Finnish lakes, the pH generally ranges from 5.1 to 7.3 in autumn (Henriksen *et al.* 1997). During summer, the pH in receiving waters is considerably higher, especially in eutrophic lakes. The maximum summer pH value observed was 10.3 (0–2 m depth), and the 99th percentile of approximately 35 500 measurements of pH was 8.9 (summers 1990–1997, Antikainen, unpublished data). To avoid high pH values, thought only to occur in extreme cases in aquatic systems, the assay solutions in this study were buffered to pH 7 or pH 8. The use of a somewhat higher pH value would have more realistically described the maximum P availability in eutrophic waters. However, unbuffered assays with high pH would have generated overestimates of the P availability in most waters, particularly as regards conditions during the agricultural loading period. In the sorption-desorption experiments, almost twice as much P was released from riverine particles to P-free nutrient solution at pH 9 as at pH 7 (I); however, even at pH 9 only 3% of the

PP was released during 24 hours (I). Bruning and Klapwijk (1984) conducted batch assays with low and high concentrations of lake sediment, which resulted in assays with 'low' pH (maximum 8.2) and 'high' pH (maximum 10.3). The mean availability of sediment P at low pH was 37%, whereas at high pH it was 79% (Bruning and Klapwijk 1984). Both these observations suggest that during a production and pH maximum, a somewhat higher proportion of available P may be released from particles than that presented in this study.

As regards the ionic composition and ionic strength, the conditions in the dual culture assays resembled those in freshwater lakes. The brackish coastal waters of Finland receive substantial agricultural and municipal P loading (Pitkänen 1994). Compared with lake water, the coastal waters have higher ionic strength, higher concentrations of sulphate and divalent cations and higher mean pH. An increase in ionic strength should suppress desorption and thus PP availability (Hartikainen and Yli-Halla 1982). On the other hand, the higher average pH and higher concentrations of sulphate and divalent cations should promote desorption of P and thus its availability (Hartikainen 1981, Caraco *et al.* 1989, Hartikainen and Yli-Halla 1982, 1996). The conclusion is that the potential availability of PP in the coastal waters may differ to some extent from that in freshwater systems, but whether it is higher or lower is uncertain.

A possible factor rendering unavailable dissolved P to an available form is ultraviolet radiation, present in surface waters but almost absent under assay conditions. Dissolved organic matter can be degraded by sunlight into products stimulating the growth of microorganisms in aquatic systems (Moran and Zepp 1997). However, the importance of photochemical reactions in influencing P availability is largely unknown.

The results obtained by algal assays do not give accurate results for anoxic conditions. Possibly the most important factor governing the release of available P under these conditions is the amount of P bound by reductant-sensitive Fe. This information might have been obtained by fractionations of P by sequential extractions. As they were not performed, the release of P in anaerobic conditions cannot be assessed.

Finally, it is possible that unialgal assays underestimate true potentially available P in natural planktonic communities (Boström *et al.* 1988a).

The possible underestimation is closely connected to the issue of the mechanisms by which unavailable P is made available. In the case of the PP fraction, desorption appeared to play a marked role. For example, on average 50% of available P was already released from the concentrated river water samples by dilution with P-free nutrient medium (I). In the case of soil samples, the corresponding proportion was 26% (III). Dorich *et al.* (1980) also found that a significant amount of available P was released already by placement of riverine particles in P-free medium. However, the possibility cannot be excluded that some specific enzyme or excreted substance, for example, would in a natural community render a higher proportion of P into an available form than that found in the dual culture assays. Persson (1990) observed that the batch cultures of *Chlamydomonas* sp. and *Aphanizomenon flos-aquae* differed in their ability to utilise P in a variety of samples.

Release rate of algal-available phosphorus

In the dual culture assays, available P seemed to be released rapidly; the increase in the P content of algae was clearly highest during the first week of the experiment, whereas only small amounts of P were incorporated in algae during the subsequent incubation (I, III, V). Although the rate would be low, the cumulative amount of available P released during a substantially longer period might still be considerable (Golterman 1988). However, the ultimately available P, estimated using the first-order kinetics, was at the same level as the potentially available P released during the 2 to 4 week incubation in all soil samples and in 16 out of 20 wastewater samples (Fig. 8). On the other hand, the conclusion that the bulk of the potentially algal-available P is released within a few weeks under test conditions may be biased: the use of first-order kinetics in the algal-assay data is theoretically not justified, because available P consisted of at least two or three fractions with probably different release rates (see section 3.2). However, even if the calculations underestimate the ultimately available P, a very slow P release from particles will probably have a negligible effect on eutrophication (see section 1.3).

Functionally, the dual culture assay has three rates which ultimately determine the change in algal P in the assay chamber (DePinto 1982): (i) the release rate of available P in the sample chamber, (ii) the diffusion rate of available P across the

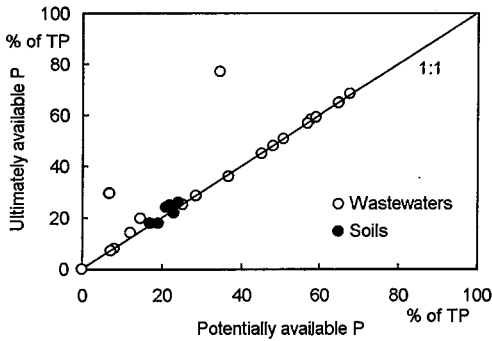


Fig. 8. Relationship between the potentially algal-available P released during 2–4 weeks of incubation and the ultimately available P extrapolated from the release rate of available P.

membrane which dividing the chambers and (iii) the uptake rate of P by the algae in the assay chamber. The release rates given by the dual culture assays should be reliable if both the diffusion of available P through the membrane and the algal P uptake occur much faster than the conversion of unavailable P to an available form. The diffusion experiments showed that dissolved orthophosphate was transported from the sample chamber to the assay chamber at a rate of $k = 2.34 \text{ d}^{-1}$ (k is the release rate coefficient in the first-order kinetics equation), and that 93% of the transported P was incorporated into algal cells within 25 hours. In the actual tests, available P was released from soils at a rate of $0.09\text{--}0.40 \text{ d}^{-1}$ (III) and from wastewater at a rate of $0\text{--}0.63 \text{ d}^{-1}$ (V), *i.e.* much slower than the rate of diffusion. As the shortest incubation period was three days in the actual tests, the prerequisite that the diffusion and algal uptake were more rapid than the release of available P was fulfilled.

Method-specific considerations

The dual culture assays were chosen for the testing of potentially algal-available P partly because the technique enabled the direct measurement of increases in algal P. It was assumed that this technique might be less liable to measurement errors than the assays in which algae and particles are mixed. Nevertheless, problems were also encountered in managing P in the dual culture assays. First, part of the added P was not bound by the algae in the control vessels (I, V). As it was not present in solution, the P may have been incorporated in bacterial cells in the sample chamber. If so, bacteria may have a dual role in the assays. On

the one hand, they increase the pool of available P by mineralising organic P, but on the other hand they compete with algae for P. As the bacterial populations in the actual tests probably exceeded those in the control vessels, the possible underestimation of algal-available P due to bacterial P uptake may be substantial. However, bacteria also act in batch assays, unless samples are sterilised and an axenic algal stock is used. Second, the P balance of the vessels was usually negative, *i.e.* some P remained in the vessels after the emptying of both chambers during the termination of the assays. This was due partly to the attachment of sample particles to the walls of the vessels and to the membrane, which should not affect the results obtained for algal-available P. However, the negative mass balance may also be caused by the underestimation of algal P, particularly in paper I. The dilution of algal suspensions with distilled water prior to digestion (not performed in I) increased the values obtained for TP. However, the same applied to river waters, soil suspensions and wastewaters, which supports the observation of Turtola (1996) that dilution with distilled water (1:4) prior to digestion with persulphate increases the results. The PP resistant to digestion has been found to include algal-available P (Engle and Sarnelle 1990). If both algal P and sample P were underestimated by insufficient digestion, the errors should partly counteract each other.

Eight river water samples were concentrated by centrifugation, micro- or ultrafiltration before testing. In general, there was no clear difference in the PP availability between concentrated and unconcentrated samples, although the samples concentrated by centrifugation tended to have a higher proportion of algal-available P (I). As centrifuging did not retain the finest particles, which may have the highest ability to retain P (Hartikainen 1979, Klotz 1988), the values for centrifuged samples may be too high. In terms of the filtrations, P was probably sorbed on suspended solids and onto the filtration device, which may also have affected the results. On the other hand, no difference in algal-available PP was observed between the two aliquots of a sample of which one portion was unconcentrated and the other was concentrated by ultrafiltration (I). The samples tested in paper I were stored for a long time before the assays. During storage of the water samples, some degradation of organic matter probably occurred as their concentration of DRP

tended to increase (I). In the concentrated samples, however, the relative changes in P were small (I).

3.1.3 Comparison between the dual culture assay and a chemical determination

The dual culture assays and the determination of reversibly adsorbed P are based on the same main principle: P desorbed from a sample is bound by a sink (algae or Fe-hydroxide), which maintains a concentration gradient and promotes further desorption of P. In the unconcentrated river water samples, the amount of P retained by the Fe-hydroxide coated filter paper strips always exceeded DRP (II). In addition, the amount of retained P correlated with the DRP concentration ($r = 0.96$, $P < 0.001$) but not with PP concentration. Both these observations suggest that P bound by paper strips originated mainly from the DRP fraction. However, DRP was not measured from test suspensions after the determination, and thus this assumption could not be confirmed. If all DRP was captured by Fe-hydroxide, on average 3% (range 1–4%) of PP was also sorbed by the strips in the unconcentrated samples. The corresponding proportion in the concentrated samples was 4% (2–5%). In the calculations, DUP was considered to be inert. However, since P belonging to the DUP fraction may also be sorbed onto Fe-oxides, this assumption may not be valid (see Sharpley 1993a).

As DRP also seemed to be the main source of

algal-available P in the unconcentrated samples (see section 3.2), the proportion of TP utilised by the algae in the dual culture assays correlated with that retained by the paper strips (Fig. 9a). However, in the case of PP, no correlation existed between the methods (Fig. 9b). Although the levels of the results were similar, the utilisation of PP in dual culture assays varied over a wider range than the amount of PP bound by the paper strips. Particulate P retained by the paper strips exceeded algal-available P in 4 out of 5 concentrated samples, but the opposite applied for 6 out of 8 unconcentrated samples. As averaged over the 13 samples tested by both methods, 3.5% of PP was retained by Fe-hydroxide impregnated filter paper strips, whereas 4.3% of PP was utilised by the algae.

In the determination of reversibly adsorbed P the test suspension was not buffered. During the determination, the pH decreased from the approximately neutral value by an average of 0.6 units in the case of unconcentrated samples and 1.3 units in the case of concentrated samples (II). The protons causing the decrease in pH may have originated in the hydrolysis of Fe^{3+} . Two filter papers retained more P than one filter paper (II). The increase in the strip number may have increased the strength of the P sink, or alternatively the surface onto which particles can be attached. Despite the rinsing with water some attached particles may have been carried over to the step in which P bound to the iron coatings was dissolved by sulphuric acid. In this case, P in these particles may have been partly released, resulting in the overestimation of reversibly adsorbed P.

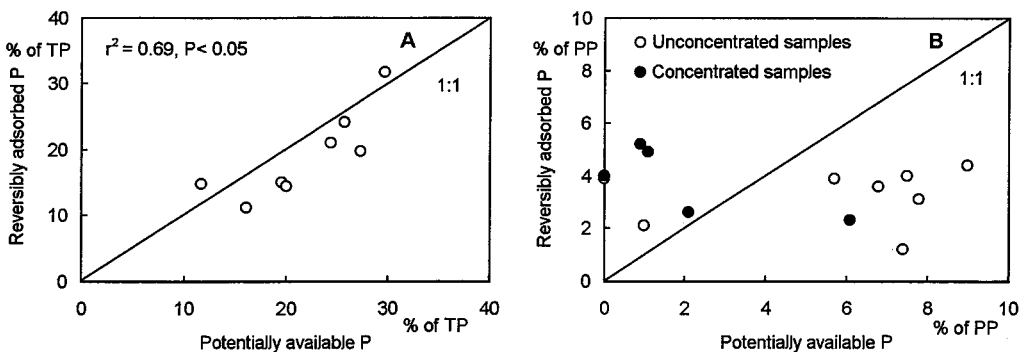


Fig. 9. Relationship between the potentially algal-available total P (a) and particulate P (b) and the amount of P retained by Fe-hydroxide impregnated filter paper strips, i.e. reversibly adsorbed P.

Provided that the dual culture assays gave unbiased results, the nonexistent correlation between the results obtained by the two methods for PP could be attributed to the combined effect of the decrease in pH and attachment of suspended solids to the paper strips in the determination of reversibly adsorbed P (II). As these artefacts can substantially affect the apparent P availability, the determination is not recommended as a surrogate for algal assays until these problems have been solved.

3.2 Potential availability of the phosphorus fractions

The TP concentration exceeded the concentration of potentially available P in all materials tested in this study, except the municipal wastewaters of St Petersburg. As regards river waters and municipal wastewaters, there was a weak but significant correlation between algal-available P and TP (Fig. 10). In the municipal wastewaters, no correlation between these two P fractions was observed, whereas in the river waters the correlation was strong ($r = 0.92$, $P < 0.001$). However, closer examination of the relationship revealed that TP was also a poor indicator of available P in river waters. For example, in the TP range of 200 to 400 $\mu\text{g l}^{-1}$, almost no change in algal-available P was observed (Fig. 10). The fact that TP did not describe potentially algal-available P was probably due to the different composition of TP in each sample. The P fractionation employed here, *i.e.* the partitioning of TP into PP, DRP and DUP, has been widely used in aquatic monitoring and was

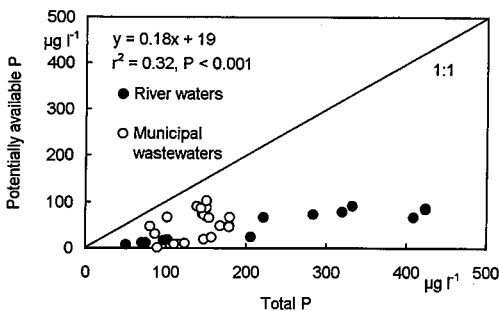


Fig. 10. Relationship between total P and potentially algal-available P in unconcentrated river waters and municipal wastewaters. Note that most municipal wastewater samples were diluted before being tested.

originally chosen as a compromise between the predictive power and the ease of handling (Broberg and Persson 1988). Neither of the algal-assay methods allowed the explicit measurement of the availability of the P fractions, but tentative estimates of the availability could be made from the results obtained by the dual culture assays.

3.2.1 Dissolved phosphorus

Most DRP appeared to be available to algae. In the first place, the concentration of DRP decreased rapidly in the assay suspension. However, some DRP was detected particularly in the first harvest of tests with river waters, suggesting that a small portion of DRP in these samples was not readily utilised by algae (I). Second, algal-available P exceeded or was at the same level as DRP in all samples, except in three samples from the rivers discharging into lake Pyhäjärvi (Fig. 11). The lowest availability of DRP was found in a sample taken from the river Pyhäjoki in early September: the concentrations of DRP and algal-available P in this sample were 24 and 11 $\mu\text{g l}^{-1}$, respectively. The high availability of DRP was also supported by the determination of reversibly adsorbed P (see section 3.1.3). During the pretreatment of 5 samples from the river Paimionjoki by ultrafiltration, DRP was not appreciably concentrated in the samples (I). This observation indicates that DRP in river waters consisted of low molecular weight substances. The results presented above suggest that DRP provides a rather good estimate of the minimum amount of available P.

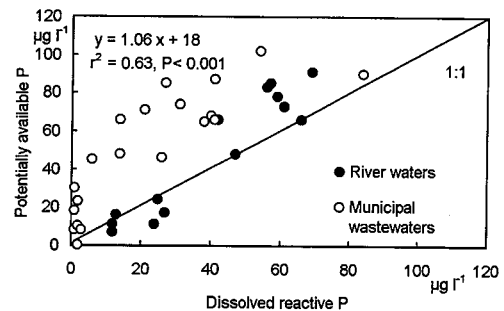


Fig. 11. Relationship between dissolved reactive P and potentially algal-available P in unconcentrated river waters and municipal wastewaters. See note in Fig. 10.

In contrast to DRP, DUP appeared to be entirely unavailable in river waters; the amount of DUP taken from the vessels always equalled or exceeded the amount put into the vessels (I). The low concentrations of DUP in soil suspensions did not allow the estimation of its availability (III). However, in purified municipal wastewaters, an average of 22% (0–74%) of DUP disappeared during the assay and was probably converted into an available form (V). The dual culture assays are liable to underestimate DUP availability, because in each harvest some DUP that might have become available later was removed from the assay. Furthermore, part of the DUP in the vessels may represent P in, or reacted with, organic products excreted by the test algae (see Ripl and Lindmark 1979). Corresponding underestimation of DRP availability is rare because the concentration of DRP in the harvested suspensions was low (see above). From the DP fraction, on average 80% appeared to be available in river waters and 58% in municipal wastewaters.

As regards natural waters, the results presented above mostly support the assumption of Lee *et al.* (1980) that DRP is entirely available, whereas DUP tends to be inert. On the other hand, Boström *et al.* (1988a) considered the algal-available fraction of dissolved P to be usually smaller than DRP and always less than DRP + DUP. According to their review, the ratio of DRP to potentially available dissolved P varies from 0.7 to 10. If dissolved orthophosphate was the only P form directly taken up by the algae in the dual culture assays, most of the DRP had either converted into or already existed in this form. The latter alternative is not supported by the observation that DRP has usually been 3 to 7 times as high as the immediately available P as determined by various techniques of short-term algal assays (Boström *et al.* 1988a). On the other hand, most studies on immediately available P have been conducted on lake waters; the river waters and municipal wastewaters may have had a high ratio of true orthophosphate to P forms liable to be converted to orthophosphate in the DRP analysis.

A crucial step in the P fractionation is the separation of the particulate and dissolved phases by filtration. The absorbance of turbidity blanks of filtered undigested samples was usually negligible, which indicates that the Nuclepore filters (pore size 0.4 μm) removed most particulate matter from the samples. Turtola (1996) found that filtration

through Nuclepore 0.4 and 0.2 μm filters resulted in similar DRP concentrations for water samples containing soil. She explained the lack of difference by the fact that, due to clogging, the filters probably retained particles smaller than their pore size. However, some colloidal matter passed through the filters; the concentration of DRP was on average 6 $\mu\text{g l}^{-1}$ lower in samples filtered with a dialysis tubing (0.0024 μm pore size) than in samples filtered with Nuclepore 0.2 μm filters (*ibid.*). The low availability of DRP in the rivers discharging into lake Pyhäjärvi might be due to dissolved or colloidal P associated with humic substances, perhaps originating from forested areas and peatland. The rivers were sampled during a relatively dry period, when the load from agricultural areas was low.

DUP represents P forms capable of passing through a membrane filter but requiring digestion to convert them into reactive P. In natural waters, the DUP fraction may include *e.g.* nucleic acids, adenosine phosphate, phospholipids and inositol phosphates (Nanny *et al.* 1995). DRP and DUP are sometimes assumed to represent dissolved inorganic P and dissolved organic P, respectively. However, some of dissolved organic P is also included in the DRP fraction, whereas inorganic polyphosphates may be included in the DUP fraction (Broberg and Persson 1988). Since polyphosphates are normally easily hydrolysed, especially when the hydrolysis is aided by enzymes (*ibid.*), it seems that DUP in river waters consisted mainly of dissolved or colloidal organic P, perhaps in highly resistant humic substances. According to Kortelainen (1993) the majority of humic substances in Finnish lakes are not retained by the commonly used membrane filters. The hypothesis of DUP representing largely P in humic substances was supported by the observation obtained during the concentration of river waters by micro- and ultrafiltrations (I): the final concentrates were dark brown and contained higher concentrations of DUP than the original samples. Golterman (1973) also found that 'humic-bound' P was not easily available to algae. The fact that part of DUP in municipal wastewaters appeared to be available suggests that this fraction of DUP may have been composed of hydrolysable polyphosphates of detergent origin, *i.e.* dissolved inorganic P. Young *et al.* (1982) also reported a part of DUP in municipal effluents to be available to algae.

3.2.2 Particulate phosphorus

The availability of PP depended on its source. Of the P in the surface soil of agricultural land, 17 to 24% (mean 20%, III) appeared to be available. Despite a higher proportion of acid ammonium acetate-soluble P in the Aurajoki soils (22–28 mg dm⁻³) than in the Jokioinen soils (5–9 mg dm⁻³), no clear differences between the two soils was found in the *proportion* of algal-available P in total soil P (III). Phosphorus extracted with acid ammonium acetate (Vuorinen and Mäkitie 1955) should reflect the labile P. However, as the Aurajoki soils were richer in P than the Jokioinen soils, the *absolute* amount of algal-available P, *i.e.* as expressed per gram of dry soil, was on average 19% higher in the Aurajoki soils (III). Krogstad and Løvstad (1991) found that RP (total reactive P) amounted to the algal-available P in Norwegian soils. For the soils studied here, RP was approximately at the same level as algal-available P estimated by batch assays but lower than that estimated by dual culture assays (III). However, RP did not correlate with algal-available P as tested with either of the techniques (III).

In river waters, in which PP consisted mainly of eroded soil particles, the PP availability ranged from 0 to 13% (mean 4%), *i.e.* it was substantially lower than in surface soil. In the municipal wastewaters 0 to 54% (mean 25%, V) of PP appeared to be utilised by the algae. In the wastewaters, PP probably consisted of P bound by precipitation chemicals and organic matter.

Finally, it is interesting to compare the results of this study with those of Howarth *et al.* (1995). They assessed the burial of biogeochemically active P in marine sediments from the values presented in the literature for the inputs of dissolved and particulate P to the oceans of the world and from the P forms found in marine bottom sediments. Howarth *et al.* (1995) found that the burial of P likely to have been in 'reactive' form exceeded the estimated input of dissolved P, which suggests that some of the PP input to the oceans has been biogeochemically active. The proportion of biogeochemically active PP was estimated to range from 23 to 69%. However, it must be noted that the average residence time of P in seawater before burial in the sediments is approximately 4000 years (Howarth *et al.* 1995).

3.3 Agriculture vs. municipalities as sources of available phosphorus

On the basis of the specific areal P load determined for small agricultural drainage basins, the diffuse load of P originating from agriculture has been estimated as 2000 to 4000 t a⁻¹ in Finland (Rekolainen 1989a). Of this, approximately 25% is in the form of DRP (Pietiläinen and Rekolainen 1991) and the rest consists mainly of PP; the proportion of DUP is unknown but probably small. If all of the DRP load (500–1000 t a⁻¹) and 4% of the PP load (1500–3000 t a⁻¹) can be utilised by the algae, the diffuse load of potentially algal-available P from agriculture equals 560 to 1120 t a⁻¹, *i.e.* 28% of the TP load from this source. As almost 90% of the available load consists of DRP, it can be concluded that to abate P-induced eutrophication, agricultural water protection measures should generally be focused on the reduction of DRP loss. However, the proportion of different P fractions in the available P may vary considerably with the erodibility and P status of the soil.

The average proportion of the potentially algal-available P in the samples from the agriculturally loaded rivers examined here was only 20% (range 12–30%). However, as only a relatively small number of river water samples was tested, the conclusion that a lower proportion of P is available in the rivers than in runoff is unwarranted. As estimated from the algal-assay data and the intensive nutrient monitoring carried out in 1988–1994, the mean flow-weighted concentration of algal-available P in the river Paimionjoki was 46 µg l⁻¹ (temporal range 4–91 µg l⁻¹). Of this, 74% consisted of DRP and the rest of PP (Fig. 12). A similar calculation for the surface runoff from the Aurajoki field showed that the mean concentration of algal-available P was 310 µg l⁻¹ (temporal variation 73–700 µg l⁻¹), of which 93% consisted of DRP (Fig. 12). The data for the Aurajoki field applied here consisted of a relatively low number of instantaneous samples and probably underestimated the PP fraction (Ekholm, unpublished data). This data was used in the estimation of available P concentrations, because the more extensive data used in the modelling efforts did not include DUP.

The proportion of agricultural land in the drainage basins of the rivers varied from 22 to 43%, the rest being mainly forested areas and peatland. It may be asked whether the availability of agricul-

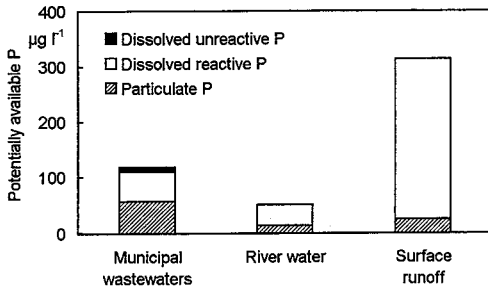


Fig. 12. Mean concentrations of potentially algal-available P in purified municipal wastewaters, the river Paimionjoki and surface runoff from the Aurajoki field.

tural P losses can be accurately derived from this data. However, as the specific P load from agricultural areas is approximately ten times as high as that from forested areas (Rekolainen 1989a), most P carried by the rivers can be assumed to have originated from agricultural land. This assumption is further supported by the observation of Pietiläinen and Ekholm (1992) that on average 90% of the suspended solids transported by a small agricultural river originated from the surface of the fields as opposed to channel bank erosion.

The direct P load from animal husbandry has been estimated to be 300 t a^{-1} in Finland, *i.e.* approximately 10% of the total agricultural P loading (Finnish Environment Institute 1996). However, as the availability of P in agricultural point sources, such as leakage from fodder silos and manure storage, has been reported to be relatively high (see IV), the significance of these point sources in eutrophication is higher than their proportion of the total agricultural load.

In the purified municipal wastewaters, on average 36% (range 0–67%) of TP was in an algal-available form. Although the within-plant variation was high, a greater average proportion of TP (50%) was available in the three nitrifying plants than in the two plants with no nitrification but a post precipitation unit (20%, V). Statistical tests partly confirmed this difference; the plant in Tampere was, however, included in both groups, which is logical because the plant was only partially nitrifying (V). The concentration of algal-available P in the municipal wastewaters was on average $120 \mu\text{g l}^{-1}$ ($0\text{--}310 \mu\text{g l}^{-1}$), and was higher in the nitrifying plants than in the post precipitation plants; the sample with no algal-available P

was taken from a post precipitation plant. A total of 48% of the algal-available P in the wastewaters originated from the particulate fraction, the rest consisting mainly of DRP; the proportion of algal-available DUP in the total algal-available P was 8% (Fig. 12). The fact that only 44% of available P in municipal wastewaters consisted of DRP mainly reflects its low concentration in the effluents. As DRP concentrations were low particularly in the post precipitation plants, it seems that dissolved orthophosphate is efficiently precipitated with the post-precipitation chemicals (mainly Al).

In addition to a higher concentration of DRP, the availability of PP was higher in the effluents from the nitrifying plants. Nitrification may have slightly increased P availability. First, partly due to lime fed to the process in the nitrifying plants, effluent pH tended to be higher in these plants (V). An increase in pH favours the release of P from Fe compounds (Snoeyink and Jenkins 1980), the only precipitating agents used in the nitrifying plants. Second, the longer process in the nitrifying plants may have favoured the release of organic P by allowing a more efficient degradation of organic matter. In addition to the treatment method, problems in the operation of the plant seemed to increase P availability (V).

The results suggest that the more efficient is the purification process, the lower is the biological, as well as chemical, reactivity of residual P. This assumption was further supported by the observation that the average TP availability in the purified municipal wastewaters of the plants in St Petersburg was twice as high as in the Finnish plants (Table 9). An average of 66% of effluent P was in the form of DRP in the two Russian plants, which do not have chemical P precipitation.

The P load from municipalities to Finnish surface waters was 250 tons in 1996 (data base on wastewater treatment plants of the FEI). Provided that the results obtained for the five plants reflect the general situation in Finland, the potentially algal-available P load from municipalities would be 90 tons per year.

Most studies on the availability of P in agricultural runoff have dealt with the PP fraction only. As discussed in paper I, the availability of PP in the agriculturally loaded rivers of Finland is lower than that in *e.g.* the USA and Canada. The low availability might reflect the high ability of Finnish soils to retain P (Hartikainen 1979). It

Table 9. Total P, dissolved reactive P and potentially algal-available P in purified municipal wastewaters of St Petersburg.

Plant sample	Total P $\mu\text{g l}^{-1}$	Dissolved Algal- reactive P available P	
		— % of Total P	—
Central plant			
Nov. 12, 1996	1400	94	100
Apr. 23, 1997	3500	26	65
June 9, 1997	1400	84	68
Sept. 2, 1997	1400	47	98
Nov. 5, 1997	1200	96	94
Northern plant			
Nov. 12, 1996	1800	82	100 ¹
Apr. 23, 1997	820	75	83
June 9, 1997	590	34	21
Sept. 2, 1997	670	65	77
Nov. 5, 1997	330	58	77
Mean	1300	66	78

¹ = The actual result was 103%.

has been estimated that more than half of the fertilizer P not utilised by the plants can be retained by soil in forms practically unavailable to plants (Yli-Halla 1991). However, of all the Nordic studies on the availability of PP in agricultural runoff, the lowest values were obtained in this study; those from Norway were on average 23 to 30%, and those from Sweden 41% (Table 10). Although there is considerable variation in climatic conditions, soils, topography and the structure of agriculture between the Nordic countries (IV), it seems that in addition to the true differences, the wide variation in the results reflects the different methodologies used in the availability testing. This assumption is supported by the fact that the difference is highest between the results obtained in this work for southern Finland and

those obtained for the Uppsala region in Sweden (Persson 1990), which have similar environmental and edaphic conditions (IV). One factor accounting for the relatively low availability of PP in this study is the assay pH. As already discussed, it was buffered here to pH 7 or 8, whereas in most assays on algal-available P the pH is not regulated and seldom even reported. Table 10 also shows some other methodological differences between the assays conducted in the Nordic countries.

The availability of TP in agricultural runoff has been estimated in three Nordic studies (Table 11). These results confirm the crucial role of methodological factors in the results obtained. As in the case of PP, the lowest values were obtained in this study; those presented by Källqvist and Berge (1990) are almost twice as high and those presented by Kauppi and Niemi (1984) for P in small Finnish agricultural drainage basins more than three times as high as the results obtained in this work. Kauppi and Niemi (1984) conducted batch assays with *Selenastrum capricornutum* on samples which had been stored frozen. The methods used by Källqvist and Berge (1990) are shown in Table 10.

The P availability in the effluents from the Finnish municipal treatment plants was also lower than that obtained elsewhere (V). Methodological factors probably play a role here too. In addition, the relatively low availability of P in the Finnish wastewaters can be explained by the efficient purification processes applied in the plants (TP reduction 87–98%).

Table 11 shows the availabilities of TP and PP in runoff (mostly agricultural) and municipal wastewaters according to those investigators who have studied both sources by the same method. The data is consistent in that a higher proportion of P is available to algae in municipal wastewaters than in agricultural runoff.

Table 10. Potential availability of particulate phosphorus in waters from Nordic agricultural catchments. Modified from IV.

Country Sample type	Algal-available P as % of particulate P		Characteristics of the assay technique				Reference
	Mean	Range	Type	Sample pretreatment	pH in bioassay	Test organism	
Finland Rivers, agricultural area	4	0-13	DCA	Particles concentrated by various methods or used without any pretreatment	Buffered at 7 or 8	<i>Selenastrum</i> sp.	I, this study
Norway Surface runoff, agricultural area	30	22-46	BA	Samples sterilised by γ -radiation	Not presented	<i>Selenastrum</i> sp.	Recalculated from Berge & Källqvist (1990)
Drainage water, agricultural area	28	0-58	BA	"	"	"	"
Ditch water, agricultural area	23	0-45	BA	"	"	"	"
Sweden Runoff, agricultural area	41	?	BA	Particles concentrated, fractionated and frozen	7.3-11.0	<i>Chlamydomonas</i> sp.	Persson (1990)
River, agricultural and forested areas, wastewater loading	41	?	BA	"	"	"	"

Table 11. Potentially available P in runoff and municipal wastewaters according to investigators who have studied both sources by the same method.

Reference	Algal-available P			
	Runoff ¹		Municipal wastewaters	
	Mean	Range	Mean	Range
As % of total P				
Kauppi and Niemi (1984)	75	27–100 ²	–	59–83 ³
Källqvist and Berge (1990)	37	7–66	–	29–100 ²
This study	20	12–30	36	0–67
As % of particulate P				
DePinto <i>et al.</i> (1981) and Young <i>et al.</i> (1982)	18	0–40	55	–
Källqvist and Berge (1990) ⁴	27	0–58	–	0–100 ²
Persson (1990)	41	–	> 90	–
This study	4	0–13	25	0–54

1 = Mostly agricultural.

2 = Actual result exceeded 100%.

3 = Most tests on wastewater failed due to too dense algal population.

4 = Recalculated from Berge and Källqvist (1990).

3.4 Actual availability of phosphorus: effects of pH and ambient phosphorus concentration

As discussed by Kauppi and Niemi (1984), there is a time lag between the agricultural loading period and the onset of algal production in southern Finland. Most agricultural runoff enters the waters during the autumn rains and during the snow-melt period occurring in early spring, sometimes already in winter (Ekholm and Kallio 1996). On the other hand, marked algal production begins usually only in May, when most particles have settled out of the productive water layer. The production usually declines in September. Although municipal wastewater discharges are more evenly distributed among the seasons, a major part of the loading also enters the waters outside the production period.

Whether P is released from or bound to the particles depends largely on the concentration of dissolved orthophosphate and the pH in the surrounding solution. The concentration of DRP in agriculturally loaded lakes and estuaries ranges from values below the detection limit (approximately $2 \mu\text{g l}^{-1}$) during the productive season up

to $50 \mu\text{g l}^{-1}$ outside the productive season (VI, Ekholm 1992, Knuutila *et al.* 1992, 1994). The sorption experiments conducted with concentrated river waters at pH 7 and 9 reflect the conditions during these two periods (see section 3.1.2). At pH 7, the EPC ranged from 0 to $75 \mu\text{g l}^{-1}$ (mean $22 \mu\text{g l}^{-1}$) and at pH 9 from 8 to $151 \mu\text{g l}^{-1}$ (mean $50 \mu\text{g l}^{-1}$, I). These values suggest that the release of potentially available PP is not inhibited by the concentration of dissolved orthophosphate during the production period, *i.e.* the concentration of dissolved orthophosphate (\leq DRP concentration) is lower than EPC. However, the opposite may sometimes apply during other seasons, which accentuates the potential significance of summer season resuspension on the release of available P.

No measurable quantities of P were released from the sample with the highest ability to retain P to a P-free solution at pH 7 (I). This result supports the suggestion that particles may also act as a sink for P in receiving waters (Taylor and Kunishi 1971, Hartikainen 1979). However, it should be noted that the results from the sorption experiments are uncertain because the experiments were conducted on concentrated samples. Concentration

of the river waters by centrifuging or micro- or ultrafiltration probably affected the P-status of the particles (I).

3.5 Cycling of phosphorus in an agriculturally loaded lake

Actual release of potentially available P is regulated by the physical factors light, temperature and wind. Light and temperature regulate primary production, which in turn modifies the chemical environment. Wind produces currents, which affect the fate of particles during the ice-free period. In this section the cycling of P in a shallow lake which receives a substantial load from agricultural sources is discussed. Particular attention is paid to the consideration of whether the results obtained for the potential and actual availability of P under laboratory conditions are also valid for lake conditions.

3.5.1 Phosphorus balance

Lake Pyhjärvi efficiently retains incoming nutrients. On average, 87% of the external TP load was retained in the lake or removed with the fish catch (Fig. 13). On the basis of the observations for one year, the retention of DRP seemed to be even higher (VI). In six other agriculturally loaded Finnish lakes, the retention of TP ranged from 24 to 78% and that of DRP from zero to 50% (only three observations on DRP retention, VI). Most P entering lake Pyhjärvi is bound to eroded soil particles. Although these particles are fine (Huttula 1994), the relatively long water residence time (3 years) probably results in most particles settling on the bottom of the lake. On the other hand, the high retention of DRP is probably attributable to the facts that the water is clear (Secchi depth 2–5 m) and that the lake seldom stratifies thermally in summer. Under these conditions most of the water volume is productive and available P in this P-limited lake (Sarvala and Jumpanen 1988) is efficiently taken up by algae and ultimately by zooplankton and fish. This hypothesis was supported by the observation that the concentration of DRP in the lake was predominantly below the detection limit ($2 \mu\text{g l}^{-1}$). In contrast to DRP, the input of DUP from the drainage basin equalled its outflow from the lake (VI),

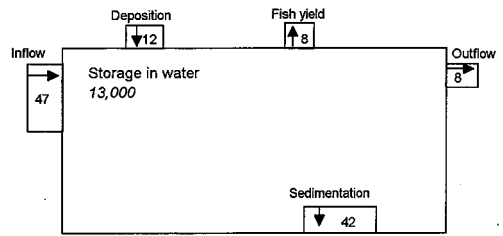


Fig. 13. Long-term balance (years 1980–1992) of total P in lake Pyhjärvi. The figure in italics denotes mean storage (kg), whereas other figures denote mean fluxes (kg d^{-1}). The storage in fish biomass is omitted.

which suggests that no net retention of DUP occurred in the lake. Furthermore, the concentration of DUP in the lake appeared to be almost constant (approximately $6 \mu\text{g l}^{-1}$). These observations support the result from the algal assays that DRP is highly available, whereas DUP is inert and does not become available even via the effect of sunlight (see section 3.2.1).

Although the net retention of P is high in lake Pyhjärvi, the internal load supplies substantial amounts of P to the water column, especially during the ice-free period. During this period, the internal loading of P was two orders of magnitude higher than the external loading (Table 12). As the internal loading of TSS was also substantial, the major mechanism of internal P loading appeared to be the wind-induced resuspension of inorganic benthic matter.

Table 12. Balance of total P and total suspended solids in lake Pyhjärvi during the ice-free period in 1992 (VI).

Component	Total P kg d^{-1}	Total suspended solids kg d^{-1}
Input	17	1 300
Outflow	18	830
Storage change	60	1 800
Sedimentation		
net	61	1 330
gross	6 000	3 200 000
Internal loading	6 060	3 200 000

3.5.2 External vs. internal loading of algal-available phosphorus

In this section, the effect of anoxia and the resuspension of bottom sediments on the pool of available P in lake Pyhäjärvi is discussed. During a strong O₂ deficiency observed in March 1988, the concentration of TP at the central deep was markedly elevated. Assuming that the P had been released from the bottom, a release rate of P was calculated (4.5 kg d⁻¹, VI). Assuming further that the release continued at this rate until the ice break-up, an estimate for the total amount of P released due to anoxia was obtained. This amount, 760 kg of P, was probably in a highly available form and equalled approximately 14% of the external annual load of available P (Table 13). However, this high P release occurs only seldom (once during the 13 study years) and thus plays a minor role in the long-term nutrient balance of the lake. As the lake stratifies only occasionally during summer, the P release due to anoxia is probably negligible at this time. This pattern is inverse to that found in two small agriculturally loaded lakes in southern Finland in which occasional anoxia during summer resulted in a marked release of P from the bottom (Knuuttila *et al.* 1994).

The contribution of resuspension to the available P pool is difficult to estimate from the present data. As regards inorganic matter, two alternative approaches were applied (VI). The inorganic benthic matter probably represents the soil originally eroded from the fields in the drainage basin, transported to the lake and eventually settled to the bottom. In the first approach, the resuspension of inorganic matter was estimated by multiplying the internal loading of TSS (Table 12) by the mean value for residue on ignition in the settling matter (83%, Krogerus, unpublished data). To convert this amount to P, the value was multiplied by the mean P content of the surface sediments in the erosive bottoms of the lake (0.75 mg g⁻¹, Kauppila 1993). Finally, an estimate of the release of available P was obtained when the above value was multiplied by the proportion of algal-available P in bottom sediments. Dual culture assays showed that the mean availability of P in the sediment layer of 0–2 cm was 4% (Krogerus and Ekholm, unpublished data), a somewhat higher value than that obtained for the settling matter in lake Villikkalanjärvi (2.6%, I) and for the bottom sediments of lake Lappajärvi (0%, I). The ap-

Table 13. Internal and external loading of algal-available P in lake Pyhäjärvi in 1992 (VI). The loadings are presented as annual mean values.

Source	Algal-available P kg d ⁻¹
Internal loading	
Anoxia	< 2
Resuspension of	
– inorganic matter	1
– organic matter	≤ 20
Total	≤ 23
External loading¹	15

¹ = Assuming that 50% of P in atmospheric deposition and 2% of incoming particulate P are available.

proach suggested that the P release is 32 kg d⁻¹ (as an annual mean), twice the annual external loading of algal-available P (Table 13). In separate sorption studies it was found that the release of algal-available P from resuspended bottom matter is never inhibited by the concentration of dissolved orthophosphate in lake Pyhäjärvi (VI).

In the second approach, the P desorption was estimated by multiplying the annual external load of PP (14 t a⁻¹, VI) by its mean availability (4%) and assuming that half of the available P is released before the particles settle to the bottom ('external loading') and half afterwards due to resuspension ('internal loading'). By this approach, the desorption from the resuspended inorganic matter would be only 0.8 kg d⁻¹. This amount is small compared with other sources of available P (Table 13). This approach reflects the likelihood that before permanent sedimentation, matter is resuspended several times; thus, if P is released during resuspension, the sediments will gradually lose their available P reservoirs. In the first approach, it was assumed that the P status of the resuspended matter would remain constant. The hypothesis that the resuspension of inorganic P contributes only a small amount of algal-available P is in accordance with the observation of Knuuttila *et al.* (1994), who observed a marked resuspension event in the agriculturally loaded lake Villikkalanjärvi which resulted in no increase in the DRP concentration of the water. Therefore, the second approach is likely the more realistic.

The TP storage of lake Pyhäjärvi tends to in-

crease in late summer (VI). In July–August 1992, the mean TP concentration of the water increased by $9 \mu\text{g l}^{-1}$ (Fig. 14a) and the TP storage by 270 kg d^{-1} . However, during this time, the external load of the lake was negligible (14 kg d^{-1}). Shortly after TP began to increase, the biomass of blue-green algae increased (Fig. 14b) and eventually a bloom occurred in September, suggesting that the P input consisted largely of available P forms. If the observed P increase consisted entirely of available P, the internal load of available P would have been 20 kg d^{-1} as expressed as an annual mean value, *i.e.* higher than the external load of available P (Table 13). The mechanism by which available P was translocated from the bottom to the water remained unclear. As the concentration of TSS in the water did not increase with TP (Fig. 14b), it appears that

resuspension of inorganic matter was not responsible for the TP increase. The increase may have been caused by the resuspension of P-rich organic bottom matter. Owing to its lightness, organic matter is eroded at slower current velocities than inorganic matter; in lake Pyhjärvi it can be detached from the whole bottom area, except in the very small central deep (Huttula 1994). Alternatively, the internal load may have reflected the vertical migration of benthic blue-green algae or germination of their resting forms (see Osgood 1988). The above hypotheses would suggest that the internal loading of P in lake Pyhjärvi reflects the cycling of P already involved in the aquatic food web, *i.e.* of P with high initial availability, rather than the release of new reserves of available P.

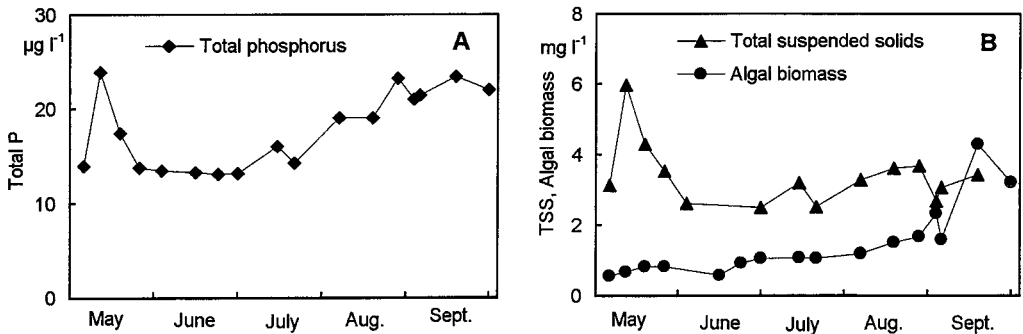


Fig. 14. Concentrations of total P and total suspended solids (TSS) and biomass of algae in lake Pyhjärvi during the ice-free period of 1992. Algal biomasses are taken from Malve *et al.* (1994). Note that the concentration of dissolved reactive P is below $2 \mu\text{g l}^{-1}$.

3.6 Assessment of the loss of available phosphorus from agricultural land

3.6.1 Origin of dissolved reactive phosphorus in surface runoff

Dissolved reactive P appears to comprise most of the algal-available P in agricultural runoff. A crucial question related to the choice of appropriate measures to reduce the agricultural DRP loss is whether P is mostly desorbed from soil particles remaining in the soil or from those detached from the soil (see Yli-Halla *et al.* 1995). As desorption of P in dilute solution is rapid (see Logan 1982, I),

a substantial amount of P might be released from the surface soil during its short contact with rain or snowmelt water. In this case, erosion control measures may not effectively reduce the DRP loss. However, if eroded particles markedly supply DRP to runoff, the opposite applies. The origin of DRP also has implications for the testing of P availability from agricultural sources. The tests have generally been performed on eroded soil particles (*e.g.* Sagher 1976, Dorich *et al.* 1980, 1984a, b, 1985, DePinto *et al.* 1981, Young *et al.* 1985, Persson 1990, Sharpley *et al.* 1991, Sharpley 1993a, b) rather than on soil samples (Sagher 1976, Krogstad and Løvstad 1991, III), which

may lead to underestimation of the potential of soil as an algal P source.

As discussed in section 3.2, 0 to 13% of P was available in suspended solids in the agriculturally loaded rivers, whereas in surface soils the proportion was 17 to 24%. When presented as available P per gram of dry matter, the values were 0 to 0.18 mg g⁻¹ and 0.24 to 0.36 mg g⁻¹, respectively. In addition, the EPC values of the particles concentrated from the river waters were 0 to 75 µg l⁻¹ (I), whereas the EPC of Jokioinen and Aurajoki soils, determined by Yli-Halla *et al.* (1995), were 61 to 83 µg l⁻¹ and 670 to 1100 µg l⁻¹, respectively. It is tempting to attribute the higher EPC and the amount of available P in soil to the fact that eroded soil particles have already lost most of their available P during transport from a field to a river. The driving force in this P loss may have been the widening of the water-soil ratio. Yli-Halla *et al.* (1995) estimated the contribution of eroded soil to DRP loss from the relationship between P release and the water-soil ratio in the Aurajoki and Jokioinen soils. If suspended soil in surface runoff had the same P release characteristics as the bulk of surface soil, it can have contributed a maximum of 16 to 38% of the DRP in runoff. The rest of DRP was assumed to have originated from the soil left in the field (Yli-Halla *et al.* 1995).

The conclusion that eroded soil particles contribute to DRP loss is still far from certain. Alternatively, erosion may have selectively removed the finest particles with the strongest ability to bind P and, consequently, the lowest tendency to release P. Furthermore, drying of the soils tested in paper III may have increased their P availability (see Klotz 1988). Finally, the amount of P in riverine particles retained by Fe-hydroxide impregnated paper strips (6–64 µg g⁻¹, mean 36 µg g⁻¹, II) was not lower than that in cultivated soils of Finland (8–64 µg g⁻¹, mean 31 µg g⁻¹, Yli-Halla 1989).

3.6.2 Modelling the concentration of dissolved reactive phosphorus in surface runoff

The design of agricultural water protection measures would benefit from a relatively simple model by which the effect of different agricultural management practices on DRP loss could be predict-

ed. The model should be applicable to various soil and crop types under different environmental conditions, and should be based on easily available data. In this study, an attempt was made to model the concentration of DRP in runoff from the Aurajoki and Jokioinen fields by the Sharpley equation (VII). However, the effort was largely unsuccessful; the original equation overestimated by a factor of 110 to 1600 the mean DRP concentrations in the surface runoff from the plots with different winter cover, crop and P status (Fig. 15a). In addition, there was no correlation between the simulated and observed mean concentrations of DRP. Daniel *et al.* (1993) also found the equation to overpredict the concentrations of DRP by a factor of 1.7 for pasture plots and 100 for tillage plots in Arkansas, USA. Furthermore, the equation significantly accounted for the variation in observed DRP concentrations for pasture plots only (Daniel *et al.* 1993). On the other hand, the Sharpley equation accurately simulated DRP in cropped and grassed watersheds in the southern Great Plains, USA (Sharpley *et al.* 1985, Sharpley and Smith 1989, 1993).

The reason for the overprediction of DRP in surface runoff from the Finnish soils remained unidentified. It is possible that the water-soil ratio derived from the TSS concentration in runoff by Eq. 6 (section 2.5) overestimated the true ratio and subsequently the release of P. This hypothesis is correct if P was released from the soil remaining in the field rather than from eroded soil transported by surface runoff to the edge of the field (where sampling was performed). In addition, the eroded soil particles may have had a higher ability to bind P than the bulk soil. The value of runoff duration applied in the modelling approach (30 min) was probably too low for the Finnish conditions (see Posch *et al.* 1992). However, the use of a higher value would have resulted in an even more pronounced overestimation (see Eq. 4). In addition, the equation predicts DRP in individual runoff events. As the interval between the recordings of cumulative runoff was several days at Aurajoki and Jokioinen, the values for runoff volume may have represented the cumulative runoff volumes of several individual events. However, due to the inverse relationship between DRP and runoff volume in the Sharpley equation (Fig. 16), too high values for runoff volume should result in the underestimation, not overestimation of DRP.

To obtain better simulations for DRP, several serial modifications of the Sharpley equation were made. Although the fit between the observed and simulated mean concentrations of DRP for each treatment was improved by the modifications, the correct level of results could only be achieved by calibration. The first modification consisted of estimating the amount of desorbable P by water extraction instead of Bray extraction (Fig. 15b). The substitution was based on the observation that water-extractable P well illustrates the P status of Finnish mineral soils (Hartikainen 1982b). In addition, water-extractable P has been reported to reflect the concentration of DRP in surface runoff from agricultural soils (Yli-Halla *et al.* 1995, Pote *et al.* 1996). In contrast, as judged from the regression line between DRP and Bray extractable P, which intercepts the x-axis at 12 mg kg^{-1} , the Bray solution appears to extract P forms that will not be desorbed from the soils tested during the runoff process (the corresponding intersection for water-extractable P was -0.4 mg kg^{-1} , Fig. 17). Furthermore, the Bray extraction is not routinely used in Finland.

The second modification consisted of excluding the runoff term ($V^{-0.424}$) as no correlation between DRP and V was observed in either of the fields (Fig. 15c). As a result, the temporal variation in DRP was predicted entirely by the variation in the TSS concentration (see Eq. 12). The relationship between TSS and simulated DRP was dependent on the value of the P buffer power of the soil (Fig. 16). The higher its value in the range 0–0.576, the less sensitive was DRP to changes in TSS. When the buffer power exceeded 0.576, the opposite applied and the relationship between TSS and DRP became negative, *i.e.* eroded soil became a sink for DRP. Due to a low buffer power (0.386–0.417), TSS substantially affected simulated DRP at Aurajoki. However, at Jokioinen, the values for buffer power were 0.529 to 0.550, so near to 0.576 that TSS exerted almost no effect on DRP (VII). These model assumptions were partly supported by the observed relationship between DRP and TSS in the surface runoff. Despite marked variation, DRP was positively related to TSS at Aurajoki in the low concentration range of TSS; with higher TSS concentrations, DRP reached a more constant level (*cf.* Figs. 16 and 18a). At Jokioinen, the relationship between TSS and DRP was less clear at low TSS concentrations (Fig. 18b).

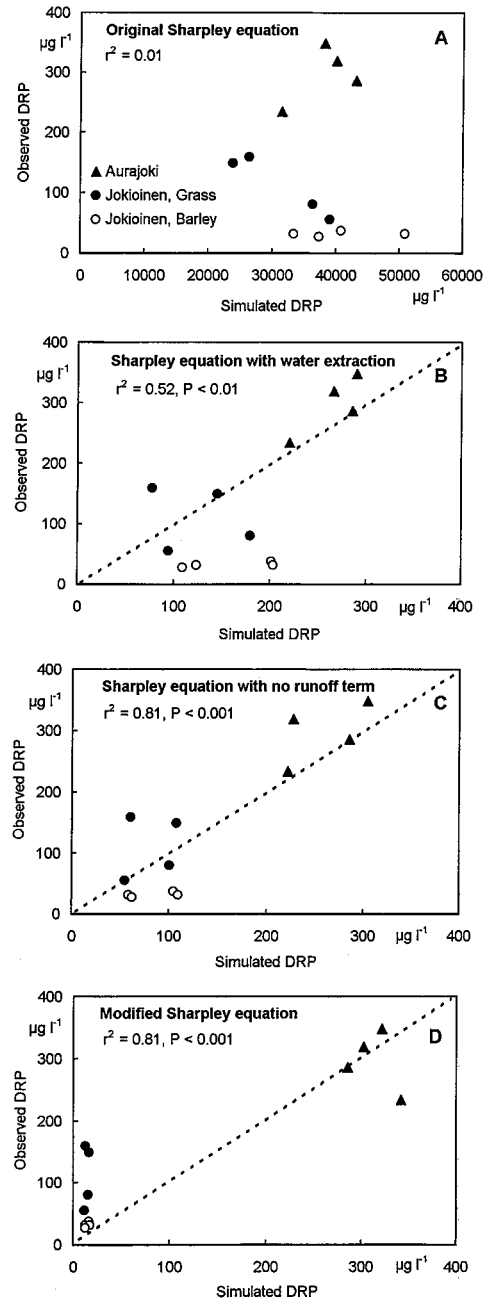


Fig. 15. Observed and simulated mean concentrations of dissolved reactive P (DRP) in the surface runoff from the Aurajoki and Jokioinen soils as simulated with the original Sharpley equation (a), the Sharpley equation with desorbable soil P estimated from water extractions (b), the Sharpley equation with no runoff term (c) and the final modification (d).

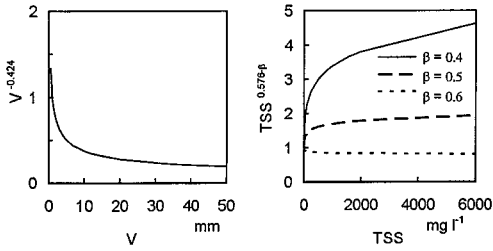


Fig. 16. Relative effects of runoff volume (V) and the concentration of suspended solids (TSS) in the Sharpley equation. β is a constant that describes the P buffer power of the soil.

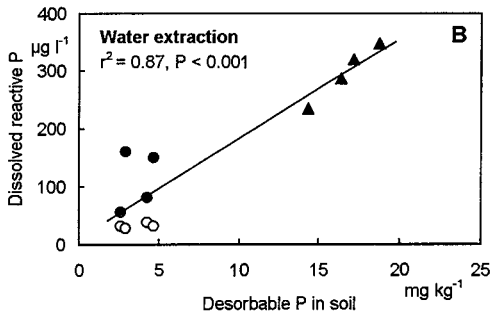
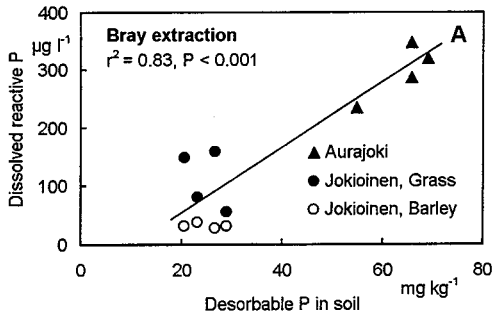


Fig. 17. Relationship between Bray extractable P (a) and water extractable P (b) in surface soil and dissolved reactive P in surface runoff.

In the original Sharpley equation, buffer power also directly affects the level of DRP (see Eq. 11); the higher its value, the higher the simulated DRP. The effect of buffer power on DRP is very strong and appears to be an artefact. Therefore, the third modification consisted of excluding the term $10^{6\beta-1.152}$ from the equation. However, the exclusion did not further improve the fit between the

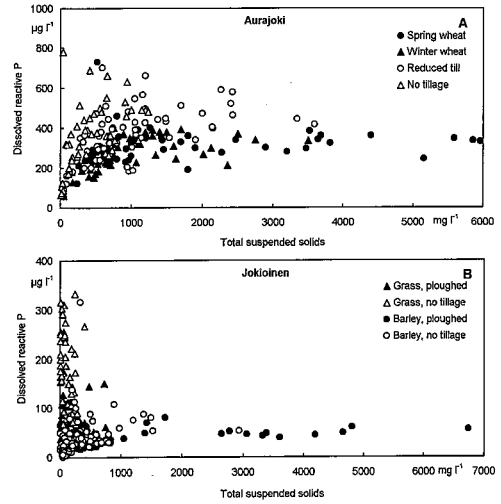


Fig. 18. Relationship between the concentrations of total suspended solids and dissolved reactive P in the surface runoff from the Aurajoki (a) and Jokioinen (b) soils.

simulated and observed mean concentrations (Fig. 15d). According to the final modified equation,

$$DRP = \gamma K_B P_D D_b t^\alpha e^{-3.13+0.071SA} TSS^{0.576-\beta} \quad (13)$$

DRP in runoff depends *e.g.* on TSS concentration in runoff, and on the P status and buffer power of soil. This appears reasonable. The concentration of TSS provides information on several crucial factors. First, it reflects the intensity with which surface runoff and surface soil have interacted. In this way, the effect of snow cover and soil frost are also taken into account, as erosion and consequently TSS concentration are affected by these typical Finnish winter conditions. This finding also suggests that soil aggregation, needed to calculate the effective depth of interaction, and bulk density could be excluded from the equation. Second, TSS concentration is the reciprocal of the water-soil ratio, which according to laboratory experiments influences desorption of P; the higher the TSS concentration, the greater is the amount of P that can be either desorbed from or sorbed to eroded soil particles during transport from field to surface waters (Sharpley *et al.* 1981a, b, Yli-Halla *et al.* 1995, Yli-Halla and Hartikainen 1996). Whether the exchange of P occurs between runoff and surface soil or at a later stage between runoff and eroded soil particles (Sharpley *et al.* 1981c,

Yli-Halla *et al.* 1995), the amount of P that will be desorbed or sorbed is a function of soil P status and the P buffer power of the soil.

As already mentioned, the modified equations gave a reasonable level of DRP only after calibration. The correction factor was derived from the ratio of observed and simulated mean concentration of DRP in the ploughed spring wheat plot at Aurajoki. The calibrated equation underestimated DRP in the reduced-tillage and untilled plots at Aurajoki and in all plots at Jokioinen, particularly in the grass experiment. As regards Aurajoki, the underestimation is partly due to the fact that labile P of the 0–25 cm soil layer did not reflect the enrichment of fertilizer P in the top soil layer of the reduced-tillage and untilled plots. As most of the runoff probably occurred in the uppermost soil layer, the labile P of the 0–25 cm layer, used in simulations, underestimated that of the interactive soil layer in these plots (see Table 7). With regard to the grass experiment at Jokioinen, the release of P from the killed grass residues was a likely P source, particularly in the untilled plots. Plant residues may also have contributed to DRP at Aurajoki (*cf.* Schreiber and McDowell 1985).

Yli-Halla *et al.* (1995) showed that when the Aurajoki and Jokioinen soils were extracted with water according to the procedure of Hartikainen (1982b), the concentration of P formed in the extraction solution (water-soil ratio 100:1 and 250:1) was at the same level as the flow-weighted mean concentration of P in the surface runoff from these soils. Despite the several modifications to the Sharpley equation, the mean DRP level for each treatment could be best predicted solely from labile P. As estimated by water extraction, this variable accounted for 87% of the variation in the mean DRP concentrations, whereas the modified equation accounted for 81% of the variation (Figs. 15c, d, and 17). However, the equation might have performed better if the model coefficients K , α and β had been measured for the soils.

Provided that the assumptions of the modified equation are correct, DRP concentration in surface runoff will increase with increasing soil loss if the P buffering power of the soil is weak. The practical implication would be that agricultural management practices reducing erosion result in the decline of DRP losses, particularly if they are directed towards easily erodible soils with high labile P and low P buffer power. However, the benefit may be nullified by the effects of the enrich-

ment of fertilizer P in the interactive soil layer and by the elevated amount of plant residues left on the soil surface (Logan 1982, Gaynor and Findlay 1995). To develop further the Sharpley equation, it should be tested under widely differing climatic and edaphic conditions. In particular, the dependence of DRP on (i) runoff volume and duration and (ii) TSS should be assessed.

4 Concluding remarks

Results obtained by simple laboratory experiments on P availability are sometimes dismissed by the argument that aquatic ecosystems are so diverse and complex that nearly all P will eventually be utilised by the biota in these systems. According to this view, the current national strategy in which the measures to reduce P are based on TP load, is correct. However, there are arguments to suggest that some P will remain unavailable to biota. First, the P in Finnish cultivated soils is largely unavailable to plants (*e.g.* Yli-Halla 1990, 1991). It is unlikely that the P forms unavailable to plants in terrestrial systems would become 'bio-available' in aquatic systems. Second, even if most P would eventually become available, the most important P fractions from the viewpoint of eutrophication are those which are easily available; the contribution of the slowly released P forms is probably small compared with all other P fluxes, particularly in eutrophic waters. Even if the release may be accelerated under some environmental conditions, such as anoxia, these conditions are relatively rare. Furthermore, they are usually a consequence of excess external loading of easily available P. Thus, although all assays tend to underestimate the potential availability of P (see Peters 1981), this underestimation does not suggest that all P is available.

Therefore, it is reasonable to combat eutrophication by targeting readily available P forms. As regards agricultural P loading, the most available P fraction is dissolved reactive P, whereas particulate P in river waters seems to contribute only slightly to the available P pool. In some, probably rare conditions, eroded soil particles may even reduce the load of readily available P (see Taylor and Kunishi 1971, Green *et al.* 1978, Hartikainen 1979, Dorioz *et al.* 1998, van der Molen *et al.* 1998). An example of such conditions would be a river receiving point source effluents with high dissolved P concentra-

tion and agricultural runoff with a high concentration of eroded soil. In addition, if aesthetic considerations are omitted, the turbidity caused by suspended particles may be regarded as beneficial, as it reduces the euphotic water layer and consequently algal productivity. It has also been suggested that clay particles decrease algal productivity by increasing the settling of planktonic algae (Avnimelech *et al.* 1982). However, if P is desorbed to a marked extent from the detached soil particles in the early phases of erosion processes, an effective reduction of dissolved reactive P also calls for erosion control. Admittedly, the reduction of the load of dissolved reactive P from agricultural land is impeded by the fact that its origin remains partly uncertain. Models cannot be used in the planning of agricultural P-reduction measures until sufficient information exists on the reactions controlling the release of dissolved reactive P from soil and the subsequent transport of P to receiving waters.

Due to several methodological factors, the estimates for the potential algal-availability of P presented in this study may be too low. To eliminate some of the analytical uncertainty, assays under widely different laboratory conditions should be performed using the same material. The conditions should include, for example, those prevailing in eutrophic brackish coastal waters. To examine whether the wide variation in the proportion of the available fraction of total P, presented in more than 50 laboratory-scale studies, is caused by differences in sample material or assay techniques, comparisons using samples from various countries would be useful.

The different availabilities of various P forms have implications for the monitoring of pollution sources and receiving waters. In addition to TP, the analysis of DRP should be included in the monitoring of all major P sources. The measurement of DRP should be performed using an appropriate filter, such as Nuclepore polycarbonate filters of 0.4 μm pore size. In Finland, this P analysis is currently included only in the monitoring programmes of some diffuse sources. The measurement of DRP in the receiving waters during the production period may appear frustrating as the concentrations are often negligible. However, it has been estimated that the P requirements of algae are satisfied at DRP concentrations as low as approximately $2 \mu\text{g l}^{-1}$ (see Grobbelaar and House 1995), which is near the detection limit of the analysis. Thus, if measurable quantities of DRP

exist in the productive water layer during the ice-free period, the information is highly useful. In such cases, some other factors than P probably limit the growth of planktonic algae.

5 Summary

Eutrophication of many inland and coastal waters is attributed to the excess supply of P. In the beginning of the 1970s, municipal wastewaters were a substantial P source to Finnish waters, whereas currently more than half of the anthropogenic P load originates from agriculture. Phosphorus from both these sources consists of several different forms. In the receiving waters, algae readily use only a part of the P, whereas some P forms may become available slowly or they may be entirely inert. In order to efficiently abate eutrophication, the P reduction measures should be targeted towards algal-available P rather than total P. The aim of this study was to estimate what portion, and which forms of the P originating from agriculture and municipalities can potentially be transformed into forms which can be utilised by planktonic algae. In addition, the actual release of this potentially algal-available P was examined under Finnish conditions. Furthermore, with regard to the loss of agricultural P, efforts were made to estimate the sources of available P and to model the loss of dissolved reactive P in surface runoff. The data was largely derived from laboratory experiments. In addition, observations on lake nutrient balances and soil and runoff data from two experimental fields were examined. In the following, the main findings of this study are summarised.

By which experimental techniques can the potentially algal-available P be reliably determined?

The use of suitable methodology is crucial in the testing of potentially algal-available P. In this study, the potential availability was approximated by two algal-assay techniques (dual culture assays and batch assays) and by a chemical method (the determination of reversibly adsorbed P). Batch assays, in which algae and particles are mixed, have often been considered the most reliable technique. However, tests with soil samples revealed that the dual culture assays, in which algae and P-carrying

particles are separated from each other, generally gave higher values for the potentially algal-available P than the batch assays. The result indicates that algal surface-bound enzymes do not markedly affect the availability of soil P to a chlorophycean *Selenastrum capricornutum* Printz. The dual culture assays are labourious, but for the time being cannot be replaced by the relatively simple chemical method. The true potentially algal-available P is probably underestimated to some extent by the dual culture assays; especially under conditions of high pH or anoxia the availability of particulate P may be higher than indicated by the assays. In addition, due to a relatively short incubation period, problems in P determination and possible P uptake by bacteria, the assays may underestimate available P.

Is it possible to approximate the potentially algal-available P by simple routine P analyses?

The P fractionation employed here could only partly predict the potential availability of P. Most of the dissolved reactive P, analysed from a filtered sample by a molybdenum blue method, appeared to be available. By contrast, dissolved unreactive P, which represents the P forms capable of passing a filter but requiring digestion to react with molybdate, appeared to be inert in the agriculturally loaded rivers. However, in the purified municipal wastewaters, an average of 22% (0–74%) of the dissolved unreactive P appeared to be converted into an available form. Of the total amount of P in the filtered samples, an average of 80% appeared to be available in the river waters and 58% in the municipal wastewaters. Particulate P, obtained as the difference between total P and dissolved P, showed variable availability. The proportion of available particulate P was 0 to 13% (mean 4%) in water of the agriculturally loaded rivers, 17 to 24% (mean 20%) in the surface soil of agricultural land and 0 to 54% (mean 25%) in the purified municipal wastewater. Due to wide variations in the availabilities and concentrations of the individual P fractions in the samples tested, their total P content was a poor absolute or relative indicator of the algal-available P. The determination of dissolved reactive P appears to offer a reliable measure of the minimum amount of algal-available P. It is suggested that this P fraction be included in the monitoring of P sources and their recipients.

What proportion of P in agricultural runoff and purified municipal wastewaters is potentially available to algae?

Provided that the samples studied here correctly reflected the overall situation in Finland, it can be estimated that 28% of the diffuse total P load originating from agriculture is potentially available to algae. The corresponding value for total P load from municipalities is 36%. The values indicate that 560–1120 and 90 tons, respectively, of algal-available P enters surface waters annually from these two sources. The potentially available P from agriculture primarily consisted of dissolved reactive P, whereas available P in purified municipal wastewaters was composed of dissolved unreactive P and particulate P in addition to dissolved reactive P. Thus, the measures for agricultural P control should be targeted towards the reduction of dissolved reactive P rather than of total P. The values for the potentially algal-available P obtained in this study were generally lower than those obtained elsewhere. The discrepancy is attributed to differences in methodology and in the materials tested. It should be noted that the results presented here are valid for freshwater lakes; the availability of particulate P may differ to some extent in brackish water systems, such as the coastal waters of the Baltic Sea.

What are the origins of algal-available P in agricultural runoff and can the P loss be estimated by a simple model?

Dissolved reactive P in surface runoff may originate from several different sources. For example, it may be desorbed from soil particles remaining in the field or from those detached from the field, or it may be released from decaying plant residues left on the soil surface. The algal assays showed that surface soil of agricultural land was richer in algal-available P than suspended particles in agriculturally loaded rivers. As the riverine particles were mainly composed of eroded soil particles, the observation above suggests that dissolved reactive P is markedly desorbed from eroded soil particles during the erosion process. Therefore, the agricultural treatments which reduce erosion should also diminish the loss of dissolved P. However, the beneficial effect of reduced tillage may be nullified by the concomitant increase in P leaching due to the enrichment of fertilizer P in the interactive soil layer and the elevated amount of plant residues left on the soil surface. The modelling efforts sug-

gested that the factors controlling the loss of dissolved reactive P from cultivated soil are still partly unknown. The empirical equation applied in this study (the Sharpley equation) produced substantial overestimations for the concentration of P in the surface runoff from two experimental fields. In addition, there was no correlation between the simulated and observed mean concentrations for each agricultural treatment. Although the correct level of results could only be achieved by calibration, the fit between the observed and simulated mean concentrations for each treatment was improved when a series of modifications was made to the equation. Provided that the assumptions of the modified equation are correct, the concentration of dissolved reactive P in surface runoff will increase with increasing erosion if the P buffering power of the soil is weak. This suggests that if erosion control measures are used to reduce the loss of available P, the measures should be directed towards easily erodible soils with high P status and low P buffering power.

To what extent is potentially available P actually released in receiving waters?

The observations on P balances of the agriculturally loaded lake Pyhäjärvi (southwestern Finland) support the results of the algal assays that dissolved reactive P is readily utilised by algae, whereas dissolved unreactive P is largely inert. Although the lake efficiently retained the incoming P, a substantial amount of available P was supplied from the bottom of the lake during the productive season. The mechanism of the P release remained unidentified, but it appeared not to include the resuspension of inorganic matter. Nevertheless, it seems that the release of P from the bottom mainly reflects the cycling of readily available P forms in the lake, rather than the activation of previously unavailable P reserves.

6 Yhteenveto

Liiallisen ravinnekuorman seurauksena pintavesien perustuotanto kasvaa, ts. ne rehevöityvät. Yksi rehevöitymiseen liittyvistä ongelmista on planktonlevien määrän lisääntyminen. Planktonlevien vaatimuksiin suhteutettuna fosfori on ravinne, jota on sisävesissämme luontaisesti vähiten. Siten järvemme ovat erityisen herkkiä fosforikuormitukselle. Typen ohella fosforilla on merki-

tystä myös jokisuistojen ja rannikkovesien rehevöitymisessä. Yhdyskunnat olivat 1970-luvun alkupuolella yksi suurimmista vesien fosforikuormittajista, mutta jätevesien tehostuneen puhdistuksen ja pesuaineiden alentuneen fosforisisällön vuoksi yhdyskuntien osuus on enää vain 5 % ihmisen aiheuttamasta fosforin kokonaiskuormituksesta. Nykyisin suurin fosforin lähde on maatalous, jonka osuus fosforin kokonaiskuormituksesta on 60 %.

Vesiensuojelutoimet ovat kohdistuneet fosforin osalta kokonaisfosforikuormituksen vähentämiseen. Sekä yhdyskuntien että maatalouden fosforipäästöt sisältävät kuitenkin monia eri fosforimuotoja. Levät voivat välittömästi käyttää osan niistä, kun taas jotkin fosforimuodot muuntuvat vain vähitellen leville käyttökelpoisiksi, ja osa fosforista voi jäädä pysyvästi käyttökeltottomaan muotoon. Jotta rehevöitymistä voitaisiin tehokkaasti torjua ja vähentää, tulisi kuormituksen alentamistoimet suunnata kokonaisfosforin sijasta leville käyttökelpoiseen fosforiin.

Tämän tutkimuksen tavoitteena oli arvioida, mikä osuus ja mitkä muodot maatalouden ja yhdyskuntien fosforipäästöistä ovat leville potentiaalisesti käyttökelpoisia. Lisäksi pyrittiin arvioimaan laboratorioskokeilla määritetyn potentiaalisesti käyttökelpoisen fosforin vapautumista maatalouden kuormittamissa järvissä. Maatalouden päästöjen osalta pyrittiin myös selvittämään, mikä on käyttökelpoisen fosforin alkuperä sekä mallintamaan erään käyttökelpoisen fosforijakeen pitoisuutta pintavalunnassa. Tutkimuksessa tarkasteltu aineisto perustui pitkälti laboratorioskokeisiin. Lisäksi käsiteltiin maatalouden kuormittaman järven fosforitaseaineistoa sekä huuhtoutumiskentiltä kerättyä maaperä- ja pintavalunta-aineistoa. Seuraavassa esitetään tutkimuksen tärkeimmät tulokset.

Miten potentiaalisesti käyttökelpoinen fosfori voidaan kokeellisesti määrittää?

Fosforin käyttökelpoisuudesta saatu arvio riippuu suuresti käyttökelpoisuuden määrittämismenetelmästä. Tässä tutkimuksessa fosforin potentiaalinen käyttökelpoisuus arvioitiin ensisijaisesti levätestimenetelmällä, jossa leviä kasvatettiin kahdesta neljään viikkoa niin, että levien ainoa fosforinlähde oli tutkittava näyte. Kasvatus tehtiin kaksiosaisessa astiassa, jossa levät ja näyte oli erotettu toisistaan suodatinkalvolla (*dual culture assays*). Kahden huuhtoutumiskentän pintamaa-

näytteistä fosforin käyttökelpoisuus arvioitiin edellisen menetelmän lisäksi myös niin, että levät ja tutkittavat hiukkaset olivat kosketuksessa toisiinsa (*batch assays*). Jälkimmäistä menetelmää on aiemmin pidetty luotettavimpana testimenetelmänä. Lisäksi maatalouden kuormittamien jokien vesi- ja kiintoainenäytteistä määritettiin käyttökelpoinen fosfori kemiallisella menetelmällä, jossa näytteistä vapautunut fosfori sidottiin rauta-hydroksidilla kyllästettyihin suodatinpaperiliuskoihin (*determination of reversibly adsorbed P*).

Menetelmä, jossa levät ja tutkittavat hiukkaset oli erotettu toisistaan antoi suurempia tuloksia peltomaan potentiaalisesti käyttökelpoiselle fosforille kuin menetelmä, jossa levillä oli suora kontakti maahiukkasiin. Tulos viittaa siihen, etteivät levien solunseinään kiinnittyneet entsyymit juurikaan edistä testeissä käytetyn viherlevän (*Selenastrum capricornutum* Printz) kykyä käyttää maa-ainekseen sitoutunutta fosforia. Menetelmä, jossa levät ja hiukkaset on erotettu toisistaan on työläs. Sitä ei kuitenkaan vielä voida korvata työssä testatulla kemiallisella menetelmällä.

Tässä tutkimuksessa esitetyt tulokset fosforin käyttökelpoisuudesta aliarvioivat jonkin verran todellista potentiaalista käyttökelpoisuutta. Käyttökelpoisuus voi olla suurempi erityisesti vesissä, joiden pH on korkea tai redox-potentiaali matala. Lisäksi eräät koetekniset seikat (lyhyehkö kasvatusaika, ongelmat fosforin määrittämisessä ja mahdollinen fosforin sitoutuminen bakteereihin) ovat voineet vaikuttaa siihen, että tulokset ovat liian pieniä.

Voidaanko potentiaalisesti käyttökelpoisen fosforin pitoisuutta arvioida rutiiniluontoisella fosforimäärittäyksellä?

Tutkimuksessa sovelletulla rutiiniluontoisella fosforin fraktioinnilla voitiin selittää fosforin potentiaalinen käyttökelpoisuus vain osittain. Suurin osa liuenneesta reaktiivisesta fosforista, joka määritettiin suodatetusta näytteestä molybdeenisämenetelmällä, vaikutti olevan käyttökelpoista. Sen sijaan liennut ei-reaktiivinen fosfori vaikutti olevan leville käyttökelpotonta jokivesinäytteissä. Tämä fosforijae koostuu niistä fosforimuodoista, jotka läpäisevät suodatinkalvon mutta vaativat peroksidisulfaattilla tehdyn hajotuksen reagoidakseen molybdaatin kanssa. Puhdistetussa yhdyskuntajätevedessä keskimäärin 22 % (0–74 %) liuenneesta ei-reaktiivisesta fosforista muuttui levätestien aikana käyttökelpoiseen muotoon. Liunneen fosforin kokonaismäärästä (liennut

reaktiivinen fosfori + liennut ei-reaktiivinen fosfori) keskimäärin 80 % oli jokivesissä ja 58 % jätevesissä käyttökelpoista. Hiukkasmaisen fosforin pitoisuus saatiin vähentämällä näytteen kokonaisfosforipitoisuudesta liunneen fosforin pitoisuus. Tämän fosforijakeen käyttökelpoisuus vaihteli näytteen alkuperän mukaan. Jokivesissä 0–13 % (keskimäärin 4 %) hiukkasmaisesta fosforista oli leville käyttökelpoista, peltojen pintamaassa vastaava osuus oli 17–24 % (keskimäärin 20 %) ja puhdistetuissa asumajätevesissä 0–54 % (keskimäärin 25 %).

Näytteiden kokonaisfosforipitoisuus kuvasi huonosti leville käyttökelpoisen fosforin suhteellista tai absoluuttista määrää. Tämä johtui näytteiden välisistä vaihteluista eri fosforijakeiden käyttökelpoisuuksissa ja pitoisuuksissa. Liennut reaktiivinen fosfori näyttää kuvastavan suhteellisen hyvin leville käyttökelpoisen fosforin minimimäärää. Siten tämä fosforijae olisi hyvä sisällyttää eri päästölähteiden sekä näiden purkuvesistöjen seurantaohjelmiin.

Mikä osuus maatalouden valumavesien ja puhdistettujen asumajätevesien fosforista on potentiaalisesti leville käyttökelpoista?

Olettaen, että tässä työssä testatut näytteet olivat riittävän edustavia, voidaan maataloudesta peräisin olevan hajakuormituksen arvioida sisältävän 28 % potentiaalisesti käyttökelpoista fosforia. Karjatalouden ns. suorissa fosforipäästöissä osuus on todennäköisesti jonkin verran korkeampi. Yhdyskuntien fosforikuormituksesta noin 36 % koostuu potentiaalisesti käyttökelpoisesta fosforista. Kun edellä esitetyillä osuuksilla kerrotaan vastaavat kokonaisfosforikuormitukset, saadaan maatalouden käyttökelpoisen fosforin hajakuormitukseksi 560–1120 tonnia vuodessa ja yhdyskuntien käyttökelpoisen fosforin kuormitukseksi 90 tonnia vuodessa.

Maataloudesta peräisin oleva käyttökelpoinen fosfori oli lähinnä liennutta reaktiivista fosforia. Tulos osoittaa, että maatalouden fosforikuormituksen vähentämistoimet olisi kohdistettava kokonaisfosforin sijasta liunneeseen reaktiiviseen fosforiin. Myös yhdyskuntien osalta vesiensuojelutoimet olisi hyvä kohdistaa tähän fosforijakeeseen. Tutkimuksessa saatiin viitteitä siitä, että puhdistusprosessin poistaessa tehokkaasti liennutta reaktiivista fosforia, myös hiukkasmaisen fosforin käyttökelpoisuus laskee.

Tässä tutkimuksessa saadut arviot potentiaali-

sesti käyttökelpoisesta fosforista ovat matalampia kuin useimmat aiemmin esitetyt arviot. Tämä johtuu toisaalta erilaisista testausmenetelmistä ja toisaalta näytteiden välisistä eroista. Tämän tutkimuksen tulokset ovat sovellettavissa makean veden ympäristöön. Rannikkojemme murtoveteen kohdistuu myös huomattava maatalouden ja asutuksen fosforikuormitus. Hiukkasmaisen fosforin käyttökelpoisuus voi jonkin verran poiketa murtoveden ja makean veden välillä.

Mistä lähteistä maatalouden valumavesien käyttökelpoinen fosfori on peräisin? Voidaanko käyttökelpoisen fosforin huuhtoutumista ennustaa empiirisellä mallilla?

Pintavalunnan liennut reaktiivinen fosfori voi olla peräisin monesta eri lähteestä. Se on voinut vapautua maa-aineksesta joko välittömästi sadetai lumensulamiseden sekoittuessa pellon pintakerrokseen tai vasta myöhemmin sen jälkeen kun maa-aines on erodoitunut valumaveteen. Liennutta reaktiivista fosforia voi myös huuhtoutua esimerkiksi pellon pinnalle jätetystä kasviaineksesta. Levätestit osoittivat, että huuhtoutumiskenttien pintamaassa oli enemmän leville käyttökelpoista fosforia kuin maatalouden kuormittamisen jokivesien kiintoaineessa. Koska jokivesien kiintoaine pitkälti koostui erodoituneista maa-hiukkasista, ero käyttökelpoisen fosforin määrissä viittaa siihen, että fosforia on vapautunut maa-hiukkasista eroosiotapahtuman alkuvaiheessa.

Edellä esitetyn tuloksen mukaan eroosiota ja hiukkasmaisen fosforin kulkeutumista vähentävien maanviljelytoimien pitäisi vähentää myös liunneen reaktiivisen fosforin huuhtoutumista. Käytännössä viljelymenetelmät, joissa maan muokkautusta kevennetään eivät kuitenkaan välttämättä vähennä, vaan saattavat jopa lisätä liunneen fosforin huuhtoutumista. Tämä johtuu lannoitefosforin rikastumisesta aiempaa voimakkaammin valumaveden kanssa reagoivaan pintamaakerrokseen sekä fosforin huuhtoutumisesta kasvinjäänteistä.

Mallilaskelmat osoittivat, että liunneen reaktiivisen fosforin huuhtoutumiseen vaikuttavat tekijät tunnetaan vielä puutteellisesti. Tutkimuksessa sovellettu empiirinen, ns. Sharp-ley'n yhtälö yliarvioi huomattavasti eri tavoin käsitellyiltä peltolohkoilta tulevan pintavalunnan fosforipitoisuuksia. Yhtälö ei myöskään pystynyt kuvaamaan eri viljelymenetelmien välisiä suhteellisia eroja fosforipitoisuuksissa. Tässä tutkimuksessa Sharp-ley'n yhtälöä muunneltiin mm. arvioimalla desorp-

tiokykyinen fosfori Bray-uuton sijasta vesiuuton perusteella ja poistamalla liunneen reaktiivisen fosforin ja valunnan määrän välinen yhteys. Modifioitu yhtälö kuvasi alkuperäistä paremmin eri viljelymenetelmien välisiä eroja, mutta ei tuottanut oikeaa tulostasoa ilman kalibrointia. Mikäli muunnellun yhtälön oletukset ovat oikeita, liunneen reaktiivisen fosforin pitoisuus pintavalunnassa nousee eroosion kasvaessa vain maan fosforinpuskurikyvyn ollessa heikko. Mikäli eroosion torjuntaa halutaan käyttää myös liunneen fosforin huuhtoutumisen vähentämiseen, tulisi toimet kohdentaa eroosioherkille pelloille, joilla on korkea fosforitila ja matala fosforinpuskurikyky.

Missä määrin potentiaalisesti käyttökelpoinen fosfori todella vapautuu vesissä?

Maatalouden kuormittaman Säkylän Pyhäjärven fosforitaseet tukivat levätestien antamaa käsitystä siitä, että levät käyttävät nopeasti järveen tulevan liunneen reaktiivisen fosforin, kun taas liennut ei-reaktiivinen fosfori ei muunnu käyttökelpoiseen muotoon. Suurin osa ulkoisesta fosforikuormituksesta laskeutui Pyhäjärven pohjalle tai poistui järvestä kalansaaliin mukana. Tuotantokauden aikana järven pohjalta vapautui huomattavasti käyttökelpoista fosforia, mutta vapautumisen mekanismeja ei voitu selvästi osoittaa. Vaikka osa pohjalle laskeutuneesta epäorgaanisesta hiukkasmaisesta fosforista siirtyi tuulen vaikutuksesta uudelleen veteen, ei tästä aineksesta ilmeisesti juurikaan vapautunut leville käyttökelpoista fosforia. Vaikuttaakin siltä, että aiemmin käyttökelpottomat fosforimuodot, kuten jokien tuoma eroosioainekseen sitoutunut fosfori, eivät muunnu järven pohjalla käyttökelpoiseen muotoon. Siten käyttökelpoisen fosforin vapautuminen Pyhäjärven pohjalta olisi osa helposti käyttökelpoisen fosforin kiertoa järvestä.

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I believe that the first steps are the most important ones in almost everything. Thus, I would like to start my acknowledgements by warmly thanking the persons who were especially influential during the early years, most of them being around in more recent years too.

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Petri Ekholm

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