

# Phosphorus in surface runoff and drainage water affected by cultivation practices

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## PREFACE

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To Ari, Matti, Riku and Sara

Jokioinen, 31 August 1999

Eila Turtola

## LIST OF ORIGINAL ARTICLES

This paper is a summary and discussion of the following articles, which in the introductory chapter are referred to by their Roman numerals:

- I Turtola, E. 1996. Shortcomings of Finnish standard methods for determining phosphorus in water samples containing soil particles. *Boreal Environment Research* 1: 17–26.
- II Turtola, E. 1989. Effect of storage and sulphuric acid addition on analytical results of nitrogen and phosphorus in water samples containing eroded material. *Aqua Fennica* 19(2): 109–112.
- III Turtola, E. & Paajanen, A. 1995. Influence of improved subsurface drainage on phosphorus losses and nitrogen leaching from a heavy clay soil. *Agricultural Water Management* 28(4): 295–310.
- IV Turtola, E. & Jaakkola, A. 1995. Loss of phosphorus by surface runoff and leaching from a heavy clay soil under barley and grass ley in Finland. *Acta Agriculturae Scandinavica Sect. B, Soil and Plant Science* 45: 159–165.
- V Turtola, E. & Kemppainen, E. 1998. Nitrogen and phosphorus losses in surface runoff and drainage water after application of slurry and mineral fertilizer to perennial grass ley. *Agricultural and Food Science in Finland* 7: 569–581.
- VI Turtola, E. & Yli-Halla, M. 1999. Fate of phosphorus applied in slurry and mineral fertilizer: accumulation in soil and release into surface runoff water. *Nutrient Cycling in Agroecosystems* 55(2): 165–174.

Eila Turtola was fully responsible for papers I and II.

In paper III, Eila Turtola initiated the study and Arja Paajanen did the data processing. Both participated in the interpretation of the results and writing, Eila Turtola having the main responsibility.

Antti Jaakkola set up and carried out the experiment described in paper IV, and Eila Turtola did the data processing. Both participated in the interpretation of the results. Eila Turtola wrote the paper and Antti Jaakkola commented on the manuscript.

Erkki Kemppainen set up and carried out the experiment described in paper V, and Eila Turtola did the data processing. Both participated in the interpretation of the results. Eila Turtola wrote the paper and Erkki Kemppainen commented on the manuscript.

Eila Turtola and Markku Yli-Halla planned the study described in paper VI. Eila Turtola did the data processing and both participated in the interpretation of the results and the writing.

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## ABSTRACT

To improve the water quality of Finnish lakes, rivers and coastal areas, knowledge is needed of management practices aiming to reduce losses of phosphorus (P) from agriculture. In the present study, the P load on the aquatic environment through surface runoff and drainage water was estimated by investigating water and soil samples taken from field experiments. The aim of the study was, first, to investigate errors associated with determinations of different P fractions in surface runoff and drainage water samples and, second, to highlight some cultivation practices and processes in runoff/soil interaction that might induce high P losses from agricultural soil to watercourses.

The experiments were carried out on soils originally quite poor in plant-available P at two experimental sites, one at Jokioinen, southwestern Finland, and one at Toholampi, western Finland. The Jokioinen site was situated on a heavy clay soil (Vertic Cambisol) with a 2% slope and the Toholampi site on a fine sand soil (Gleyic Podzol) with a 0.5% slope. The two 2–2.6 ha fields, with plots of 0.11–0.16 ha, had facilities to measure and collect surface runoff and drainage water, and allowed farming practices to be carried out with normal size machinery. The effect of different fertilizing and cropping practices on P losses was studied on both soils but the influence of subsurface drainage improvement only on the heavy clay soil. Water samples for investigating errors in P determinations were obtained from the heavy clay soil.

Suspended soil particles, which are typical of spring and autumn flow from cultivated clay soils, were the principal source of errors in determinations of different P fractions in the water samples. In peroxodisulphate digestion, which is used for determining total P, adding more sulphuric acid than is recommended in current standard methods increased the values by 5–7% but they were still 6–11% lower than those obtained by HF digestion. In dissolved orthophosphate P determination, Nuclepore (0.2 and 0.4  $\mu\text{m}$ ) and Sartorius PFN (0.45  $\mu\text{m}$ ) filters produced the same results although the release of orthophosphate from colloids passing through the filters was not totally eliminated, even with Nuclepore 0.2  $\mu\text{m}$  filters. The presence of suspended particles led to considerable overestimation (77%) of orthophosphate if the filtrates were stored and sulphuric acid was used as a preservative.

On both the heavy clay and the fine sand, grass ley decreased particulate P loss compared with barley although the proportion of surface runoff was increased in grass ley cultivation. However, the dissolved orthophosphate P losses were higher from ley, mostly due to surface application of fertilizers, which resulted in high dissolved orthophosphate P concentrations in surface runoff, indicating direct losses from applied P. On the fine sand, immediate ploughing after application of slurry in autumn reduced P losses efficiently. On the heavy clay, peak concentrations of orthophosphate P in drainage water indicated fast preferential movement of orthophosphate from the surface through macropores, while the podzolized fine sand profile efficiently retained P. Study of the fine sand showed that surface application of fertilizers on grass ley increased the amount of inorganic P and soil test P values in the top layer (0–5 cm), and the mean flow-weighted concentration of dissolved orthophosphate P in surface runoff rose linearly with the values of soil test P, thereby multiplying the P losses. Very shallow soil sampling (< 5 cm) is needed to assess the P loading potential in a soil with surface-applied P.

On the heavy clay, the contribution of drainage water to total discharge (drainage+surface runoff) rose from 10–40% to 50–90% when the subsurface drainage system was improved. The drainage water contained relatively high amounts of suspended soil particles and particulate P both before and after the drainage improvement, surface soil being the most probable origin of the particles. Contrary to wood chips, topsoil as backfill material was able to reduce particulate P losses from the field. The 25% lower losses of dissolved orthophosphate P after the improvement indicated efficient sorption of orthophosphate in the new drain trenches.

# 1 INTRODUCTION

Phosphorus (P) is the major nutrient controlling eutrophication in many aquatic systems (Fisher et al. 1995), e.g. in most Finnish lakes and near the coastline of the Archipelago Sea, southwestern Finland (Kauppi 1984, Kirkkala et al. 1998). Agricultural runoff contributes a significant portion of P inputs to aquatic systems (Iserman 1990, Sharpley et al. 1994). In Finland, the contribution of agriculture to the human induced P load, estimated at 60% (Ekholm 1998), has resulted in an increased occurrence of blue-green algal blooms and other eutrophication problems (Kauppi et al. 1993). Monitoring of small catchments influenced by agriculture shows that, contrary to the P load from built-up areas and industry, there has been no decrease in the load from agriculture (Kauppi 1984, Rekolainen 1989, Rekolainen et al. 1995, Rosenström et al. 1996).

To improve the water quality of rivers, lakes and coastal waters, there is a need for cultivation practices aimed at reducing losses of P from agricultural soils. The P loss from agriculture is greatest in southern and western Finland, in a 100–200 km wide belt along the coast of the Baltic Sea, where the percentage of agricultural land is the highest in the country. Rivers loaded with suspended soil particles and nutrients leached from fields flow through cultivated areas towards the Baltic Sea. Data collected for voluntary soil analyses show that the cultivated soils are clayey (>30% clay fraction) in the plough layer in 55–66% of the field area (Kurki 1982). Towards Middle Finland, the percentage of silt and sand soils increases, the percentage of agricultural land decreases and lakes become more abundant.

It is essential to measure the particulate and dissolved orthophosphate P fractions in runoff waters from agricultural soils, as the losses of these fractions are induced by different mechanisms (erosion and desorption). Moreover, the availability of the fractions for algal growth varies. Dissolved orthophosphate P is generally considered to be 100% algal available (Walton and Lee 1972, Herve and Kauppi 1986, Sharpley et al. 1991, Ekholm 1994), whereas particulate P can exist in many chemical forms in undissolved

colloids and larger particles. Bioassay experiments showed that only 0–13% (mean 5%) of the particulate P in river water samples was potentially available for algal growth (Ekholm 1994). With the aid of anion exchange resin extraction, Uusitalo et al. (1999) estimated that 5–10% of the particulate P in surface runoff samples from two clay soils was potentially bioavailable. Suspended particulate P consists of various soil P pools: labile P, secondary P bound to Fe and Al oxides, primary P bound to Ca (apatite P), and organic P. During transport and progressive dilution of the runoff water, labile P and secondary P are partly desorbed from the particles, thus contributing to the loss of dissolved P. Desorption of P is enhanced by a decrease in the concentration of background electrolytes (Barrow 1983, Yli-Halla and Hartikainen 1996).

Problems of water clogging and heavy surface runoff are endemic to heavy clay soils, owing to low hydraulic conductivity. In dry clay soil, water tends to pass quickly through cracks and macropores as preferential flow (Talsma and van der Lelij 1976, German and Bewen 1981, Bronswijk et al. 1995) but after wetting, swelling and closure of the cracks, infiltration slows down dramatically (Bouma and Wösten 1979). Moreover, during snowmelt, the macropores of frozen soil may be blocked by ice, reducing hydraulic conductivity and water percolation (Bottcher et al. 1981). As a result of low conductivity, snowmelt and rainwater are easily channelled to surface runoff, particularly on sloping fields.

The route of runoff water, whether along the surface or through the soil to a subsurface drainage system, would be expected to influence P losses from a field. Erosion of soil particles is induced by the mechanical action of raindrops and surface runoff (Bottcher et al. 1980, Rose 1998, Agassi and Bradford 1999), but during infiltration and flow through soil pores, some suspended particles, and thus particulate P, may be sieved from the water. As surface runoff water moves along the soil surface and soil pores near the surface, the dissolved orthophosphate P held in soil pores is removed, water-soluble soil P compounds are dissolved, and some of the inorganic P sorbed on soil surfaces is released

into the surface runoff water. Although dissolved orthophosphate P in the soil solution (in concentrations of 0.003–0.7 mg l<sup>-1</sup>, Wiklander and Anderson 1974, Beek and Riemsdijk 1982, Bohn et al. 1985) is often the main source of orthophosphate in runoff, some dissolved orthophosphate P is contributed by decaying crop residues (Timmons et al. 1970, Burwell et al. 1975, Ulén 1984).

When P is applied to the surface soil (0–10 cm) only, the P status of the subsoil tends to be much lower than in the plough layer (0–25 cm). In the case of deep infiltration, therefore, the slow movement of water through the subsoil, where the equilibrium concentration is lower, may allow sorption of dissolved orthophosphate P from the percolating waters (Hartikainen 1979, Sharpley and Syers 1979a). The subsurface placement of mineral fertilizers to spring-sown arable crops that began in Finland in the 1960s' has improved the efficiency of P fertilization, and annual soil tillage prevents P from accumulating on the topmost (0–5 cm) soil. In contrast, P in mineral fertilizers is applied almost exclusively to the surface in grasslands, causing a potential risk of P losses. Surface application of fertilizer P has been shown to induce larger losses of dissolved P in surface runoff than does incorporation of fertilizer (Timmons et al. 1973, Uhlen 1978b). Therefore, different water pathways and cropping practices may be characterized by different P fractions and magnitudes of P loss.

The P-sorption properties of acid soils are dominated by their contents of poorly crystalline Al and Fe oxides (Breeuwsma and Silva 1992, Lookman et al. 1995). Due to the high content of Al and Fe oxides in Finnish acid soils (Kaila 1965, Hartikainen 1979), residual fertilizer P accumulates in Al- and Fe-bound forms (Hartikainen 1989). However, by raising the P saturation of the sorbing mineral surfaces, the fertilizer inputs affect the amount of labile P and the equilibrium concentration between sorbed P and dissolved orthophosphate shifts towards a higher concentration in the soil solution (Hartikainen 1979, 1989). P fertilizer applied to the soil surface, in particular, tends to saturate the fixing sites at the surface and locally to raise the concentration of dissolved P in the soil solution (Biggar and Corey 1969, Oloya and Logan

1980). Heavy, long-lasting applications of P in slurry or manure can saturate the fixing sites and even increase the P saturation of the whole soil profile (Smet et al. 1996, Holford et al. 1997, Laves and Thum 1984). Moderate and more short-term surface applications of slurry or manure, such as reported by Sharpley and Smith (1995), Lyngstad and Tveitnes (1996), Ginting et al. (1998), Vervoort et al. (1998) and Hooda et al. (1999), influenced P status mainly in the 0–5 or 0–10 cm layer.

The degree of P saturation (DPS) of poorly crystalline Al and Fe oxides has been used as an indicator of the residual P-sorption capacity of soil and to identify soils from which high P loads might be expected to enter watercourses. Holford et al. (1997) found, for example that P leaching began when 17–38% of the sorption capacity of soil horizons had become saturated. In the Netherlands, a DPS of 25% is considered critical for P movement in surface and subsurface waters (Zee et al. 1987). The increase in P saturation raises the values of commonly measured, agronomically based values of soil test P. The increase in readily extractable P in surface soil correlates with higher concentrations of dissolved orthophosphate P in surface runoff water (Nelson and Romkens 1974, Sharpley et al. 1977, Pote et al. 1996, Sibbesen and Sharpley 1997). In Finland, however, the database relating soil test P to the concentration of dissolved orthophosphate P in surface runoff is limited to only a few soils (Yli-Halla et al. 1995).

The aim of this study was twofold: 1) to investigate errors associated with determinations of different P fractions in surface runoff and drainage water samples, and 2) to highlight some cultivation practices and processes in the runoff/soil interface that may induce high P losses from agricultural soil to watercourses. The introductory chapter is a summary of six separate papers (I–VI). The accuracy of standard methods for determining total P and dissolved orthophosphate P in water samples containing suspended soil particles is discussed with reference to the accuracy of measured P losses. Some improvements to the accuracy of the analytical procedures are suggested. Investigations on the effect of different cultivation practices on particulate and dissolved orthophosphate P losses from



two sites, a heavy clay soil and a fine sand soil, originally with low or moderate P status are presented with a discussion on ways of mitigating the losses. The cultivation practices include installation of an improved subsurface drainage system, and barley and grass ley cropping with different P fertilization rates and application

practices. The influence of soil P status on the loss of dissolved orthophosphate P in surface runoff is attributed to the accumulation of surface-applied P in the topsoil. Finally, the losses of P are evaluated in terms of crop uptake of P to better estimate the short and long-term environmental risks of P application practices.

## 2 MATERIAL AND METHODS

### 2.1 The experimental sites

The experiments were carried out on two experimental fields at Jokioinen, southwestern Finland (see details in Jaakkola 1984) and at Toholampi, western Finland (Fig. 1). At Jokioinen the frost and snowcover extend from November to April, interrupted by snowmelts (Table 1). Typical of the Toholampi site are occasional snowmelts during the winter, the main snowmelt in March–April and frost until late May or early June (Table 1).

The Jokioinen soil, with a mean slope of 2% (1–4%), was silty or heavy clay in the plough layer and heavy clay in the subsoil according to the Finnish textural classification (Table 2). The clay in the experimental field was illitic, with moderate crack development and was classified as a Vertic Cambisol (FAO 1988) and a very fine Typic Cryaquept (Soil Survey Staff 1992). The soil was rather impermeable, as shown by measurements of saturated hydraulic conductivity and the volume of macropores (Table 2, III). Within the profile, the conductivity fell off sharply in the deeper layers, indicating a high tendency towards surface and near-surface runoff instead of deep percolation and drainage flow. The soil was rather poor in readily extractable P ( $P_{Ac}$ , determined as P dissolved in acid ammonium acetate, pH 4.65, Vuorinen and Mäkitie 1955) compared with the average  $P_{Ac}$  of clay soils in Finland in 1981–1985 found in the voluntary soil analyses ( $7.5 \text{ mg l}^{-1}$ , Kähäri et al. 1987) (Table 2). The soil was also poor in other inorganic P fractions as determined by a modified Chang and Jackson method (Hartikainen 1979); the exception was the NaOH-soluble fraction (Table 3).

The values of water extractable P ( $P_w$ ) were near the  $P_{Ac}$  values.

At the Toholampi site, the slope ranged from 0.30 to 0.74%, with a mean value of 0.54%. Sideways the mean slope was 1.1%. Texturally the field was fine sand and was classified as Gleyic Podzol (FAO 1988) and Aquic Haplocryod (Soil Survey Staff 1992). The 25–35 cm horizon was a spodic horizon, characterized by an abundance of oxalate-extractable Fe and Al and a relatively high amount of organic C (V). Over most of the field, the albic horizon and the upper part of the spodic horizon had been ploughed into the  $A_p$  horizon. The percentage of silt and clay was somewhat higher below the 35 cm depth than above it (Table 2). The values of saturated hydraulic conductivity were relatively low (V, Table 2), indicating a tendency towards surface runoff instead of deep percolation and drainage flow. The  $P_{Ac}$  value of the surface soil ( $6.4 \text{ mg l}^{-1}$ ) was lower than the average for fine sand soils in Finland in 1981–1985 according to voluntary soil analyses ( $11.5 \text{ mg l}^{-1}$ ; Kähäri et al. 1987).

The drainage system of the Jokioinen site (referred to below as heavy clay soil) consisted of 16 plots, 33 m x 33 m (0.11 ha), each with a separate pipe system to allow measurement and analysis of drainage water flow by means of tipping buckets (Fig. 1). The tile drainage pipes were laid in 1962, 16.5 m apart and at a depth of about 1 m. In 1975 they were connected to plastic cross pipes to form the 16 drainage plots. In 1991, new plastic drainage pipes were laid at the same depth but at 0.3 m from the old ones and connected to the same plastic cross pipes. The surface water, in turn, was collected from four

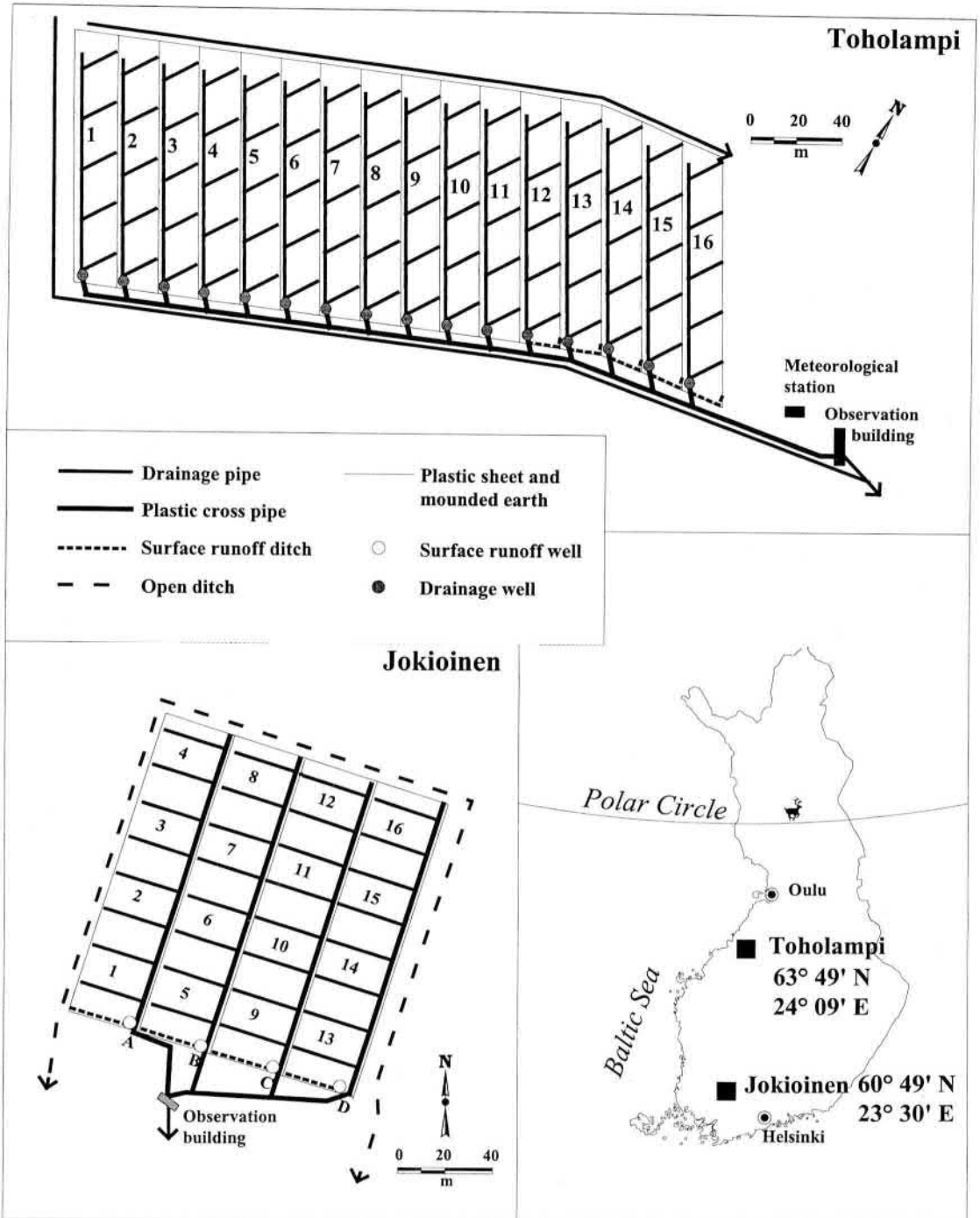


Figure 1. Location and maps of the experimental fields.

parallel areas, 33 m x 140 m (each consisting of four drainage plots), into an open ditch at the lower edge of the field, and conducted via wells ( $\varnothing$  0.6 m) for measurement and analysis (Fig. 1).

The flow-weighted water samples were collected with funnels conducting 0.1% of the total discharge to plastic containers for further sampling and chemical analysis. The field was sur-



Table 1. Total precipitation, maximum amount of water in snow in spring, number of snowmelts in winter-spring before the final snowmelt, dates of snow cover and frost and maximum frost depth during the experimental years (Jokioinen: 1 June – 31 May, Toholampi: 1 Sept. – 31 Aug.).

Year	Total precip. (mm)	Max. water in snow (mm)	Snow cover (date)	Snowmelts depth (cm)	Frost (date)	Max. frost
Jokioinen						
1980–1981	715	227	23.10 – 24.4	–	27.10 – 8.5	33
1981–1982	740	121	14.11 – 17.4	1	27.11 – 1.4	17
1982–1983	643	49	8.12 – 3.4	1	15.12 – 26.4	61
1983–1984	675	190	16.11 – 15.4	1	12.11 – 17.4	34
1984–1985	710	126	21.11 – 27.4	1	12.12 – 19.5	64
1985–1986	579	81	25.11 – 7.4	1	18.11 – 28.4	52
1986–1987	608	69	6.12 – 13.4	–	4.12 – 17.5	105
1987–1988	691	101	7.11 – 27.4	2	8.11 – 5.5	26
1988–1989	695	74	29.10 – 1.3	1	25.10 – 9.4	21
1989–1990	670	83	21.11 – 9.4	2	21.11 – 16.3	7
1990–1991	589	112	14.11 – 4.4	–	22.11 – 4.4	14
1991–1992	638	57	16.12 – 26.4	1	5.12 – 12.3	25
1992–1993	529	44	29.10 – 24.3	1	23.10 – 28.4	42
1993–1994	602	84	14.11 – 10.4	–	22.10 – 28.4	57
1994–1995	660	73	18.12 – 15.4	1	4.11 – 18.4	28
1995–1996	576	113	16.11 – 18.4	–	1.11 – 22.4	48
1996–1997	623	80	12.12 – 1.4	–	14.12 – 2.5	30
1997–1998	688	45	24.11 – 30.3	1	23.10 – 30.4	45
1998–1999	614	118	6.11 – 10.4	–	8.11 – 16.4	35
Average						
1980–1999	644		20.11 – 10.4		15.11 – 21.4	39
Toholampi						
1992–1993	594	86	10.10 – 5.4	1	15.10 – 26.5	62
1993–1994	534	150	11.11 – 10.4	–	16.10 – 12.6	58
1994–1995	671	95	8.11 – 19.4	1	10.11 – 3.6	69
1995–1996	486	120	29.10 – 20.4	–	3.11 – 9.6	66
Average						
1966–1996	583		18.11 – 13.4		9.11 – 30.5	63

rounded by open ditches, mounded earth and, after 1991, by plastic sheeting extending from the surface to a depth of 1 m to prevent water flow from outside. After 1991, the four surface runoff areas were also isolated from each other by plastic sheeting and 0.3 m high ridges of mounded earth.

The drainage system at Toholampi (referred to below as fine sand soil) consisted of 16 plots, 16 m x 100 m (0.16 ha), each with a separate pipe system to allow measurement and analysis of the drainage flow by means of tipping buckets (Fig. 1). The plastic drainage pipes were laid in 1989, 16 m apart and at a depth of about 1.05 m. They were connected to plastic cross pipes, that carried the drainage water to wells

( $\varnothing$  0.3 m) from where the water was conducted to an observation building for volume measurement. The surface runoff was collected at the lower end of five drainage plots (12, 13, 14, 15 and 16) into 0.2 m deep open ditches strengthened with concrete (Fig. 1). From there the water was conducted through plastic pipes for measurement and analysis. The flow-weighted water samples were collected with funnels conducting 0.24% of the total discharge to plastic containers for further sampling and chemical analysis. The plots were isolated hydrologically from each other and from the surrounding area with 0.3 m high ridges formed of mounded earth and with a plastic sheeting extending to a depth of 1.5 m.

Table 2. Particle size distribution, saturated hydraulic conductivity ( $K_{sat}$ ), content of organic carbon (Org. C), pH (1:2.5 soil:water suspension) and plant-available phosphorus ( $P_{Ac}$ ) in different soil layers of the experimental fields.

	Particle size fractions (%)			K <sub>sat</sub> (cm h <sup>-1</sup> )	Org. C (%)	pH <sub>water</sub>	P <sub>Ac</sub> (mg l <sup>-1</sup> ) <sup>1</sup>
	<0.002	0.002–0.02	0.02–0.2 mm				
Jokioinen							
0–25	61	16	23	62	2.7	5.9	3.4
25–40	83	8	9	0.63	0.6	6.3	0.2
40–80	90	6	4	0.0046	0.4	6.9	0.2
Toholampi							
0–25	5	17	75	0.63	5.0	5.7	6.4
25–35	4	22	72	0.88	2.6	5.2	4.1
35–60	9	30	62	–	0.3	5.3	2.7

<sup>1</sup> Acid ammonium acetate (pH 4.65) extractable phosphorus (Vuorinen and Mäkitie 1955)

Table 3. Phosphorus fractions (mg kg<sup>-1</sup>) in different soil layers of the experimental fields.

	NH <sub>4</sub> F <sup>1</sup>	NaOH	H <sub>2</sub> SO <sub>4</sub>	Total inorg.P	Org.P	Total P
Jokioinen 1990						
0–25	90	354	149	593	780	1373
25–60	53	135	133	321	505	826
60–90	58	112	226	396	515	911
Toholampi 1991						
0–20	163	55	146	364	455	819
20–40	53	36	242	331	262	593
40–60	24	46	424	494	155	649
60–90	13	60	480	553	115	668

<sup>1</sup> Summed with NH<sub>4</sub>Cl fraction

Table 4. Fertilizing method and amounts of N, P and K fertilizer (kg ha<sup>-1</sup>) for barley and grass ley in the heavy clay soil at Jokioinen, in 1980–1982.

Crop	Fertilizing method	Fertilizer amount					
		Low			High		
		N	P	K	N	P	K
Barley	Placement, 8 cm depth	50	21	40	100	42	80
Grass ley	Surface application, split into two equal portions	100	42	80	200	84	160

## 2.2 Field experiments

The effect of different cropping and fertilizer application practices on P losses was studied on heavy clay soil in 1980–1982. The aim was to compare total, particulate and dissolved orthophosphate P losses during barley and grass ley cultivation with different P fertilization rates and application practices (IV). The P losses through

both surface runoff and drainage water were measured. For barley, the NPK fertilizer was incorporated between the seed rows at a depth of c. 8 cm. For grass ley, the fertilizer dose was split into two equal portions, both broadcast on the soil surface. The annual amounts of P applied for barley were 21 and 42 kg ha<sup>-1</sup>, and for grass ley 42 and 84 kg ha<sup>-1</sup> (IV, Table 4).

In 1987–1993, the influence of subsurface

Table 5. Amounts of N, P and K fertilizer (kg ha<sup>-1</sup>) and cropping (soil surface condition during winter period in parentheses: p = ploughed, s = stubble, sc = stubble cultivated, ww = winter wheat, t = timothy) on surface runoff plots A, B, C and D and in the corresponding drainage plots 1–4, 5–8, 9–12 and 13–16, in the heavy clay soil at Jokioinen, in 1980–1998.

Year	Fertilizer N, P, K	Plot			
		A, 1–4	B, 5–8	C, 9–12	D, 13–16
1980	75, 32, 60 <sup>1</sup>	timothy (t)	spring barley (p)	timothy (t)	spring barley (p)
1981	75, 32, 60 <sup>1</sup>	timothy (t)	spring barley (p)	timothy (t)	spring barley (p)
1982	75, 32, 60 <sup>1</sup>	timothy (t)	spring barley (p)	timothy (p)	spring barley (p)
1983	106, 68, 118 <sup>2</sup>	timothy (p)	spring barley (p)	sp. barley/fallow (p)	spring barley/fallow (p)
1984	100, 22, 42	spring barley (p/ww <sup>3</sup> )	spring barley (p/ww <sup>3</sup> )	spring barley (p/ww <sup>3</sup> )	spring barley (p/ww <sup>3</sup> )
1985	106, 46, 78	wheat <sup>4</sup> (p/ww <sup>3</sup> )	wheat <sup>4</sup> (p/ww <sup>3</sup> )	wheat <sup>4</sup> (p/ww <sup>3</sup> )	wheat <sup>4</sup> (p/ww <sup>3</sup> )
1986	124, 22, 42	wheat <sup>4</sup> (p)	wheat <sup>4</sup> (p)	wheat <sup>4</sup> (p)	wheat <sup>4</sup> (p)
1987	0, 0, 0	bare fallow (p)	bare fallow (p)	ryegrass (p)	timothy (t)
1988	0, 0, 0 <sup>5</sup>	bare fallow (p)	spring barley (p)	spring barley (p)	timothy (t)
1989	0, 0, 0	bare fallow (p)	bare fallow (p)	ryegrass (p)	timothy (p)
1990	92, 42, 78	spring barley (p)	spring barley (p)	spring barley (p)	spring barley (p)
1991 <sup>6</sup>	80, 14, 21	spring barley (p)	spring barley (p)	spring barley (p)	spring barley (p)
1992	80, 14, 21	spring barley <sup>7</sup> (t)	spring barley <sup>7</sup> (t)	spring barley <sup>7</sup> (t)	spring barley <sup>7</sup> (t)
1993	90, 12, 5	timothy (p)	timothy (s <sup>8</sup> )	timothy (p)	timothy (s <sup>8</sup> )
1994	90, 25, 50	spring barley (p)	spring barley (s)	spring barley (p)	spring barley (s)
1995	90, 18, 36	spring barley (p)	spring barley (s)	spring barley (p)	spring barley (s)
1996	90, 18, 36	spring barley (p)	spring barley (sc)	spring barley (p)	spring barley (sc)
1997	90, 18, 32	spring barley (p)	spring barley (sc)	spring barley (p)	spring barley (sc)
1998	90, 18, 32	spring barley (p)	spring barley (sc)	spring barley (p)	spring barley (sc)

<sup>1</sup> Average for barley; average for timothy: 150, 63, 120

<sup>2</sup> For barley; for timothy: 206, 112, 200

<sup>3</sup> Half of area of surface runoff plots sown on winter wheat

<sup>4</sup> Half of area of surface runoff plots sown on winter wheat, the other half on spring wheat

<sup>5</sup> For plots A and D: 0,0,0; plots B and C: 92, 42, 78

<sup>6</sup> New drainage system installed in June 1991.

<sup>7</sup> With undersown timothy+red clover mixture

<sup>8</sup> Timothy killed with glyphosate in October

drainage improvement on P losses was studied on the heavy clay soil. This time the aim was to evaluate the effects of improved subsurface drainage on total, particulate and dissolved orthophosphate P losses (III). After 29 years of cropping since the subsurface drainage system was installed, in 1962, the drains had ceased to function well. New drainage pipes were laid therefore in 1991. These were at the same depth as the old ones but 0.3 m away. Above a layer of gravel, the drain trenches were filled with either topsoil (upper part of the field) or wood chips (lower part of the field). The amount of fertilizers applied as well as the crops cultivated in 1980–1998, including the years of study III, are presented in Table 5.

The influence of slurry application time on P losses in surface runoff and drainage water was

studied in 1992–1996 in the fine sand soil (V). Cow slurry was either mixed with the surface soil or surface-applied in autumn, winter or spring on perennial grass ley. The losses were compared with those from mineral fertilized and non-fertilized soil. For P, the total amounts applied (1992–1996) were 0, 141, 119, 143 and 107 kg ha<sup>-1</sup> for the unfertilized, autumn applied slurry, winter applied slurry, spring applied slurry and mineral fertilizer treatments, respectively (Table 6).

## 2.3 Phosphorus in water

At both experimental fields, water was sampled from the containers for chemical analysis before

Table 6. N, P and K applications ( $\text{kg ha}^{-1}$ ) in fertilizer (f) and slurry (s) and month of treatment in the fine sand soil at Toholampi, during 1992–1996.

No. Treatment	1992–1993 Ploughed	1993–1994 Ley	1994–1995 Ley	1995–1996 Ley	Total
1 Control	None	None	None	None	None
2 Slurry, Sept.	196,49,136 s, Sept	193,26,163 + 91,11,11 s, Sept + f, July	201,44,154 + 91,11,11 s, Sept + f, June	None	772,141,475
3 Slurry, Dec.	226,28,172 s, Dec	207,32,192 + 91,11,11 s, Jan + f, July	192,37,218 + 91,11,11 s, Jan + f, June	None	807,119,604
4 Slurry, May	211,33,163 s, May	247,61,218 + 91,11,11 s, May + f, July	165,27,171 + 91,11,11 s, May + f, June	None	805,143,574
5 NPK, May	100,35,71 f, May	128,28,52 + 91,11,11 f, May + f, July	100,22,42 + 91,11,11 f, May + f, June	None	510,107,187

major agricultural practices, i.e. seed bed preparation and sowing, fertilization, harvest and autumn tillage. At Jokioinen, the drainage water and surface runoff were sampled 17–47 times per year, depending on the flow rate, each sample representing 5–6 mm of surface runoff or drainage water. For the experimental periods reported in articles IV and III (1980–1982 and 1987–1993), the total number of sampling occasions was 72 and 229 and the average length of sampling intervals 15 and 11 days, respectively, ranging from half a day to two months. Most of the water samples (50%) were taken in winter-spring; while 28% were taken in summer and 22% in autumn. At Toholampi, the drainage water and surface runoff were sampled 17–28 times per year, each sample representing about 7 mm of surface runoff or drainage water. For the four-year experimental period (1992–1996, V), the total number of sampling dates was 89 and the average sampling interval 16 days, ranging from half a day to four months. Reflecting the volume of water flow, most of the water samples (55%) were taken in winter-spring; while 15% were taken in summer and 30% in autumn (V).

Before analysis, the water samples were stored at 4°C. The storage time of the water samples in experiments III and IV ranged from one day to three weeks and in experiments V and VI from three days to three weeks. No preserving agent was added to the samples. There were some differences between the methods used in the

present study and the previous (SFS 3025: 1986, SFS 3026: 1986) and current (SFS-EN 1189: 1997) standard methods for determining total, particulate and dissolved orthophosphate P in water samples (Table 7). The water samples collected for experiment IV were analysed for total P with peroxodisulphate digestion according to the Finnish standard (SFS 3026: 1986, SFS-EN 1189: 1997). In experiments III and V, the amount of  $\text{H}_2\text{SO}_4$  and  $\text{K}_2\text{S}_2\text{O}_8$  added before digestion was doubled if the total P content of the samples exceeded c.  $0.4 \text{ mg l}^{-1}$ .

For dissolved orthophosphate P analysis, the water samples were filtered and orthophosphate was determined according to the method of Murphy and Riley (1962), with ascorbic acid as reducing agent. Sartorius cellulose nitrate membrane filters ACN, pore size  $0.45 \mu\text{m}$ , were used in experiment IV, and Sartorius cellulose nitrate membrane filters PFN, pore size  $0.45 \mu\text{m}$ , in experiment III; after 1992, Nuclepore polycarbonate filters, pore size  $0.2 \mu\text{m}$  were used. In experiments V and VI, only Nuclepore  $0.2 \mu\text{m}$  filters were used. Particulate P was always calculated as the difference between total P and dissolved orthophosphate P.

The shortcomings of peroxodisulphate digestion for determining total P (SFS 3026: 1986, SFS-EN 1189: 1997) was studied using surface runoff and drainflow samples from the heavy clay soil in Jokioinen. The ability of peroxodisulphate digestion to release P from suspended

Table 7. Phosphorus fractions in water samples according to standard recommendations for P analyses in Finland (SFS 3025: 1986, SFS 3026: 1986 and SFS-EN 1189: 1997) and according to methods used in the present study.

SFS 3025, 3026;	SFS-EN 1189	Present study
Dissolved PO <sub>4</sub> -P <sup>1</sup>	PO <sub>4</sub> -P <sup>7</sup>	Dissolved PO <sub>4</sub> -P <sup>9</sup>
PO <sub>4</sub> -P <sup>2</sup>	Hydrolyzeable PO <sub>4</sub> -P <sup>8</sup>	
Dissolved unreactive P <sup>3</sup>		
Dissolved total P <sup>4</sup>		
Particulate P <sup>5</sup>		Particulate P <sup>10</sup>
Total P <sup>6</sup>	Total P <sup>6</sup>	Total P <sup>11</sup>

<sup>1</sup> Measured after filtration through 0.4 µm filter; 1ml 4 M H<sub>2</sub>SO<sub>4</sub>/100 ml sample may be added after filtration for preservative

<sup>2</sup> Measured in unfiltered sample

<sup>3</sup> Calculated as difference between total P in filtrate (0.45 µm) and dissolved PO<sub>4</sub>-P

<sup>4</sup> Total P in filtrate (0.4 µm)

<sup>5</sup> Total P measured in particulate material retained on 0.4 µm filter, or calculated as difference between total P and dissolved total P (total P in filtrate)

<sup>6</sup> Measured in unfiltered sample with peroxodisulphate digestion, diluted if > 0.8 mg l<sup>-1</sup>

<sup>7</sup> Measured after filtration through 0.45 µm filter; larger pore size recommended for samples requiring filtering time longer than 10 min

<sup>8</sup> Measured after filtration through 0.45 µm filter, addition of 4.5 M H<sub>2</sub>SO<sub>4</sub>, 1ml per 100 ml of sample and boiling with 4.5 M H<sub>2</sub>SO<sub>4</sub>

<sup>9</sup> Measured after filtration through Nuclepore 0.2 µm filter

<sup>10</sup> Calculated as difference between Total P in unfiltered sample and PO<sub>4</sub>-P in filtrate (Nuclepore 0.2 µm)

<sup>11</sup> Measured in unfiltered sample with peroxodisulphate digestion, diluted if > 0.4 mg l<sup>-1</sup>

Table 8. Amounts of water sample, deionized water used for dilution and digestion reagents in five variations of peroxodisulphate digestion.

	Variation no.				
	1	2	3	4	5
Sample, ml	25	25	25	12.5	6.25
Deionized H <sub>2</sub> O, ml	0	0	0	12.5	18.75
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , g	0.25	0.25	0.50	0.25	0.25
H <sub>2</sub> SO <sub>4</sub> , mol l <sup>-1</sup>	0.033	0.057	0.057	0.033	0.033

soil particles and its effect on the value of total P was investigated by varying the digestion (I, Table 8). Total P values obtained with HF digestion (Bowman 1988) were considered a reference for the values obtained with the variations in the peroxodisulphate digestion. The effect of storage (2 – 12 weeks) was examined in experiment II.

The magnitude of errors associated with the determination of dissolved orthophosphate was investigated by removing particulate material from the samples using filters of various types (Nuclepore polycarbonate, Sartorius PFN and Sartorius ACN, pore sizes 0.2, 0.4, 0.45µm) (I). Dissolved orthophosphate values obtained after filtering the samples through cellulose acetate tubing, pore size 0.0024 µm, were considered to be unaffected by colloids and particulate mate-

rial. The magnitude of changes in orthophosphate values occurring during storage and due to the addition of sulphuric acid as preservative (1 ml 4 M H<sub>2</sub>SO<sub>4</sub> per 100 ml of sample) was also studied (II). Evaluation of the inaccuracies in total and dissolved orthophosphate P determinations permitted the error in the particulate P value to be estimated.

## 2.4 Phosphorus in soil

In paper VI, the soil P status of the fine sand soil as affected by the different P application practices was characterized by measuring P fractions with different risks to leaching. Total P (TP) in

soil was determined by wet digestion with concentrated  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}_2$  and HF (Bowman 1988). Inorganic P reserves were fractionated according to a modified Chang and Jackson method (Hartikainen, 1979), where inorganic P (TIP) was sequentially extracted with  $\text{NH}_4\text{Cl}$  ( $\text{P}_{\text{NH}_4\text{Cl}}$ ),  $\text{NH}_4\text{F}$  ( $\text{P}_{\text{NH}_4\text{F}}$ ),  $\text{NaOH}$  ( $\text{P}_{\text{NaOH}}$ ) and  $\text{H}_2\text{SO}_4$  ( $\text{P}_{\text{H}_2\text{SO}_4}$ ).  $\text{NH}_4\text{F}$  was assumed to extract P bound by Al oxide,  $\text{NaOH}$  to extract P bound by Fe oxide and  $\text{H}_2\text{SO}_4$  to dissolve P contained in apatite. The amount of total organic P (TOP) was calculated as the difference between TP and TIP. The degree of P saturation (DPS, %) of the hydrous oxides (Breeuwsma and Schoumans 1986, Lookman et al. 1995) was calculated as a molar ratio of  $(\text{P}_{\text{NH}_4\text{F}} + \text{P}_{\text{NaOH}}) / 0.5(\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}})$ . The amounts of Al and Fe in hydrous oxides ( $\text{Al}_{\text{ox}}$ ,  $\text{Fe}_{\text{ox}}$ ) were estimated by extracting samples with 0.05 M ammonium oxalate, pH 3.3 (Niskanen 1989). P bound by the hydrous oxides ( $\text{P}_{\text{NH}_4\text{F}}$  and  $\text{P}_{\text{NaOH}}$ ) was measured by the modified Chang and Jackson fractionation method referred to above.

Readily extractable P was obtained by extracting soil samples in three different ways: with 0.5 M ammonium acetate – 0.5 M acetic acid, pH 4.65 (Vuorinen and Mäkitie 1955) ( $\text{P}_{\text{Ac}}$ ); with 0.5 M  $\text{NaHCO}_3$ , pH 8.5 (Olsen and Sommers 1982) ( $\text{P}_{\text{Olsen}}$ ); and with anion-exchange resin (Sibbesen and Rubæk 1994) ( $\text{P}_{\text{Resin}}$ ). To estimate the P released from soil to runoff water, P was further extracted with water ( $\text{P}_{\text{w}}$ ) at solution-to-soil ratios of 200:1, 500:1 and 2000:1 (Yli-Halla et al. 1995).

## 2.5 Phosphorus balance

The crop uptake of P (Crop) was calculated by

multiplying the yield by its P concentration, which was determined according to Kähäri and Nissinen (1978). For the Removal, the uptake by the harvested crop (Crop) was added to the losses in surface runoff and drainage (Runoff). P balance (Balance) for the different treatments was calculated by subtracting the total amount of P removed (Removal) from the amount applied in fertilizer or slurry (Input). The content of P in slurry was determined as described by Kempainen (1989).

To compare the environmental effects of different nutrient management systems, the beneficial (crop uptake) and adverse effects (loss in runoff, accumulation in soil) of applied P were considered simultaneously. In line with the thoughts of Bertilsson (1992) and Addiscott (1995), who evaluated the environmental risks of different cropping systems per kg of end products or in terms of the achievement of the target production rather than per ha of cultivated area, the indirect environmental effects were included through 'Crop' as the divisor. The calculation method is based on the considerably higher nutrient losses from agricultural than from natural or forestry ecosystems. The term 'Crop' as a divisor accounts for the difference in the level of harmful environmental impacts of the different types of land-use (agriculture/natural or forestry) because higher crop yields, in principal, mean smaller area requirements for agricultural production. Environmental risk values of P application were estimated by calculating three values: 1) Runoff/Crop, 2) Balance/Crop and 3) (Input-Crop)/Crop. Here, Runoff/Crop represents the short-term nutrient losses in surface runoff and drainage water. Balance/Crop and (Input-Crop)/Crop represent the longer-term effects, such as accumulation in soil.



## 3 RESULTS AND DISCUSSION

### 3.1 Accuracy of phosphorus determination in water

#### 3.1.1 Total phosphorus

Digestion with acid peroxodisulphate is recommended for routine analysis of total P in runoff waters (EPA 1974, APHA 1976, SFS-EN 1189: 1997). However, several researchers (O'Connor and Syers 1975, Logan et al. 1979) have found that peroxodisulphate digestion may underestimate total P in water samples containing suspended soil particles. To avoid such underestimation, both the previous (SFS 3026: 1986) and the current Finnish standard (SFS-EN 1189: 1997) recommend that samples with total P > 0.8 mg l<sup>-1</sup> should be diluted.

The present study showed that total P values were underestimated with peroxodisulphate digestion, even with samples with total P < 0.8 mg l<sup>-1</sup> (I, Fig. 2). The higher the amount of suspended sediment in the samples the larger was the underestimation of total P with peroxodisulphate

digestion, and the results indicated that the amount of sulphuric acid relative to the amount of suspended material was critical for the release of P from the particles (I). For complete extraction of P from the suspended material, fourfold dilution was necessary, even for samples with total P < 0.2 mg l<sup>-1</sup> (I, Fig. 2).

Runoff waters tend to be most turbid during peak flows in autumn and spring, and these peak flows will often be decisive for the annual load of P from agricultural land on watercourses. The results of the present study show that the concentrations of total P obtained with the Finnish standard are too low, especially for water samples with high amounts of suspended material. With the present standard recommendation, the total P load may be underestimated by as much as 10–20% (Fig. 2, Table 9). Here, the total P losses may have been underestimated by 15% and 10% in experiments III and IV, respectively. The underestimation probably diminished the apparent differences in calculated total and particulate P losses between the treatments. For the experiment in V, the error in total P losses was smaller.

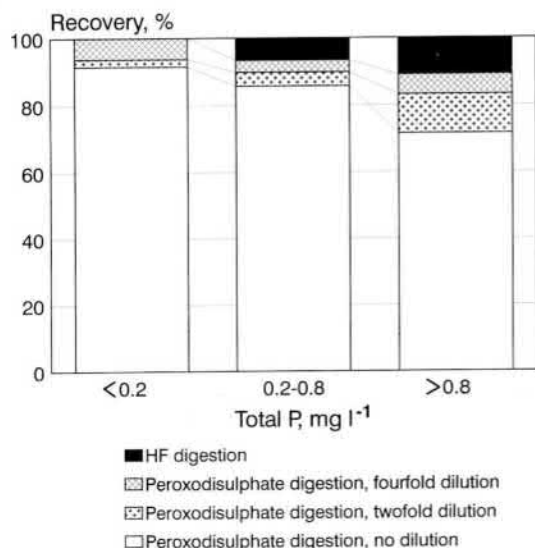


Figure 2. Percentage of increasing recovery of total P in water samples with peroxodisulphate digestion (SFS 3026, SFS-EN 1189) and different degrees of dilution compared with HF digestion (100%, modified from Bowman 1988).

#### 3.1.2 Dissolved orthophosphate phosphorus

Orthophosphate is the main form of dissolved P in runoff waters (Reddy et al. 1996, Broberg and Persson 1988). For runoff waters containing eroded particulate material, filtration through 0.45 µm filters is recommended (APHA 1976, Herve and Kauppi 1986) before analysis of dissolved orthophosphate by the method of Murphy and Riley (1962). However, determination of dissolved orthophosphate P in water samples may be unreliable if an appreciable amount of P is attached to suspended soil particles and colloids. Depending on the filters used, varying amounts of desorbable colloidal P may pass through. The strong acid used in the measurement of orthophosphate may dissolve orthophosphate from the colloidal P fraction (Logan 1982, Broberg and Pettersson 1988), leading to excessively high orthophosphate values. Orthophos-

Table 9. Example of results of different P fractions measured according to standard recommendations for P analyses in Finland (SFS 3025, 3026; SFS-EN 1189) and according to methods and suggestions of the present study (with the percentage of under- or overestimation in parentheses).

	SFS 3025, 3026; SFS-EN 1189		Present study	
			Routine method	Most accurate method
Dissolved PO <sub>4</sub> -P	0.060 <sup>1</sup>	(+20)	0.056 <sup>4</sup>	0.050 <sup>7</sup>
Dissolved total P	0.070			
Total P	0.401 <sup>2</sup>	(-14)	0.421 <sup>5</sup>	0.469 <sup>8</sup>
Particulate P	0.331 <sup>3</sup>	(-21)	0.365 <sup>6</sup>	0.419 <sup>6</sup>

<sup>1</sup> Filtration through Sartorius PFN 0.45 µm filter  
<sup>2</sup> Peroxodisulphate digestion without dilution  
<sup>3</sup> Calculated as difference between total P and dissolved total P  
<sup>4</sup> Filtration through Nuclepore 0.2 µm filter  
<sup>5</sup> Peroxodisulphate digestion with twofold dilution  
<sup>6</sup> Calculated as difference between total P and dissolved PO<sub>4</sub>-P  
<sup>7</sup> Filtration through dialysis tubing (0.0024 µm)  
<sup>8</sup> HF digestion modified from Bowman (1988)

phate release from the filters may also lead to overestimation of the real value (Bloesh and Gavrieli 1984).

In the present study (I), the orthophosphate P values after filtration through Nuclepore 0.2 µm pore size filters were 12% higher than after filtration through 0.0024 µm cellulose acetate tubing (0.056 vs. 0.050 mg l<sup>-1</sup>), which separated all colloids from the samples. The result suggests that Nuclepore 0.2 µm filtrates slightly overestimate the concentration of dissolved orthophosphate P (Fig. 3). Dissolution of colloidal P during analysis was probably the reason for the slight overestimation of the orthophosphate values when Nuclepore 0.2 µm filters were used. Similarly, Ekholm's (1994) finding that a small portion of P determined as dissolved orthophosphate is not available for algae might be ex-

plained by the release of P from colloids, which causes overestimation of the true concentration. Haygarth et al. (1995) found that concentrations of orthophosphate determined after filtration through 0.45 µm or smaller membrane filters might be over 50% larger than concentrations determined after ultrafiltration. In the study of Stamm et al. (1998) on a loamy soil, filtration through 0.45 instead of 0.05 µm filter gave 14% higher results of dissolved orthophosphate P during a drainage flow event.

The orthophosphate P values of the Nuclepore 0.2 µm, Nuclepore 0.4 µm and Sartorius PFN 0.45 µm filtrates were practically the same, but those of the Sartorius ACN 0.45 µm filtrates were higher (I). Due to their different structure, the Nuclepore filters tended to clogg more rapidly than the Sartorius filters and therefore re-

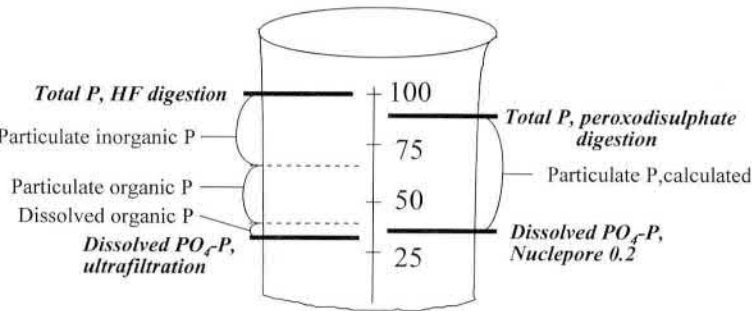


Figure 3. Phosphorus fractions in surface runoff and drainage water as determined and discussed in the present study (on the right: papers III, IV, V, IV, on the left: paper I).



tained progressively more and smaller particles. The higher values obtained with the Sartorius ACN filtrates were mainly due to dissolution of colloidal P during analysis and to some extent, to release of orthophosphate from the filter.

On the basis of the results in paper I, it can be estimated that the concentrations and losses of dissolved orthophosphate P in experiment IV, measured in 1980–1982, were overestimated for barley by 20–50% and for grass ley by 6–38% due to the use of Sartorius ACN 0.45  $\mu\text{m}$  filters. This overestimation must be kept in mind when the losses are compared with those measured after 1985. However, the overestimation of orthophosphate probably did not have as much effect on the differences between the treatments. Because the concentration of particulate P was calculated as the difference between total and dissolved orthophosphate P, the overestimation of orthophosphate values resulted in the estimates of particulate P in experiment IV being too low by 5–40%. In experiment III, the change in filter type and pore size (from Sartorius PFN 0.45  $\mu\text{m}$  to Nuclepore 0.2  $\mu\text{m}$ ) had no significant effect on the measured concentrations and calculated losses of orthophosphate P.

The amount of P, that passed through the Nuclepore and Sartorius PFN filters, but was not recorded as dissolved orthophosphate, was 0.007–0.017  $\text{mg l}^{-1}$ . This P fraction (often referred to as dissolved unreactive P, Table 7) depended on the pore size and filter type. Apparently the fraction is arbitrary in water samples containing suspended soil particles and has little value in water quality monitoring. This conclusion is supported by the finding of Ekholm (1994) that, in river water samples, the fraction appeared to be entirely unavailable for algae.

According to the Finnish standard (SFS 3025: 1986) valid until August 25, 1997, the concentration of dissolved orthophosphate P should be determined immediately. Should this not be possible, the samples should be filtered if sulphuric acid is to be added to prevent microbial growth during storage. However, in the present study (II), the addition of sulphuric acid as a preservative led to dissolution of P from the smallest colloids, which had not been entirely removed in the preceding filtration; the outcome was a large overestimation (77%) of dissolved ortho-

phosphate P. Without the addition of sulphuric acid, however, the values did not change during two weeks' storage (II). Moreover, the changes in the dissolved orthophosphate P concentration due to biological activity were probably negligible. The results of the experiment indicate that the sorption reactions of orthophosphate had reached equilibrium at the time of sampling. Ekholm et al. (1991) also found that the dissolved orthophosphate P concentration in runoff concentrates with 2.7–33.9  $\text{g l}^{-1}$  of suspended solids did not change during storage of up to one year at 4°C.

### 3.1.3 Particulate phosphorus

Particulate P is usually determined as the concentration of total P in material retained on 0.2–0.45  $\mu\text{m}$  filters (Broberg and Persson 1988), but it has also been calculated as the difference between concentrations of total P in unfiltered and filtered water samples (SFS 3026: 1986, Table 7). Calculation of the concentration of particulate P as the difference between total P values measured in unfiltered water and in the filtrate leads to underestimation of particulate P due to (1) incomplete extraction of total P by peroxodisulphate digestion and (2) incomplete separation of colloids by the filters (I). If the recommendations of the standard methods (SFS-EN 1189 for total P and dissolved orthophosphate P, SFS 3025, 3026 for calculating particulate P) are used, the underestimation may be 20–25% (see Table 9). An alternative and less laborious way to estimate particulate P might be to calculate the difference between the values of total P in unfiltered water and of dissolved orthophosphate in the filtrate (Fig. 3); colloidal P would then be included in the particulate fraction. The true concentration of particulate P might be slightly overestimated, since dissolved organic P would be considered as particulate. However, dilution of the samples with a total P concentration above 0.2  $\text{mg l}^{-1}$  probably gives less erroneous values for particulate P (Table 9). The suggested procedure, with dilution of the samples with a total P concentration above 0.4  $\text{mg l}^{-1}$  was used in the present study (III, IV, V).

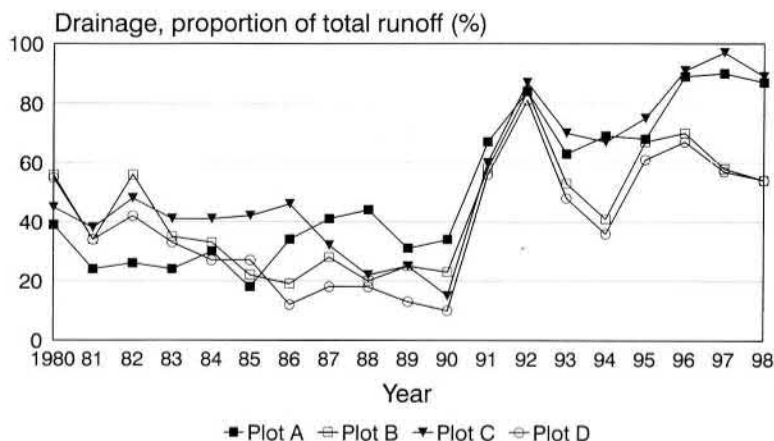


Figure 4. Proportion of drainage of total runoff (drainage + surface runoff) in the heavy clay soil at Jokioinen in 1980–1998.

### 3.2 Phosphorus losses as affected by cultivation practices

#### 3.2.1 Surface runoff and drainage water

##### *Functioning of the subsurface drainage system*

Since 1950, agronomic considerations have caused 80% of clay soils in southern Finland to be drained with subsurface drains placed at a depth of 1 m to lower the ground-water table, especially during sowing and harvest-ploughing. After 10–20 years of cultivation, however, many of the drains no longer function well (Puustinen et al. 1994) and the amount of surface runoff tends to increase. This was also the case on the heavy clay soil at Jokioinen, where the partitioning of total runoff (drainage + surface runoff) to drainage water and surface runoff was very much dependent on the functioning of the subsurface drainage system.

Before the subsurface drainage system was improved, drainage accounted for only about 15–35% of the total discharge (III, Fig. 4). At that time, most of the water was discharged to open ditches as lateral flow either on the soil surface or in the upper, more permeable zones. As the subsoil was almost impermeable, the negligible water movement to the drains was along cracks and old root channels near the trench (III). Due to the low volume of macropores in the surface soil, as little as 5–10 mm of rain was able to induce surface runoff. Surface runoff was particu-

larly heavy in spring during and just after snowmelt (III).

After the drainage improvement, however, when water running in the upper layers or along the soil surface reached the site of a new drain, it infiltrated and passed to the drain through the permeable backfill, even during heavy rains and spring snowmelt. As a consequence, drainage flow increased dramatically: to 80–90% of the total discharge (III). Two years after the improvement, the proportion of drainage flow diminished to 50–70% of the total, partly due to the grass cover on the soil (III, Fig. 4). The grass established in 1992 was ploughed in on some plots in autumn 1993 (Table 5). Seven years after the drainage improvement the permeability of the new drain trenches was still high on autumn-ploughed plots, as seen from the considerable proportion of drainage flow (Fig. 4).

From the runoff data for years preceding and following the drainage improvement (Table 10), it can be estimated that, after the improvement, at least 60% of the drainage water passed straight through the new drain trenches.

##### *Cropping*

Partitioning of total runoff to surface runoff and drainage flow was influenced by cropping as well as by functioning of the subsurface drainage system. In the experiment with barley and grass ley on the heavy clay soil (IV), ley cultivation with no soil tillage for three years increased the pro-

Table 10. Mean annual runoff (mm) and losses of total P (TP), particulate P (PP) and dissolved orthophosphate P (PO<sub>4</sub>-P) (kg ha<sup>-1</sup> a<sup>-1</sup>) in surface runoff and drainage water from the heavy clay soil in Jokioinen before and after the subsurface drainage improvement in 1991, averaged over all plots and treatments.

		Before subsurface drainage improvement 1980–1990 <sup>1</sup>	After subsurface drainage improvement 1992–1998 <sup>2</sup>
Precipitation		656	611
Runoff	Surface runoff	199	79
	Drainage water	81	196
TP	Surface runoff	0.85	0.29
	Drainage water	0.25	0.63
PP	Surface runoff	0.74	0.23
	Drainage water	0.19	0.57
PO <sub>4</sub> -P	Surface runoff	0.11 <sup>3</sup>	0.06
	Drainage water	0.06 <sup>3</sup>	0.06

<sup>1</sup> Cultivation: cereals 61%, grass ley 28%, bare fallow 11%

<sup>2</sup> Cultivation: cereals 79%, grass ley 21%

<sup>3</sup> Plots with surface application of fertilizer in 1980–1982 excluded

portion of surface runoff as compared with barley. The average surface runoff from barley (ploughed in autumn) accounted to 44–66% of the annual total runoff (Table 11), the proportions in autumn, winter-spring and summer being 42–68%, 61–85% and 14–44%, respectively. From the grass ley, surface runoff averaged 58–70% of the annual total runoff (Table 11), the proportions being higher than from barley throughout the year (52–78%, 70–91% and 28–50% in autumn, winter-spring and summer, respectively). After the subsurface drainage had been improved, the annual proportion of surface runoff from soil ploughed in autumn was 10–30%, but due to cultivation of the ley rose once more, to 50%, as noted above (Fig. 4).

Likewise in the fine sand soil, the proportion and amount of surface runoff were higher during the ley years of the study than in the first year, when barley was grown and the soil was ploughed in autumn. The general pattern of water flow from ploughed soil was marked by dominance of drainage flow in autumn and surface runoff in spring. Surface runoff from ploughed soil averaged 40–52% of the annual total runoff (Table 12), the figures for autumn, winter-spring and summer being 11–30%, 95–96% and 73–

88%, respectively (V). However, surface runoff from the ley accounted for as much as 83–100% of the annual total runoff, on average, and water discharge from the field during the occasional snowmelt in winter and the final snowmelt in March consisted entirely of surface runoff. During the ley years, the proportion of surface runoff in autumn, winter-spring and summer was 31–100%, 100% and 49–100%, respectively. In autumn there was substantial drainage flow after snowmelt from frozen ploughed soil, whereas drainage flow from frozen sand soil decreased to zero during perennial ley cultivation (V).

On the fine sand soil, one obvious reason for the more abundant surface runoff from grass ley than from ploughed soil was the larger amount of water in snow owing to the higher precipitation in winter and the somewhat larger snow accumulation on the grass covered surface (V). A larger proportion of precipitation as snow tends to produce more surface runoff, as snowmelt water does not efficiently infiltrate to frozen soil, especially if occasional snowmelts and freezing have filled the largest pores with ice. However, the frozen ploughed soil was porous due to recent tillage, thus promoting water penetration and drainage water flow, especially in autumn,

Table 11. Mean annual runoff (mm) and concentrations of total P (TP), particulate P (PP) and dissolved orthophosphate P ( $\text{PO}_4\text{-P}$ ) ( $\text{mg l}^{-1}$ ) in surface runoff and drainage water from barley (soil ploughed in autumn) and perennial grass ley on heavy clay soil in consecutive years of the experiment IV. NPK-fertilizing treatments: (1) 21  $\text{kg ha}^{-1}\text{a}^{-1}$  P for barley, 42  $\text{kg ha}^{-1}\text{a}^{-1}$  P for grass ley, (2) 42  $\text{kg ha}^{-1}\text{a}^{-1}$  P for barley, 84  $\text{kg ha}^{-1}\text{a}^{-1}$  P for grass.

Heavy clay		Barley			Grass ley		
		1980	1981	1982	1980	1981	1982
Runoff	Surface runoff	109	301	183	139	250	225
	Drainage water	136	156	165	101	106	122
TP	Surface runoff	0.22	0.39	0.51	0.19	0.62	0.89
	Drainage water (1)	0.18	0.31	0.54	0.11	0.26	0.46
	Drainage water (2)	0.16	0.21	0.31	0.11	0.27	0.52
PP	Surface runoff	0.15	0.24	0.39	0.094	0.23	0.24
	Drainage water (1)	0.13	0.21	0.45	0.054	0.12	0.25
	Drainage water (2)	0.11	0.13	0.25	0.050	0.10	0.24
$\text{PO}_4\text{-P}$	Surface runoff	0.072	0.15	0.12	0.10	0.39	0.65
	Drainage water (1)	0.051	0.10	0.087	0.054	0.14	0.21
	Drainage water (2)	0.051	0.076	0.055	0.060	0.17	0.28

Table 12. Annual runoff (mm) and mean concentrations of total P (TP), particulate P (PP) and dissolved orthophosphate P ( $\text{PO}_4\text{-P}$ ) ( $\text{mg l}^{-1}$ ) in surface runoff and drainage water from barley (soil ploughed in autumn) and perennial grass ley on fine sand soil in consecutive years of the experiment V. P-fertilizing treatments: (1) unfertilized, (2) slurry surface applied in September (with immediate ploughing in 1992), (3) slurry surface applied in December, (4) Slurry surface applied in May (with immediate harrowing in 1993), (5) NPK fertilizer surface applied in May (fertilizer placement in 1993).

Fine sand			Barley		Grass ley	
			1992–1993	1993–1994	1994–1995	1995–1996
Runoff	Surface	Unfertilized (1)	110	161	261	151
		Slurry, Sept. (2)	98	376	329	135
		Slurry, Dec. (3)	78	234	244	139
		Slurry, May (4)	118	316	327	140
		NPK, May (5)	109	207	258	145
	Drainage		120	22	3.0	5.8
TP	Surface	Unfertilized (1)	0.60	0.16	0.12	0.11
		Slurry, Sept. (2)	0.73	2.5	1.6	0.72
		Slurry, Dec. (3)	3.1	9.8	12	0.64
		Slurry, May (4)	0.56	0.41	0.55	0.79
		NPK, May (5)	0.79	0.42	0.77	0.76
	Drainage		0.021	0.019	0.018	0.070
PP	Surface	Unfertilized (1)	0.57	0.075	0.069	0.026
		Slurry, Sept. (2)	0.69	0.32	0.27	0.16
		Slurry, Dec. (3)	2.5	1.7	3.3	0.27
		Slurry, May (4)	0.52	0.15	0.18	0.18
		NPK, May (5)	0.72	0.17	0.19	0.39
	Drainage		0.014	0.015	0.015	0.068
$\text{PO}_4\text{-P}$	Surface	Unfertilized (1)	0.025	0.081	0.046	0.086
		Slurry, Sept. (2)	0.042	2.2	1.3	0.56
		Slurry, Dec. (3)	0.60	8.1	9.0	0.37
		Slurry, May (4)	0.042	0.26	0.37	0.61
		NPK, May (5)	0.072	0.25	0.58	0.37
	Drainage		0.007	0.004	0.003	0.002

whereas hydraulic conductivity seemed to be lower in the frozen grass ley surface soil. During the winter-spring period, however, most of the pores had probably already been closed by earlier meltwater freezing in the pores, thus increasing the proportion of surface runoff from ploughed soil, too.

The observed increase in surface runoff from perennial grass ley was, however, contradictory to a common idea of a beneficial impact of perennial grass ley on soil structure, with higher permeability as a consequence. While most studies have been conducted on small plots, here the experimental plots were large enough to permit normal agricultural practices with a higher frequency of wheeled traffic and compactive load on the edges of the field. The greater tendency to surface runoff on the grass ley may thus be explained by the heavy wheel traffic and the lack of frequent soil tillage. Whereas in arable fields the surface soil is loosened frequently by annual ploughing, resulting in an increase in the pore space on the surface layer (Anderson 1961), in perennial grass cultivation, the bulk density of the surface soil (0–20 cm) has been found to increase (Douglas et al. 1992a) and pore space and hydraulic conductivity to decrease (Hofstra et al. 1986, Douglas et al. 1995) due to wheeled traffic. However, according to measurements of Douglas et al. (1992b) and Koppi et al. (1992), the upmost soil layer (1–1.5 cm) of perennial grassland had more pore space than the underlying soil, and the difference was associated with the presence of the crowning area of the living sward. Due to consolidation of the surface soil during grass cultivation, the depth of interaction between soil and surface runoff may be reduced. When studying surface runoff from perennial ley, Nash and Murdoch (1997) and Sharpley et al. (1996) noted that surface runoff moved mainly in the 0–2 cm layer of the soil surface. On ploughed soil, the much higher surface roughness of the tilled layer creates larger depression storage of water on the surface, thus allowing time for infiltration and drainage. Consequently, the proportion of surface runoff from perennial grassland may be greater than from arable, annually tilled soil.

An increase in the proportion of surface runoff from perennial ley compared with that from

barley was also observed on a loam soil in southern Norway (Uhlen 1978a). Young and Mutchler (1976) measured more surface runoff from alfalfa plots during the spring snowmelt than from ploughed maize plots and attributed the difference to smaller depressional storage of water and longer-lasting frost on the alfalfa plots. On fine loamy sand and sandy loam soils with a slope of 10% in Denmark, however, Hansen and Nielsen (1995) found that grass covered plots had less surface runoff than wheat-covered and fallow plots. Cropping practices may, then, have different effects on the infiltration rate, depending on the soil type, slope and climate.

### 3.2.2 Total and particulate phosphorus

#### *Water flow routing*

Before the subsurface drainage of the heavy clay soil was improved in 1991, the higher amount of surface runoff resulted in concentrated, high-erosive flows, especially at the lower edge of the field. The concentrations of suspended solids and particulate P in surface runoff were therefore high in the surface runoff from ploughed soil (Fig. 5), especially in autumn and after snowmelt in spring (III). Due to the large amount of surface runoff and higher concentrations of total P and particulate P, surface runoff was the main route of P loss (Fig. 6). On the heavy clay soil in 1980–1982, surface runoff transported 51–60% and 71–84% of the total P losses from ploughed soil (barley) and fertilized grass ley, respectively. The respective proportions for particulate P were 50–73% and 64–83% (IV). In 1983–1990, the proportion of total P and particulate P transported with surface runoff was even higher due to the increase in surface runoff (data not shown). On the fine sand soil in 1992–1996, surface runoff transported 95–100% of the total P and 93–100% of particulate P losses, the largest proportion occurring on the fertilized grass ley (V).

The improvement to subsurface drainage changed the water flow paths on the heavy clay soil by increasing the proportion of drainage flow. Thereafter, the large water volumes discharged through the drains backfilled with topsoil had considerably lower concentrations of



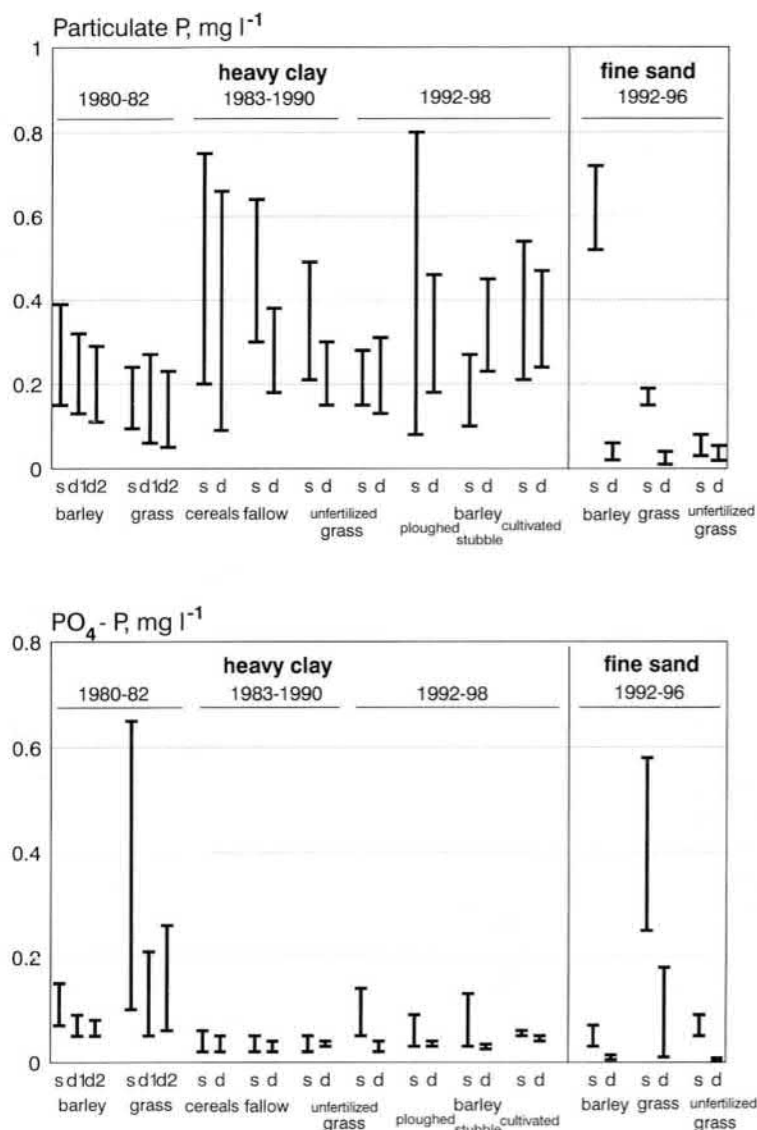


Figure 5. Range of annual mean particulate P (above) and dissolved orthophosphate P (PO<sub>4</sub>-P, below) concentrations (mg l<sup>-1</sup>) in surface runoff (s) and drainage water (d) during the experimental years on the heavy clay soil at Jokioinen and the fine sand soil at Toholampi. d1 = concentration from plots receiving P fertilizer 21 kg ha<sup>-1</sup> a<sup>-1</sup> (barley) and 42 kg ha<sup>-1</sup> a<sup>-1</sup> (grass ley); d2 = concentration from plots receiving P fertilizer 42 kg ha<sup>-1</sup> a<sup>-1</sup> (barley) and 84 kg ha<sup>-1</sup> a<sup>-1</sup> (grass ley). On the heavy clay; unfertilized grass on the right killed with glyphosate; on the fine sand: autumn and winter applications of slurry excluded.

suspended solids and particulate P than had the surface runoff, which constituted most of the total runoff before the improvement. On an impermeable clay soil in England, Catt et al. (1998) noted that the absence of under-drainage was the main reason for increased surface runoff and P loss. However, in the present study, the trenches filled with wood chips were not effective in reducing the particulate P concentrations of the infiltrating surface runoff (III). After the drainage improvement, the proportion of total P transported in surface runoff was 3–50% and 51–56%

from barley (ploughed) and grass ley, respectively. For particulate P, the respective proportions were 3–50% and 44–49%.

Surface runoff is regarded a more important pathway of P to the aquatic environment, especially for particulate P and suspended soil particles (e.g. Bengtson et al. 1984, Catt et al. 1998). The same was true on the fine sand soil and also on the heavy clay soil of the present study before the subsurface drainage improvement. However, the drainage water from the heavy clay soil contained relatively large amounts of suspend-

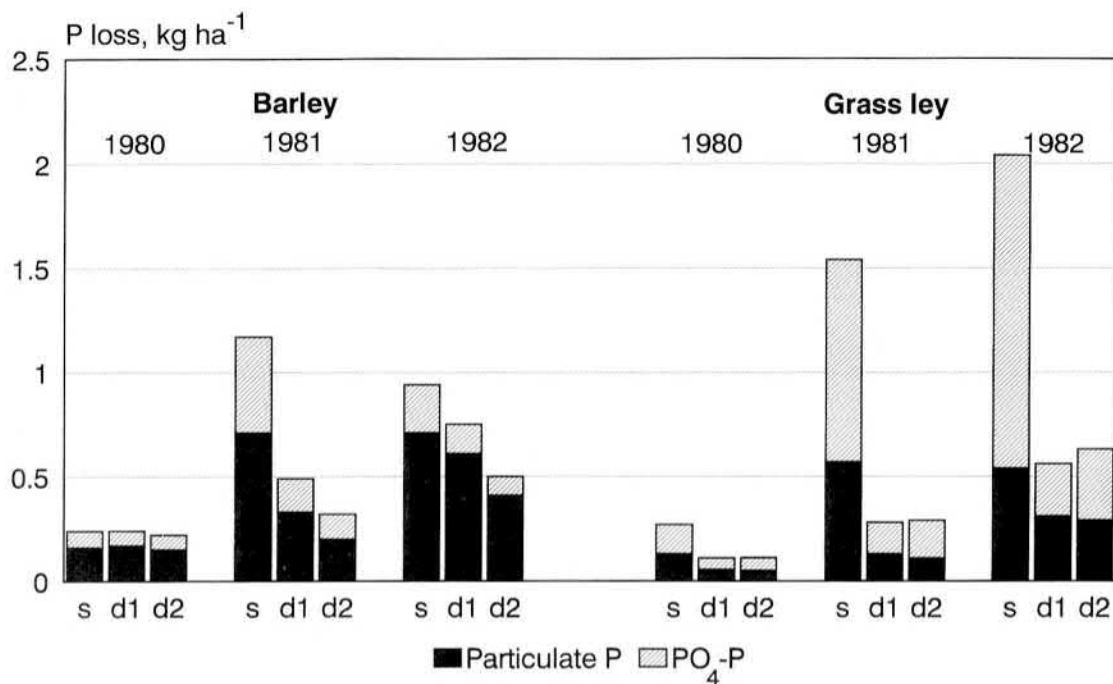


Figure 6. Annual losses (kg ha<sup>-1</sup> a<sup>-1</sup>) of particulate P and dissolved orthophosphate P (PO<sub>4</sub>-P) in surface runoff (s) and drainage water (d) from barley (soil ploughed in autumn) and perennial grass ley on the heavy clay soil in 1980–1982 in the experiment IV. d1 = P loss in drainage water from plots receiving P fertilizer 21 kg ha<sup>-1</sup> a<sup>-1</sup> (barley) and 42 kg ha<sup>-1</sup> a<sup>-1</sup> (grass ley); d2 = P loss in drainage water from plots receiving P fertilizer 42 kg ha<sup>-1</sup> a<sup>-1</sup> (barley) and 84 kg ha<sup>-1</sup> a<sup>-1</sup> (grass ley).

ed particles and particulate P both before and after the improvement although the concentrations were lower than in surface runoff, especially during the peak flows before the drainage improvement (III, IV).

The high concentrations of particulate P, and hence of total P, in drainage water found here were probably of surface origin, as they followed the concentration patterns of surface runoff fairly closely. Deeper soil horizons might be an additional source of suspended soil particles in the drainage water but, on the basis of laboratory studies, Pilgrim et al. (1978) suggested that velocities of flow within the soil mass are unlikely to be sufficient to detach and entrain sediment. They concluded that the source of the sediment was at the ground surface and that raindrop impact was the primary agent of particle detachment and entrainment. Øygarden et al. (1997) likewise found evidence that the tillage of levelled silty clay loam soil with an unstable structure affected particle loss to the drainage system. Their results indicated that particles can be

eroded from the plough layer and transported through macropores and cracks into the backfill and from there directly to drain pipes. Moreover, Laubel et al. (1999) showed with tracer analysis using <sup>137</sup>Cs that particulate matter in drainage water from sandy loam soil derived from topsoil. However, deeper soil horizons may produce minor amounts of suspended soil particles that then enter the drainage water, as clay particles may become suspended through dispersion (Miller and Baharuddin 1987), especially in the case of low free electrolyte concentration and 2:1 minerals (e.g. illite, smectite) with a higher negative charge than 1:1 minerals (kaolinite) (Rengasamy 1983, Seta and Karathanasis 1996). The net negative charge is the primary factor in clay dispersion, and an increase in pH has a great dispersive effect, especially for illitic clays (Chorom and Rengasamy 1995).

The smaller concentrations of particulate P in drainage water than in surface runoff (Fig. 5) were probably a result of sieving action, as postulated by Sharpley and Syers (1979a). In drain-

age water from a clay soil, Culley et al. (1983) found smaller suspended solids and particulate P concentrations when drains were installed at greater depth (1.0 vs. 0.6 m). In the present study after the subsurface drainage improvement, the particles were probably sieved by the topsoil material in the trenches, as the trenches filled with wood chips were not effective in reducing the particulate P concentrations of the infiltrating surface runoff.

Based on the discussion above, efficient sieving of the particles was probably the reason why Ylärinta et al. (1996) found negligible amounts of total and particulate P losses in a lysimeter trial, in which 1.15 m deep lysimeters were filled with the heavy clay studied here. The result indicates that the major flowpaths of water were different in the lysimeters, probably due to the absence of drain trenches and large cracks. The lack of surface runoff in the lysimeters (and the impact of running water inducing particle detachment) contributed to the result. Also Ulén (1999) measured lower P concentrations in flow from clay lysimeters than in drainage water from the same clay in the field.

At decreasing water contents, the proportion of water flowing through smaller pores increased steadily and the overall velocity of water flow decreased sharply. On the heavy clay soil, the concentration of particulate P in drainage water was correlated positively with the daily amount of drainage flow (Fig. 7). Therefore, the smaller concentrations of particulate P and suspended soil particles in drainage water during the later phase of runoff events can probably be attributed to the decrease in water flow velocity, and water movement through smaller pores in the soil profile, allowing efficient sieving of the particles. Sieving of the particulate P from drainage water was, however, much more efficient on the fine sand than on the heavy clay soil (Fig. 5), possibly due to the larger size of the suspended particles in the fine sand soil than in the heavy clay soil.

As noted on the heavy clay soil in the present study, sieving soil particles and particulate P may not always be very efficient owing to open structure of the backfill or presence of large pores or cracks. In drain flow from levelled silty clay loam soil in Norway, Lundekvam (1994), Os-

karsen et al. (1996) and Øygarden et al. (1997) found particulate P concentrations similar to those in surface runoff, Schwab et al. (1977, 1980) reported high fine sediment losses in drainage water from silty clay soil, offering the tentative explanation that, once suspended in water at the soil surface, small particles remained in suspension as water moved through the soil and the drain backfill. Bottcher et al. (1981) reported that the average particulate P concentration in drainage water ranged from 0.15 to 0.22 mg l<sup>-1</sup> in silty clay soil, a value at the lower range to those measured here. Direct channelling of the water from the surface through cracks was considered the most probable cause of the high sediment and particulate P concentrations. In subsurface runoff from silty loam soil underlain by clay and clay loam, Pilgrim et al. (1978) found sediment concentrations of over 1 g l<sup>-1</sup> and attributed the high concentrations to rapid water movement through macropores. In the soil profile, suspended particles were not transported in appreciable quantities through soil pores similar in size to the particles. Laubel et al. (1999) measured particulate P concentrations of 0.18–0.88 mg l<sup>-1</sup> in drainage water from sandy loam soil in Denmark.

### *Cropping*

In 1980–1982, the total P loss (mean of the two fertilizer amounts) was 1.2 and 1.6 kg ha<sup>-1</sup>a<sup>-1</sup> from barley and grass ley, respectively. In 1984–1998 the total P losses were 0.25–2.4 kg ha<sup>-1</sup>a<sup>-1</sup> for cereals. The total P losses in experiment V on the fine sand soil, 0.67–0.88 kg ha<sup>-1</sup>a<sup>-1</sup> for barley and 0.88–2.0 kg ha<sup>-1</sup>a<sup>-1</sup> for spring-fertilized grass ley, were comparable to the losses measured on the heavy clay soil.

On the heavy clay soil, particulate P concentrations were considerably higher for barley than for grass ley especially in the surface runoff (Table 11, Fig. 5). Similarly on the fine sand soil, the lower amount of erosion from grass ley was reflected in the lower concentrations of particulate P in surface runoff (Table 12, Fig. 5). Although the cultivation of grass ley tended to promote more surface runoff, the lower particulate P concentrations resulted in smaller losses of particulate P from grass ley than from ploughed soil and cereals (Fig. 8). The effect of ley was



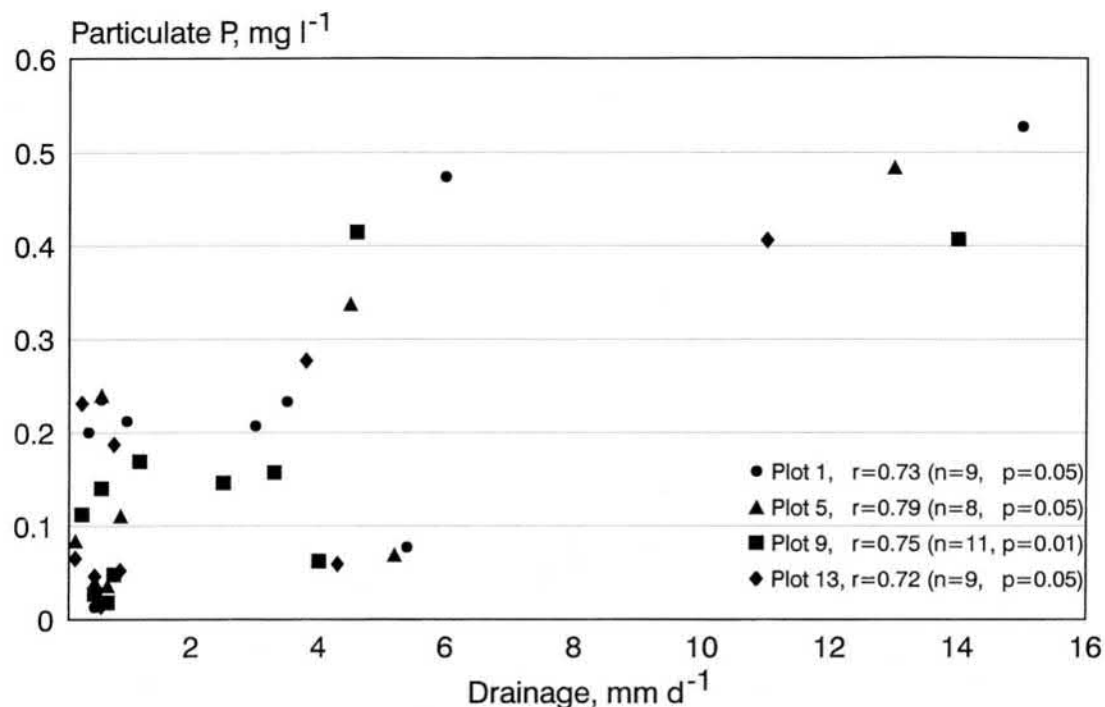


Figure 7. Concentration of particulate P in drainage water (mg l<sup>-1</sup>) plotted against daily drainage flow (mm d<sup>-1</sup>) from plots 1, 5, 9 and 13. Water samples taken in 23.4.–1.8.1997

greatest during rainy periods in spring, when the soil was not frozen during the heaviest snow-melt period (IV). In contrast, in ploughed barley plots, soil frost seemed to reduce particulate P losses efficiently when present in the springs of 1980 and 1981 (IV).

On the heavy clay soil, particulate P loss in surface runoff from barley amounted to 61–76% of total P and from fertilized grass ley to 27–48% of total P. In the drainage water, particulate P loss (averaged over the two fertilizer amounts) was 63–82% of total P from barley and 38–55% of total P from grass ley. On the fine sand soil, loss of particulate P in surface runoff from barley in 1992–1993 amounted to 91–95% of total P. The loss of particulate P from unfertilized ley in 1993–1996 was 24–60% of total P. For the spring applications of slurry and mineral fertilizer on ley, particulate P loss accounted for 23–51% of total P. The proportion of particulate P loss in drainage water was 68% of total P from the soil under barley and 50–95% from the grass ley (V).

Due to the complete vegetation cover and the

lack of frequent tillage of the surface soil, perennial grasslands have the greatest potential to reduce soil erosion and particulate P losses (Burwell et al. 1975, Skøien 1988, Eder and Harrod 1996). Particulate P losses are clearly most efficiently reduced by set-aside grasslands cultivated without fertilizer P inputs (Turtola 1993). In the present study as well, the decrease in particulate P loss was larger for unfertilized than for fertilized ley (V, Fig. 8). On the fine sand soil, particulate P losses from unfertilized grass ley (V) were even smaller than those from unfertilized set-aside grass on heavy clay soil (Turtola 1993). The higher particulate P values for treatments 4–5 were due to P accumulation on the surface soil, which also increased the P content of the eroded soil particles.

#### Fertilization

Total P losses were extremely high after autumn and winter application of slurry on the soil surface (V, Fig. 9). The simultaneous large losses of particulate P (0.9–2 and 1.9–8 kg ha<sup>-1</sup> a<sup>-1</sup> for autumn and winter applications, respectively)

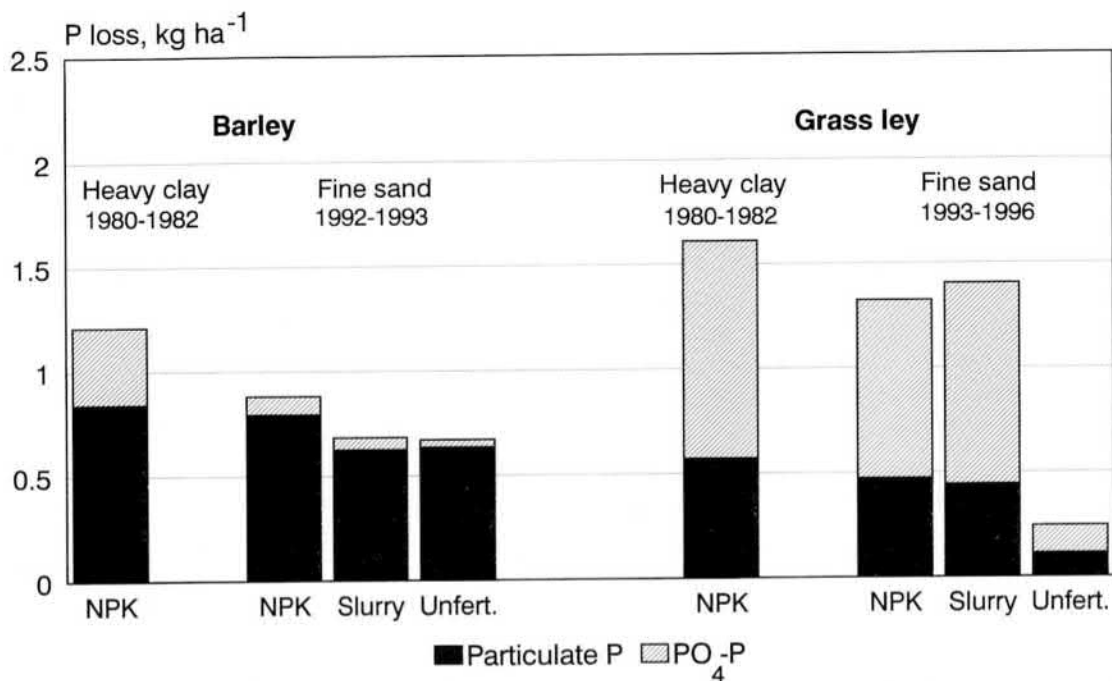


Figure 8. Average loss of particulate P and dissolved orthophosphate P ( $\text{PO}_4\text{-P}$ ) ( $\text{kg ha}^{-1} \text{ a}^{-1}$ ) from barley and grass ley on the heavy clay and on the fine sand. P-fertilizer treatments: NPK = NPK fertilizer applied in spring, Slurry = slurry applied in spring, Unfert. = unfertilized.

indicated considerable losses of slurry-derived P, in either particulate inorganic/organic or dissolved organic form. Chardon et al. (1997) measured appreciable dissolved organic P leaching from sandy soil after pig slurry application.

In the case of barley on the heavy clay, the particulate P concentration in drainage water was slightly lower on plots given the higher amount of NPK fertilizer (0.11–0.25 vs. 0.13–0.45  $\text{mg l}^{-1}$ , Table 11). The decrease in the particulate P concentration of drainage water may be explained by flocculation of the suspended particles due to increased ionic strength (Chorom and Rengasamy 1995) on plots with higher amounts of salts applied in fertilizer.

### 3.2.3 Dissolved orthophosphate phosphorus

#### Fertilization

Low infiltration of water and surface application of fertilizers proved to be a highly risky combination for P losses from ley. The surface applications of P in mineral fertilizer or slurry on grass ley in spring and summer were followed

by dissolved orthophosphate P concentration peaks of 2–10  $\text{mg l}^{-1}$  in surface runoff (IV,V), most probably due to orthophosphate dissolving directly from fertilizer granules and slurry spread on the soil surface. With the fertilizer P amount used in experiment IV, 42  $\text{kg ha}^{-1} \text{ a}^{-1}$ , dissolved orthophosphate leaching in drainage water was significantly higher from ley (P surface-applied) than from barley (P incorporated) in summer 1982, owing to peak concentrations following fertilizer broadcasting on ley (IV). With the above fertilizer amount, the mean annual concentration of dissolved orthophosphate P in drainage water was higher for grass ley than for barley and the difference increased towards the end of the experiment (0.054, 0.14, 0.21 vs. 0.051, 0.076, 0.055  $\text{mg l}^{-1}$ ) (IV, Table 11). For barley, the fertilizer amount had no effect on dissolved orthophosphate leaching in drainage water. By contrast, the fertilizer amount seemed to have a slight effect on dissolved orthophosphate leaching from ley (IV, Table 11).

Phosphorus compounds were directly lost from the surface-applied slurry in autumn and winter resulting in dissolved orthophosphate P

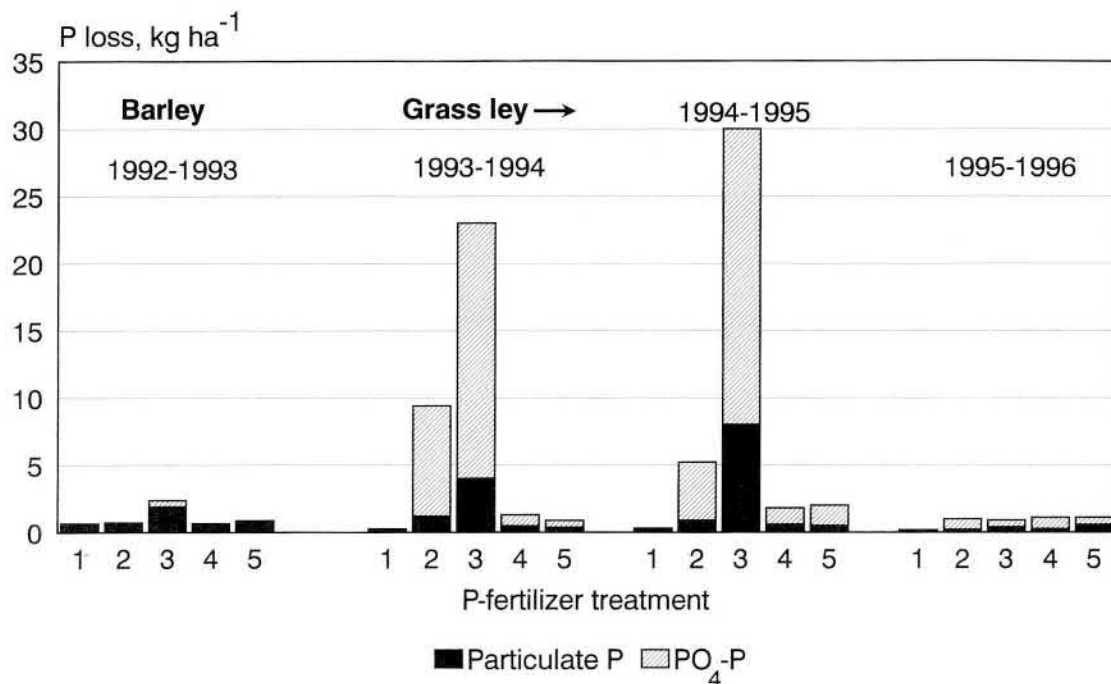


Figure 9. Annual losses (kg ha<sup>-1</sup> a<sup>-1</sup>) of particulate P and dissolved orthophosphate P (PO<sub>4</sub>-P) in surface runoff from barley (1992–1993) and grass ley (1993–1996) on fine sand soil in experiment V. P-fertilizer treatments: (1) unfertilized, (2) slurry surface applied in September (with immediate ploughing in 1992), (3) slurry surface applied in December, (4) slurry surface applied in May (with immediate harrowing in 1993), (5) NPK fertilizer surface applied in May (fertilizer placement in 1993).

losses which were higher than any previously reported losses in Finland (V, Fig. 9). The concentrations of dissolved orthophosphate P were extremely high (10–25 mg l<sup>-1</sup>) in surface runoff samples taken after surface applications of slurry in autumn and winter (V, Table 12). These concentrations were very similar to those reported by Edwards et al. (1996) for pasture fields fertilized with poultry manure. Uhlen (1978b), Brink et al. (1983) and Braun and Leuenberger (1991) measured similar high dissolved orthophosphate concentrations and losses in surface runoff from grassland after off-season manure or slurry application without incorporation.

Here incorporation of autumn-applied slurry by immediate ploughing impeded dissolved orthophosphate P leaching effectively (V, Table 12, Fig. 9). Similarly Uhlen (1978b) found that mixing the manure into the soil efficiently reduced P losses, and Bahman and Gilley (1999) reported that high dissolved orthophosphate P losses after spreading of manure on the soil surface were prevented by discing the soil to 8 cm. Bak-

er and Lafen (1982) established that surface runoff contained 110 times more dissolved P when P was broadcast on the soil surface than when it was incorporated to a depth of 5 cm. Timmons et al. (1973) observed that deep incorporation of fertilizer by ploughing down resulted in P losses through surface runoff about equal to those from unfertilized plots. However, broadcasting the fertilizer on a disced surface resulted in much higher losses. Haygarth and Jarvis (1997) estimated that, on grazed grassland, a single rainy period (50 mm) occurring some days after spreading 16 kg ha<sup>-1</sup> of P fertilizer caused P losses of 0.5 kg ha<sup>-1</sup> in surface runoff. They concluded that the weather at the time of fertilizer addition is crucial for the release of P in surface runoff from grassland.

#### *Soil phosphorus status*

Besides showing peaks after surface application of P, the dissolved orthophosphate P concentration gradually rose above the base level towards the end of the experiments (IV, V). The increas-

ing trend in the concentration of dissolved orthophosphate P from grass ley compared with that from barley was also evident in the mean annual values (Tables 11 and 12). The increase in the base level of dissolved orthophosphate P concentration in surface runoff was due to the accumulation of P in the very topmost surface soil after annually repeated broadcasting of mineral fertilizer or slurry.

The accumulation of P in the near-surface layer of soil was noted in the fine sand soil. There surface-applied P not taken up by plants or lost in surface runoff or by leaching accumulated in the 0–5 cm soil layer as  $P_{\text{NH}_4\text{F}}$  (Table 13, VI). The increase in the  $P_{\text{NH}_4\text{F}}$  values was accompanied by increases in DPS and  $P_{\text{Ac}}$ . The low level of  $P_{\text{NH}_4\text{F}}$  deeper in the profile suggested that transport of inorganic P downwards from the plough layer was minimal. Accumulation of P in the surface layer was also reflected in the amounts of P desorbed from the 0–5 cm soil layer with water at different solution-to-soil ratios (200:1, 500:1, 2000:1). In the five surface runoff plots on the fine sand soil, the soil P status in the 0–5 cm layer, measured as DPS,  $P_w$ ,  $P_{\text{Olsen}}$ ,  $P_{\text{Ac}}$  and  $P_{\text{Resin}}$ , correlated closely ( $r \geq 0.96$ ) with the mean  $\text{PO}_4\text{-P}$  concentration in the surface runoff water 1996 (VI, Table 13).

On a pasture soil, Sharpley et al. (1977) found a correlation between the dissolved orthophosphate P concentration in surface runoff and readily extractable soil P in the 0–5 cm soil layer but the correlation was less clear between the P concentration and extractable soil P in the 5–10 cm layer. Heckrath et al. (1995) and Smith et al. (1998) found that values of  $P_{\text{Olsen}}$  in the plough layer of 60 and 70 mg kg<sup>-1</sup>, respectively, were the change points for increased P leaching below 30 cm depth. Compared with the correlation between  $P_{\text{Olsen}}$  and dissolved orthophosphate P in the study of Pote et al. (1996), the dissolved orthophosphate P concentrations of the present study were at the lower range for a given value of  $P_{\text{Olsen}}$ .

However, water extractable P may be even more appropriate than  $P_{\text{Ac}}$  or  $P_{\text{Olsen}}$  for the environmental soil P test. Olness et al. (1975) and Schreiber (1988) noted a dependence between the dissolved P concentration of surface runoff and water-extractable soil P. Yli-Halla et al.

(1995) found that the concentration of dissolved orthophosphate P in the surface runoff water from two clay soils corresponded to the  $P_w$  values at solution-to-soil ratios of 250:1–100:1. In the fine-sandy soil of the present study, dissolved orthophosphate P measured in the surface runoff water was close to  $P_w$  (200:1) value (0.033 vs. 0.046 mg l<sup>-1</sup>) only in the 0 P treatment (VI). In the other treatments in which P was applied on the soil surface, dissolved orthophosphate P values were much higher than the respective  $P_w$  values (0.36–0.62 mg l<sup>-1</sup> vs. 0.12–0.16 mg l<sup>-1</sup>) (VI). According to Holford et al. (1997) and Zee et al. (1987), DPS values of 17–38% and 25%, respectively, are required before substantial P leaching will begin. The mean concentrations of  $\text{PO}_4\text{-P}$  found here in surface runoff in spring 1996 (0.53–0.62 mg l<sup>-1</sup>) from plots formerly top-dressed with slurry in autumn or spring were thus too high for the DPS value of 16.4% measured in the 0–5 cm layer.

However, the P saturation and  $P_w$  values of the present study (VI) were probably much higher in the top 1–2 cm than in the 5 cm layer as a whole. The 0–2 cm layer being the most runoff-sensitive portion of the surface soil (Sharpley and Withers 1994), especially in perennial leys (Nash and Murdoch 1997, Sharpley et al. 1996), the dissolved orthophosphate P concentrations must have been produced by a shallower surface soil with substantially higher DPS and  $P_w$ . Corroborating this, on a silt loam soil under grass Pote et al. (1996) found a high correlation between the  $\text{PO}_4\text{-P}$  concentration of runoff and the concentration of water-extractable P in the 0–2 cm soil layer. After surface application of broiler litter on hayfield, 50% of the resulted increase in resin-extractable P was concentrated in the top 3 cm of soil in the study of Vervoort et al. (1998); the lack of relationship between resin-extractable P in the top 15 cm of the soil and the dissolved orthophosphate P concentration in the surface runoff was probably due to the enrichment of P in the topmost soil layer.

Yli-Halla and Hartikainen (1996) suggested that the loading capacity of eroded soil particles can be estimated by water extraction of soil samples using high solution-to-soil ratios. In the fine sand soil of the present study, desorption of P with a solution-to-soil ratio of 2000:1 for the

Table 13. Inorganic phosphorus fractions ( $\text{mg kg}^{-1}$ ), degree of P saturation (DPS, %), P extracted with 0.5 *M* ammonium acetate – 0.5 *M* acetic acid, pH 4.65 ( $P_{Ac}$ ,  $\text{mg kg}^{-1}$ , Vuorinen and Mäkitie 1955); with 0.5 *M*  $\text{NaHCO}_3$ , pH 8.5 ( $P_{Olsen}$ ,  $\text{mg kg}^{-1}$ , Olsen and Sommers 1982) and with water at solution-to-soil ratios of 200:1 ( $P_w$ ,  $\text{mg l}^{-1}$ , Yli-Halla et al. 1995) in 0–5 cm soil layer and concentration of dissolved orthophosphate P ( $\text{PO}_4\text{-P}$ ,  $\text{mg l}^{-1}$ ) in surface runoff on the fine sand after experiment V. P-fertilizing treatments: (1) unfertilized, (2) slurry surface applied in September (with immediate ploughing in 1992), (3) slurry surface applied in December, (4) Slurry surface applied in May (with immediate harrowing in 1993), (5) NPK fertilizer surface applied in May (fertilizer placement in 1993).

Treatment	Soil, 0–5 cm								Surface runoff
	$\text{NH}_4\text{F}$	$\text{NaOH}$	$\text{H}_2\text{SO}_4$	Total inorg.P	DPS	$P_{Ac}$	$P_{Olsen}$	$P_w$	$\text{PO}_4\text{-P}$
Unfertilized (1)	132	63	150	345	10.5	6.8	49	0.046	0.033
Slurry, Sept. (2)	229	72	153	454	16.5	12.0	85	0.14	0.53
Slurry, Dec. (3)	183	73	148	404	14.6	9.8	74	0.12	0.36
Slurry, May (4)	259	85	159	503	16.6	13.0	86	0.16	0.62
NPK, May (5)	199	71	159	429	15.7	10.0	82	0.13	0.38

surface soil was 30–68  $\text{mg kg}^{-1}$ , depending on the preceding treatment. The desorption corresponded to 15–21% of the sum of P in the  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{F}$  and  $\text{NaOH}$  soluble fractions. Yli-Halla et al. (1995) studied desorption of P from surface soil in the heavy clay soil field studied here (Jokioinen) and the clay loam soil studied by Puustinen (1994) with a higher P status (Aurajoki,  $P_{Ac} = 33 \text{ mg l}^{-1}$ ). With the same solution-to-soil ratio (2000:1), desorption of orthophosphate P from the Jokioinen soil was 34  $\text{mg kg}^{-1}$  (average of two plots calculated from the data of Yli-Halla et al. 1995) while that from the Aurajoki soil was considerably higher, 122  $\text{mg kg}^{-1}$ . The desorption corresponded to 7% and 19% of the amounts of inorganic P.

### Cropping

On both soils, losses of dissolved orthophosphate P were higher from perennial grass ley than from ploughed soil (cereals). For the grass ley with spring and summer application of mineral fertilizer or slurry, the quantities of dissolved orthophosphate P lost annually were surprisingly similar on the heavy clay and the fine sand (Fig. 8).

In experiment IV, which was conducted on heavy clay soil, the losses of dissolved orthophosphate P averaged over the two fertilizer amounts were 0.15–0.60 and 0.20–1.2  $\text{kg ha}^{-1}\text{a}^{-1}$  from barley and fertilized grass ley, respectively. The respective percentage of dissolved orthophosphate as against total P losses was lower from barley than from grass ley (22–38% vs. 52–68%) due to both the lower absolute loss of dis-

solved P and the higher loss of particulate P. In experiment V, conducted on fine sand soil, the losses of dissolved orthophosphate P were 0.058  $\text{kg ha}^{-1}\text{a}^{-1}$  from barley, 0.12–0.13  $\text{kg ha}^{-1}\text{a}^{-1}$  from unfertilized grass ley and 0.52–1.5  $\text{kg ha}^{-1}\text{a}^{-1}$  from spring fertilized grass ley. The figures for dissolved orthophosphate as against total P losses were 7.6%, 40–75% and 59–75%, respectively.

In the case of barley and grass ley with spring and summer application of mineral fertilizer or slurry, the ratio of dissolved orthophosphate to total P corresponded fairly well to the results of Pietiläinen and Rekolainen (1991), who found that dissolved reactive P constituted 20–47% of the total P load from agricultural areas, with the highest proportion (47%) in an area influenced by cattle farming and grass cultivation. Hansen and Nielsen (1995) found that about two-thirds of the total P in surface runoff from grass-covered plots was in the form of dissolved orthophosphate. However, in their experiment, the loss, in  $\text{kg ha}^{-1}$ , was much smaller from grass than in treatments with ploughed, fallow or winter wheat. Uhlen (1978a, 1988) reported higher dissolved orthophosphate P losses from ley than from cereal plots. The rate of dissolved orthophosphate P leaching from ley was much higher in the present study, however.

The higher concentrations of dissolved orthophosphate P and the greater losses in surface runoff from fertilized perennial grass ley were mostly attributed to the surface application of fertilizer P on the ley in spring and summer as discussed above. However, the increase in the



concentration of dissolved orthophosphate P in surface runoff from grass ley could partly be attributed to P release from vegetation. On the fine sand soil, the average concentration of dissolved orthophosphate P in surface runoff from the unfertilized plot was slightly higher during the three ley years (0.081, 0.046 and 0.086 mg/l, respectively) than during the preceding barley year (0.025 mg/l) (Table 12).

Grass leaves have been shown to release P, especially after freezing and drying; the amounts released by barley and oats straw are much smaller P (Timmons et al. 1970, Ulén 1984). According to Sharpley (1981b), P release from growing plants can maintain concentrations of orthophosphate in plant leachate similar to those leached from unfertilized surface soil. Here, both overwintering grass leaves and grass leaves killed with glyphosate released orthophosphate to surface runoff (Fig. 5). In the study of Uhlen (1988), the dissolved orthophosphate P concentration in surface runoff from unfertilized grassland was in the range 0.1–0.2 mg/l during spring, with even higher concentrations at the outset of snowmelt. In both the present study and that of Uhlen (1988), the resulting dissolved orthophosphate P losses were 4–5 times as large as those from ploughed, unfertilized soil. Also McDowell et al. (1989) have reported that dissolved orthophosphate P concentrations in almost half of the runoff samples from unfertilized, continuous cotton exceeded 0.2 mg/l, and attributed these, in part, to the release of soluble P from crop residues.

#### *Water flow routing*

The concentrations of dissolved orthophosphate P were lower in drainage water than in surface runoff but the difference was much greater in the fine sand soil (Tables 11 and 12, Fig. 5). Due to the higher concentrations in surface runoff and the large amount of surface runoff, surface runoff was the main route of dissolved orthophosphate P losses, especially for the fine sand soil and the fertilized grass ley. On the fine sand soil, surface runoff transported 80–92% of the dissolved orthophosphate losses from barley and 99–100% from grass ley; on the heavy clay soil, the respective proportions were 53–77% and 71–85%.

The lower concentrations of dissolved orthophosphate P in drainage water than in surface runoff indicated adsorption of P during the flow of water through the soil. Lower concentrations of dissolved orthophosphate P in subsurface flow than in surface runoff have been documented already in the 1970s (Baker et al. 1975, Burwell et al. 1977, Uhlen 1978a, Sharpley and Syers 1979b). The more efficient adsorption in the fine sand soil was probably due to the high amount of Al and Fe oxides in the soil profile (VI). Reddy et al. (1996) found that on a watershed scale P retention in soils was strongly associated with Al and Fe oxide content, with the spodic horizon efficiently reducing P transport from the upland dairy and beef pastures.

On the heavy clay soil, the improvements made to the subsurface drainage reduced the loss of dissolved orthophosphate P by changing the water flow paths to favour drainage instead of surface runoff (III, Fig. 4). After infiltration, water moved mainly along large pores and in the drain trenches, where the pore walls and especially the cut walls of the trenches could adsorb dissolved P. Contrary to the P status of the filling material, the P status of the cut walls of the trenches was lower in the subsoil than in the plough layer (Table 2) thus facilitating adsorption of dissolved P. The reduction in the concentration of dissolved orthophosphate P in drainage water compared with that of drainage water and surface runoff before the drainage improvement lowered dissolved orthophosphate P losses by approximately 25% (III, Table 10).

The concentrations of dissolved orthophosphate P in drainage water showed a similar pattern to those in surface runoff (IV). Dissolved orthophosphate concentrations in drainage water on the heavy clay were higher for ley than for barley (Fig. 5), and the peak concentrations in surface runoff were accompanied by corresponding, but smaller, peaks in drainage water from the ley (IV). Towards the end of the experiment, the base level of the concentration of dissolved orthophosphate P in drainage water increased along with that of the surface runoff.

On the heavy clay, the peaks in drainage water occurred after fertilizer broadcasting followed by only 7–15 mm of drainage flow. The amount of drainage before the peak concentrations ap-

peared in the drainage water was much too small for uniform movement through the soil, and indicated rapid water and dissolved orthophosphate P movement via continuous fissures and macropores to the drainage system. The difference between the concentration of dissolved orthophosphate P in the drainage water from barley and ley plots was due to the much higher concentration in the near-surface flow of the ley, which was then reflected in the drainage water. The increase in the base level concentration in drainage water from the ley may have been partly due to gradual P accumulation on the walls of the macropores conducting water to drainage pipes, with a subsequent decrease in further adsorption.

Sharpley and Syers (1979b) likewise found lower dissolved orthophosphate concentrations in drainage water than in surface runoff and attributed this to extensive sorption of phosphate by soil components. On loam soil in Norway, Uhlen (1978a) found decreased orthophosphate concentrations in drainage water from deeper drains (0.90 m vs. 0.25 m), indicating removal of orthophosphate from the water in the 0.25–0.9 m soil layer. On clay soil, Culley et al. (1983) measured lower concentrations in water from deeper drains (1.0 vs. 0.6 m). On the contrary, the increase in the P concentration of drainage water in the study of Heckrath et al. (1995) was explained by preferential flow or transport of P in forms that made it less susceptible to sorption in subsoil (e.g. colloidal or organically associated P).

### 3.3 Phosphorus balance

Whereas the runoff losses of P, measured during a limited period, represent the immediate harmful effects of cropping practices, accumulation of P in soil leads to an increased risk of P losses in the future (Haygarth et al. 1998, Vervoort et al. 1998). On the heavy clay soil of the present study, P accumulation (Balance) was very high for the grass ley with the largest input of P (Table 14). On the fine sand soil, slurry applications in autumn and spring resulted in the highest accumulation of P in soil, partly due to the larger

amounts of P applied. Winter application of slurry induced large losses of P in runoff, which reduced the accumulation. P accumulation in the mineral fertilizer plots was lower than in plots with slurry application in spring due to the lower amount of fertilizer applied and to the higher removal in the harvested crop (V, Table 14).

On the heavy clay, grass ley cultivation with the highest P fertilization had the lowest Runoff/Crop value of all the treatments on the same soil, although runoff losses were considerable (Table 15). The environmental risk value of the treatment was therefore low when crop uptake of P was considered. On the fine sand soil, the Runoff/Crop value for the unfertilized treatment was not the lowest of all the treatments despite the very low runoff losses. There, the very small yields of the unfertilized treatment increased the environmental risk value.

The Runoff/Crop and Balance/Crop values seemed to reflect well the short- and longer-term environmental effects, respectively. Whereas the Runoff/Crop value was rather high for the unfertilized treatment on the fine sand soil, the Balance/Crop value was low due to zero input in fertilizers (Table 15). For the spring applied slurry and mineral fertilizer treatments of grass ley in both soils, the Runoff/Crop and Balance/Crop values indicated that the environmental risk was smallest for the mineral fertilizer treatment on the fine sand soil.

Except for treatment 3 on the fine sand soil, the reciprocal order of the different treatments was the same for (Input-Crop)/Crop as for Balance/Crop (Table 15). At farm level, the data on actual losses in runoff and drainage from a particular field are normally lacking, making it impossible to calculate the true balance values. However, it is relatively easy to obtain data on P input and crop uptake and so to calculate the value of (Input-Crop)/Crop. Here, the (Input-Crop)/Crop values seemed to contain the short (Runoff) and longer term (Balance) environmental risks of the different nutrient management practices.

Although little information is available on P losses from soils before cultivation, surveys of catchments have shown that the P losses tend to be an order of magnitude higher from cultivated areas than from wooded areas (Kauppi 1978,

Table 14. Phosphorus input in fertilizer and slurry, removal in harvested crop and runoff (surface runoff + drainage water) and calculated balance (Input-Removal) ( $\text{kg ha}^{-1}$ ) with percentage of applied in parentheses. Data adopted from papers IV and V.

No	Crop	Fertilizer	Input	Removal		Runoff		Balance	
				Crop					
Heavy clay soil, 1980–1982/									
1	Barley	NPK	63	26	(41)	3.9	(6.2)	33	(52)
2	Barley	NPK	126	34	(27)	3.3	(2.6)	89	(71)
3	Grass ley	NPK	126	29	(23)	4.8	(3.8)	92	(73)
4	Grass ley	NPK	252	50	(20)	4.8	(1.9)	197	(78)
Fine sand soil, 1992–1996/									
5	Grass ley	Unfertilized	0	6.4		1.4		–7.8	
6	Grass ley	Slurry, Sept.	141	45	(32)	16	(11)	80	(57)
7	Grass ley	Slurry, Dec.	119	29	(24)	57	(48)	33	(28)
8	Grass ley	Slurry, May	143	52	(36)	4.9	(3.4)	86	(60)
9	Grass ley	NPK	107	61	(57)	4.9	(4.6)	41	(38)

Table 15. Environmental risk values for the different treatments calculated from Table 14.

No Crop	Fertilizer	Runoff/Crop	Balance/Crop	(Input-Crop)/Crop
<b>Heavy clay soil, 1980–1982/</b>				
1 Barley	NPK	0.15	1.3	1.4
2 Barley	NPK	0.097	2.6	2.7
3 Grass ley	NPK	0.17	3.2	3.3
4 Grass ley	NPK	0.096	3.9	4.0
<b>Fine sand soil, 1992–1996/</b>				
5 Grass ley	Unfertilized	0.22	–1.2	–1.0
6 Grass ley	Slurry, Sept.	0.36	1.8	2.1
7 Grass ley	Slurry, Dec.	2.0	1.1	3.1
8 Grass ley	Slurry, May	0.094	1.7	1.8
9 Grass ley	NPK	0.080	0.67	0.75

1979, Rekolainen 1989, Pommel and Dorioz 1997). Apparently the first and most drastic impact of agriculture on aquatic ecosystems results from destruction of natural vegetation when land is cleared for cultivation (Kauppi et al. 1993). Agricultural systems are less sustainable than other terrestrial ecosystems such as natural or forestry systems, due to the prevailing monocultures and perturbations from the steady states, and the more open nutrient cycles (Addiscott 1995). Therefore, minimizing nutrient losses from a particular agricultural area may not always increase the overall sustainability if it leads to poor productivity. The lower the productivity of a certain agricultural area, the more agricul-

tural land is needed to approach the desired amount of production, with the result of reduction in the spare land under semi-natural or natural ecosystems. At country or global level, overall sustainability is therefore affected by 1) the amount of nutrient losses or other environmental effects from the cultivated area and 2) the size of the area needed for agricultural production. In the light of what was said before, the latter aspect might be taken into account by dividing the losses or balance values in a particular cultivated area by the nutrient uptake in the same area. The lower the value, the higher would be the environmental nutrient efficiency of the system.



## 4 GENERAL DISCUSSION

### 4.1 Estimation of phosphorus load

The phosphorus load from agricultural soils on watercourses is estimated by monitoring small catchments and by extrapolating the results obtained from field scale plots. As the measurement of truly bioavailable P in runoff water samples influenced by agriculture is very time-consuming, routine methods such as determination of dissolved orthophosphate and total P are still used for monitoring purposes. While the proportion of particulate P and dissolved orthophosphate P varies greatly between cropping practices and soils, total P losses are not very revealing about the effects of the P load on watercourses. Accurate determination of dissolved orthophosphate P must be regarded as the basis for estimation of P load from agricultural areas. However, if runoff water contains an appreciable amount of suspended soil particles, the P load cannot be estimated without determination of particulate P, which often requires determination of total P.

Determinations of the different phosphorus fractions in water samples containing suspended soil particles are prone to inaccuracy. Investigation of the accuracy of the different methods showed that suspended soil particles were the main source of error in determinations of total P and dissolved orthophosphate P in the water samples. While incomplete P release from the suspended soil particles impaired the results for total P determination, desorption of P from the particles increased the values of dissolved orthophosphate P. The errors resulted in underestimation of the particulate P values, which were calculated as the difference between total P and dissolved orthophosphate P.

According to Rigler (1973), Eck (1982) and Sibbesen (1995), a considerable amount of particulate P is associated with clay and colloid-size particles. It was evident here, too, that appreciable particulate P was associated with colloids of very small size. The nature of P in these colloids was not studied, and therefore the ratio of primary P (apatite) to adsorbed secondary P or the amount of particulate organic P is not known.

The proportion of fertilizer-derived P in the eroded particles may well be higher than in the bulk soil, due to the preferential movement of smaller particles which preferentially retain P inputs (Maquire et al. 1998) and in which the proportion of primary P is probably lower (Syers et al. 1969). Furthermore, the proportion of organically bound P or orthophosphate adsorbed to humic-metal-complexes (Gerke and Hermann 1992) is not known here.

The contribution of dissolved organic P on the losses of total P was not studied here, either. Kaila (1948) found that after extracting mineral soil samples with water (at solution-to-soil ratio of 100:1) the amount of dissolved organic P averaged 20–67% of the amount of total P in the filtered extracts. In a study on drainage water from silty clay loam, dissolved organic P accounted, on average, for less than 5% of total P (Heckrath et al. 1995). However, Chardon et al. (1997) found that dissolved organic P accounted for >70% of total P in the leachates from lysimeters filled with sandy soil and treated with animal slurry or mineral fertilizers. In drainage water from silty clay loam under grass or grass-clover, Hooda et al. (1999) estimated the amount of dissolved organic P to approach 41% of total P. The procedure of determining dissolved organic P as difference between total P in the filtrate and dissolved orthophosphate P (Heckrath et al. 1995, Chardon et al. 1997, Hooda et al. 1999) may, however, overestimate the loss of dissolved organic P. The overestimation would arise particularly in runoff waters typical for clayey soils containing small colloids in which P may be inorganically bound and would be therefore erroneously interpreted as organic.

The contribution of the different P fractions (dissolved orthophosphate and particulate P) in surface runoff and drainage water to algal-available losses of P in the present study can be estimated by assuming 1) 100% availability of dissolved orthophosphate P and 2) 5% potential algal-availability of particulate P (results of Ekholm, 1994). In the annual P losses from grass ley found here, only 1.4–7.0% of algal-available P originated from particulate P. From barley,

the contribution of particulate P to algal-available P was higher: 7.7–15% in the heavy clay soil and 31–53% in the fine sand soil. Clearly, the contribution of particulate P to algal-available P varies, depending on the abundance of suspended soil particles in water. In the surface runoff samples studied by Uusitalo et al. (1999), the proportion of particulate P as a source of bioavailable P rose from 12–33% to 31–65% when the concentration of total suspended solids increased from 0.2–0.5 g l<sup>-1</sup> to 1.0–2.5 g l<sup>-1</sup>.

According to Ekholm (1998), the average proportion of potentially algal-available P in water samples from agriculturally loaded rivers was 20%, of which the smaller part (26% in the Paimionjoki) originated from particulate P. After sedimentation, however, particulate P provides P for submerged macrophytes, which are potential nutrient pumps to the open water (Cargnan and Kalff 1980). Moreover, lake sediments can release orthophosphate P to water under anaerobic conditions or when pH increases during intensive photosynthesis (Knuuttila et al. 1994), even though the origin of the particulate P (recycled or external) is not always known (Ekholm 1998). Despite the incomplete knowledge of particulate P availability, the above findings show that water protection measures should focus primarily on reducing dissolved orthophosphate P losses, as also proposed by Ekholm (1998).

## 4.2. Soil phosphorus status – links to the load

The inherent P status of a given soil obviously has a great influence on the P load on watercourses by affecting both particulate and dissolved orthophosphate P losses. At a catchment level, a minority of fields with high soil test P levels may override larger field areas with low P status, especially in catchments with similar soil types, slopes and cultivation practices. However, in catchments with variable soil types, slopes, sub-surface drainage conditions, crop cover and soil tillage, high surface runoff and erosion potential may produce large P losses, even from fields with moderate or low P status. Therefore, all rel-

evant factors must be considered when defining critical source areas (Pionke et al. 1997) for P loss.

Heckrath et al. (1995) and Smith et al. (1998) found that the values of Olsen-P (Olsen and Sommers 1982) in the plough layer, 60 and 70 mg kg<sup>-1</sup>, respectively, were the change points for increased P leaching below 30 cm depth. In the present study, the effect of the P status of the surface soil on the loss of dissolved orthophosphate P in surface runoff was demonstrated in experiment VI. Uusi-Kämpä and Ylärinta (1996) measured P losses in surface runoff from clay soil with moderate P status ( $P_{Ac}$  7.7 mg l<sup>-1</sup>, Vuorinen and Mäkitie 1955) on plots with or without 10 m wide grass buffer strips. The P losses were comparable to those of the present study, 0.29–0.59 and 0.10–0.20 kg ha<sup>-1</sup>a<sup>-1</sup>, for particulate and dissolved orthophosphate P, respectively. However, P losses in surface runoff were higher in the study of Puustinen (1994), due to the steeper slope (7–8%) and higher P status of the clay loam soil. He measured plough layer runoff with particulate and dissolved orthophosphate P losses of 1.7–5.9 and 0.37–0.75 kg ha<sup>-1</sup>a<sup>-1</sup> respectively.

On soils with higher P status, the management practices used here (cropping, fertilizer application, drainage) would probably induce P loss changes in the same direction, although the extent of the changes might differ from the present ones. The P losses measured on cereals in this study approached the average losses from small catchments influenced by agriculture (0.9–1.8 kg ha<sup>-1</sup>, Rekolainen 1989). Although the P status of the investigated sites of the present study was low, P losses were still about ten times as high as those reported for forested catchments (0.059–0.16 kg ha<sup>-1</sup>, Rekolainen 1989), thus showing that current agricultural practices, even excluding overfertilization and high P status, have great potential to expose soil to nutrient losses. This is not surprising because the thrust of agricultural practices has been on producing higher yields, and not, until recently, on developing machinery and management strategies to minimize nutrient losses to watercourses.

To improve crop yields, the P input in mineral fertilizer in Finland in the 1950s, 1960s and 1970–1980s was 13, 19 and 30 kg ha<sup>-1</sup>a<sup>-1</sup>, respec-

tively; while in the 1990s the amounts have decreased, being  $12 \text{ kg ha}^{-1}\text{a}^{-1}$  in 1998 (Airola 1994, Yearbook of farm statistics 1998). The P input in manure is estimated to be  $8 \text{ kg ha}^{-1}\text{a}^{-1}$ . While the crop uptake has been only about  $12 \text{ kg ha}^{-1}\text{a}^{-1}$ , the inputs in fertilizers and outputs in the harvested crop in the 1970–1980s resulted in a surplus of approximately  $26 \text{ kg ha}^{-1}\text{a}^{-1}$ . Thus a progressive build-up of residual P has taken place in cultivated soils, increasing the average P content of the plough layer of clay soils from  $2200 \text{ kg ha}^{-1}$  in 1920 to  $3100 \text{ kg ha}^{-1}$  in 1995. At the same time, the average soil test P value ( $P_{\text{Ac}} = \text{P}$  extracted with acid ammoniumacetate, pH 4.65, Vuorinen and Mäkitie 1955) in surface soils has more than doubled (Saarela 1991, 1995). Despite of the past build-up of residual P, the P status of cultivated soils in Finland is still lower than in other Scandinavian countries (Steen 1997).

Although the fixed P from earlier fertilizer inputs is largely irreversible, it can gradually be released to plants when reserves of less strongly held P are exhausted. Saarela et al. (1995) reported that, without P fertilizer inputs,  $P_{\text{Ac}}$  values declined in 12 years from 20 to  $12 \text{ mg l}^{-1}$  in clay and silt soils and from 11 to  $8 \text{ mg l}^{-1}$  in sand and loam soils. To reduce P losses from agricultural soils in Finland, current recommendations for P fertilization aim to reduce P status, especially in soils rich in plant-available P. However, as stated by Sims (1998), it may well be that the soil P levels needed for economically optimum agricultural production are by definition too high in terms of water quality. In the present study, the sites with low P status still produced P losses of  $0.5\text{--}1 \text{ kg ha}^{-1}$  without P fertilization, with dissolved orthophosphate P concentrations of  $0.03\text{--}0.05 \text{ mg l}^{-1}$ , which are substantially higher than e.g. the  $0.012 \text{ mg l}^{-1}$  limit set for P concentration in lake water classified as excellent (Heinonen and Herve 1987).

Despite the low inherent soil P status found in the present study, P losses attributable to surface application of slurry in autumn and winter were larger than any P losses previously reported in Finland. The P loading risks of watercourses due to surface application of slurry are emphasized in central and northern Finland, where the cultivated area under grasses (total 680 000 ha, Statistical Yearbook of Finland 1997) is the highest

in the country. There dairy farms are not able to apply all the manure or slurry available to the often very limited area of arable crops and thus slurry is commonly applied to perennial grasses. Because of insufficient storage capacity, slurry is also applied in autumn and earlier was applied on frozen soil in winter as well. Winter application on snow-covered or frozen soil was heavily curtailed in the 1990s and forbidden by law in 1998; still, the present results strongly argue for restrictions of surface application of slurry on grasslands in autumn, too.

High dissolved orthophosphate P losses from grass ley are a result of abundant surface runoff and shallow accumulation of P after surface application of fertilizers. The present results showed that few surface applications of slurry and mineral fertilizers, irrespective of the time of application, can elevate DPS and readily extractable P at the surface, even on soil with an initial low P status. Together with the large direct P losses from surface-applied slurry and mineral fertilizer in surface runoff from the experimental plots, the present findings suggest that subsurface placement of P on perennial leys would cause a much lower P load than surface application. As high concentrations of the dissolved orthophosphate in summer runoff directly increase the risk of massive algal blooms, efforts to minimize fertilizer broadcasting should be given high priority in recommendations aimed at the improving surface water quality. During grass cultivation, fertilizer could be incorporated into the surface soil, away from the zone of extraction caused by shallow surface runoff, using a placement technique or by applying the bulk of the fertilizer P needed for the 2–3-year growing period in conjunction with sowing.

In many models describing P transport from agricultural soil, estimates of dissolved orthophosphate losses are based on the empirical equation of Sharpley et al. (1981a,b, 1985). The equation predicts the dissolved orthophosphate P concentration in surface runoff water from labile soil P, other soil characteristics, the effective depth of interaction between surface runoff and surface soil, the water-to-soil ratio and runoff volume. However, for some unknown reason, adapting the equation to two Finnish clay soils produced erroneous results (Ekholm et al.

1999). However, recent findings that water-extractable P of the surface soil may reflect the concentration of dissolved orthophosphate P in surface runoff from agricultural soils (Yli-Halla et al. 1995, Pote et al. 1996, present study) may make it unnecessary to use the rather complicated equation.

Routine soil tests, such as  $P_{Ac}$  and  $P_{Olsen}$ , have been developed to estimate plant available P. The study showed that these tests may also be used to estimate the  $PO_4$ -P loading potential. For agronomic needs the soil samples are commonly taken from the surface to a depth of 25 cm; estimation of the P loading potential, however, may require shallower sampling, especially if fertilizers are applied to the soil surface, resulting in a substantially higher P status in a surface soil layer only a few centimeters thick. For perennial leys where fertilizer or slurry is applied on the surface, samples should be taken from 0–2 or 0–5 cm layers, for example. Deeper sampling tends to severely underestimate the P load from top-dressed soils, especially for soils with an initially poor or moderate P status. However, we still lack knowledge of the depth at which the interaction between surface runoff and surface soil takes place. Depending on the cultivation practices and frost/snowmelt conditions, in Finland this may lie somewhere between a few centimeters (perennial grasslands, frozen soil) and 20–25 cm (ploughed soil).

Despite useful in showing the differences between the P loading potential between various soils, soil P analyses are often inadequate in predicting the actual P load at a given site. Estimation of the concentration of P in surface runoff must be accompanied by knowledge of the amount of surface runoff as well as of soil erosion. Processes that lower the P concentrations during water movement into deeper soil layers or along small waterways must also be taken into account. E.g. Sharpley et al. (1999) suggest that P loss from near-stream fields may have more impact on streamflow P concentrations than areas further from the channel.

As well as P losses, nitrogen (N) leaching losses from agricultural soils contribute to eutrophication in the Archipelago Sea of southwestern Finland, especially in the open sea (Kirkkala et al. 1998). As P losses and N leaching are

induced by different mechanisms, cultivation practices seeking to reduce P losses may have opposite effects on N leaching. Practices that reduce soil erosion and P losses by decreasing surface runoff tend to increase N leaching, at least temporarily, as was observed in the present study (III). However, without a well-functioning subsurface drainage system N losses from soil into the atmosphere may increase due to denitrification under more frequent anaerobic conditions. Moreover, proper functioning of the drainage system is often a prerequisite for profitable yields and higher N use efficiency, especially in clay soils. Decisions about the best practices needed to improve the water quality of the recipient watercourse must be based on knowledge of the critical nutrients for algae growth. As long as this knowledge is lacking, cultivation practices must be optimized to reduce both P and N losses.

### 4.3 Sources and sinks of phosphorus

Forces induced by raindrops and surface runoff, structural changes due to soil tillage, and inputs such as fertilization influence P losses by frequently, and often rapidly, changing the conditions on the surface. If several processes on the soil surface act to increase P loads at the same time, cultivation practices may have surprisingly dramatic and rapid effects on the actual P losses. This was demonstrated here when perennial grass cultivation produced high bioavailable P loads on watercourses, due to a simultaneous decrease in the infiltration capacity of the soil surface and P accumulation on the topmost soil.

The increase in P loss from agricultural soil takes place in successive steps, the first of which are driven by hydrological processes, such as lack of infiltration of rain or meltwater (Fig. 10). Soil management and agricultural practices affect the infiltration capacity of soil as well as the susceptibility of surface soil to erosion, decisive for particulate P losses. Depending on the porosity and roughness of the surface, water interacts with a layer of surface soil of variable thickness, and the concentration of dissolved orthophosphate P in surface runoff is determined by the desorbable P. Therefore last steps of the



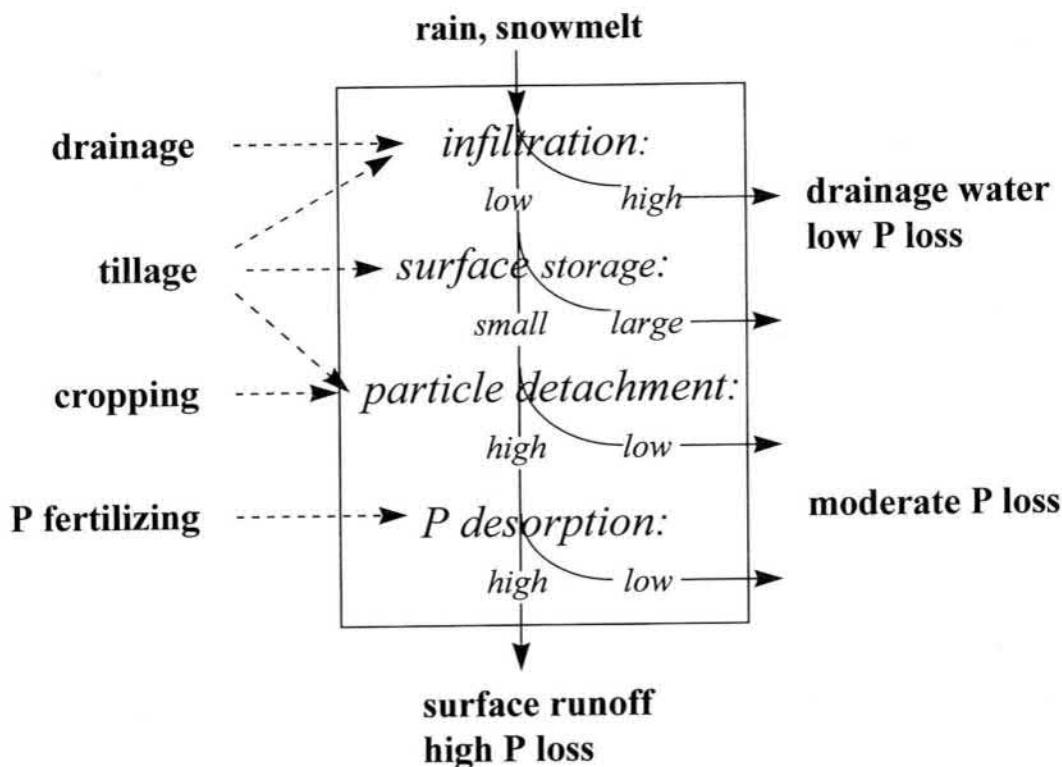


Figure 10. Schematic representation of factors affecting P losses from agricultural soil. On the left: cultivation practices; in the middle: soil processes affected by cultivation practices, with the worst and best effects; on the right: resulting P losses.

rise in P loss are driven by soil P status and fertilizing practices capable of long- and short-term increase in the P status of the surface soil.

Particulate P and dissolved orthophosphate P are mostly entrained to water from surface soil as a consequence of particle detachment and desorption from the surface. Further entrainment occurs during surface runoff transport towards the lower end of the fields but infiltration and flow through soil pores or the drain trenches may allow sieving of the particles by small pores. Moreover, deep gradient in P status between the surface and the subsoil may allow adsorption of dissolved orthophosphate P by pore walls with lower P status than the surface soil. However, sieving and adsorption are diminished by preferential flow, which transports both dissolved and particulate P from surface soil into drainage system.

On most agricultural soils, surface soil acts as a source and subsoil as a sink for both particulate and dissolved P. In the heavy clay soil,

particulate P and dissolved orthophosphate P concentrations were reduced by about 30% during transport to the drainage system, whereas in the podzolized fine sand soil the reduction was by at least 90%. However, the reduction in the dissolved orthophosphate P concentration might be appreciably lower on permeable sandy soils lacking the podzolized layer or owing to flow through preferential hydrological pathways as in the study of Hooda et al. (1999), where dissolved orthophosphate P losses through subsurface drains were 1.3–2.0 kg ha<sup>-1</sup>. Deeper soil horizons of the heavy clay soil probably make only a small contribution to the entrainment of soil particles to drainage water, although this could not be proved here. The rate of changes due to different management practices is normally slower in the subsoil than in the surface soil. Therefore, to achieve a certain reduction in P losses from agricultural soil, it may be easier to

diminish the entrainment of P in the soil surface, by curbing erosion and lowering the P status of

surface soil, than to improve the sieving or adsorption capacity of the subsoil.

## 5 CONCLUSIONS

Total P will be underestimated by the present standard recommendation for peroxodisulphate digestion. Increasing the amount of sulphuric acid relative to suspended particulate material would, however, improve the results. In routine water analysis, the colloidal P fraction should be included in full in the particulate P fraction by calculating the difference between total P in unfiltered and dissolved orthophosphate P in the filtered sample. Adopting this procedure would make it unnecessary to determine total P in the filtrate. For dissolved orthophosphate P measurement, the pore size of the filter should be as small as possible to minimize the release of orthophosphate from the small colloids passing the filter.

Management practices enhancing infiltration and drainage flow such as improvement of a poor drainage system would decrease P losses. Perennial grass ley cultivation tends to increase the proportion of surface runoff, which, together with surface application of fertilizer P, may result in high dissolved orthophosphate P losses. The surface accumulation of P during perennial grass cultivation should be diminished by employing a fertilizer placement technique and by incorporating the bulk of the fertilizer P in con-

junction with sowing. The loading potential of a soil may be estimated from the soil P status, but the P concentration must be determined from the layer that interacts most closely with the surface runoff water. On perennial grass ley, the layer of interaction between topsoil and surface runoff may be less than 5 cm thick. At farm or field level, estimation of both the direct and indirect environmental risks of different cultivation practices might be improved by simply dividing the losses or balance values by crop uptake of P.

To identify fields with the highest potential for P losses to watercourses, more data are needed on the relationship between extractable soil P and dissolved orthophosphate P in surface runoff, and on the changes in the hydraulic conductivity of the soil surface due to different cultivation practices. To develop cropping and tillage practices that reduce soil erosion, better understanding is needed of the factors governing the dispersion of clay particles into the surface runoff water. Moreover, to improve the soil's capacity to act as a filter, more research must be conducted on the adsorption of dissolved P and the sieving of particulate P along the different water paths from soil surface to the subsurface drainage system and groundwater.



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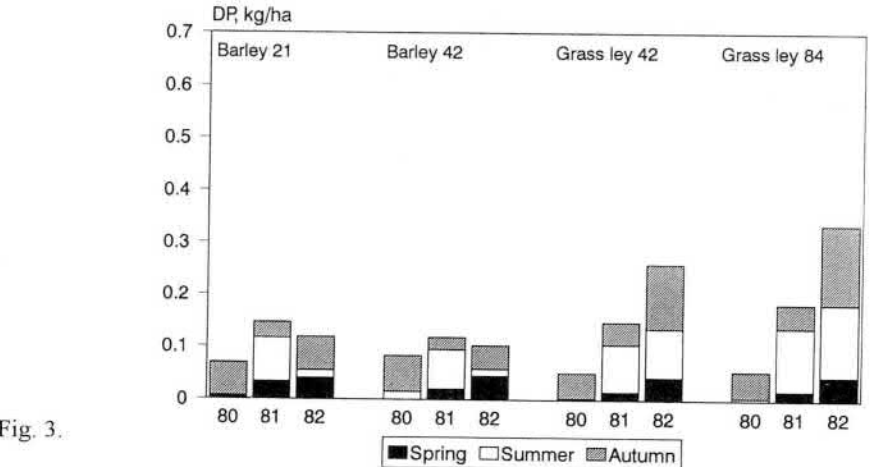
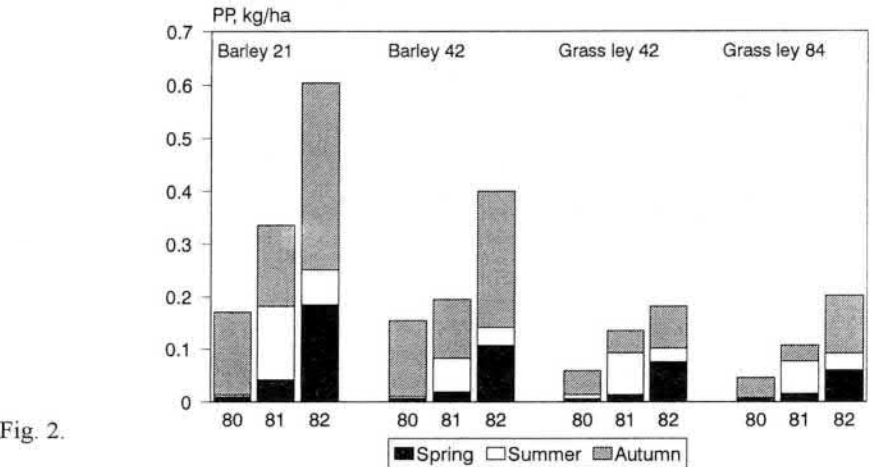
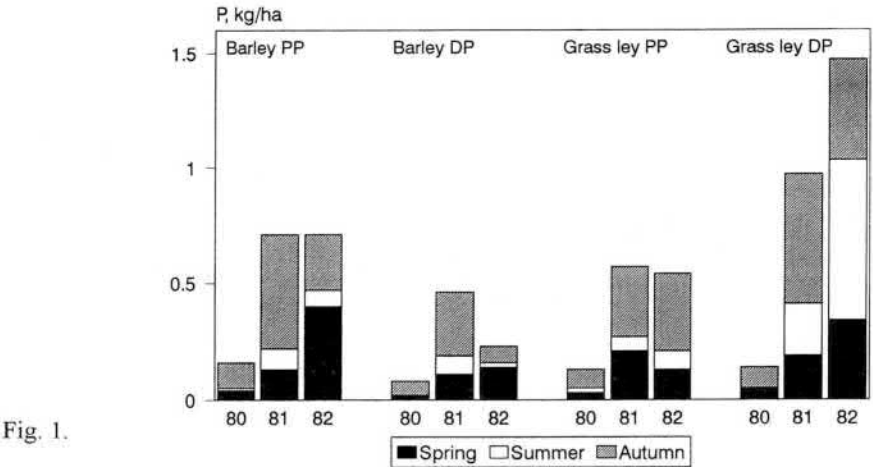
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ERRATA FOR THE ORIGINAL ARTICLES

Article IV

Correction p. 162–163

Fig. 1, Fig. 2, Fig. 3





## Article VI

*Position* p. 165, Abstract, line 12

...in the control plots...

*Correction*

...in the control plot...

*Position* p. 170, Table 4, Heading

Total inorganic P (TIP),  $P_{\text{NH}_4\text{F}}$ , degree of P saturation (DPS)...

*Correction*

$P_{\text{NH}_4\text{F}}$ , degree of P saturation (DPS)...



# Peroxodisulphate digestion and filtration as sources of inaccuracy in determinations of total phosphorus and dissolved orthophosphate phosphorus in water samples containing suspended soil particles

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Determinations of phosphorus fractions in water samples may be unreliable if an appreciable amount of phosphorus is attached to suspended soil particles. The inaccuracies in peroxodisulphate digestion for determination of total phosphorus were studied on the basis of surface runoff and drainflow samples from a clay soil. The results obtained with peroxodisulphate digestion tended to be lower than those obtained with a HF digestion method. The results of peroxodisulphate digestion indicated incomplete extraction of phosphorus, especially in samples with large amounts of suspended soil particles. More sulphuric acid, or dilution of the samples before the digestion, improved the results. Error in dissolved orthophosphate determination due to colloidal material was investigated by removing variable amounts of the material from samples before the analysis. The amounts of dissolved orthophosphate that were determined increased with the amount of suspended material in the filtrate, indicating release of orthophosphate from colloids. The described inaccuracies in total and orthophosphate phosphorus determinations may result in underestimation of the particulate phosphorus fraction.

## Introduction

Because of their dissimilar availability to algae, different phosphorus (P) fractions in runoff waters need to be quantified separately. In water qual-

ity monitoring, total phosphorus (TP) in runoff water is typically divided into particulate (PP) and dissolved, or soluble, (DP) fractions (e.g. NS 1984b, SS 1984b, DS 1985b, SFS 1986b). The PP fraction, which consists of undissolved inorganic and or-

ganic P in colloids and larger particles, is largely unavailable (Kauppi *et al.* 1993, Ekholm 1994). The DP fraction consists of both dissolved inorganic and dissolved organic P. Dissolved orthophosphate ( $\text{PO}_4\text{-P}$ ), which is the main form of dissolved inorganic P in runoff waters (Broberg and Persson 1988), is considered directly available to algae (Walton and Lee 1972, Ekholm 1994). It should be noted, however, that P recorded as DP may include also colloidal P.

Digestion with acid peroxodisulphate is recommended for routine analysis of TP in runoff waters (EPA 1971, APHA 1975, NS 1984b, SS 1984b, DS 1985b, SFS 1986b). However, several researchers (O'Connor and Syers 1975, Logan *et al.* 1979) have found that peroxodisulphate digestion underestimates TP in water samples containing appreciable soil material. To avoid the underestimation, the standards (NS 1984b, SS 1984b, DS 1985b, SFS 1986b) recommend that samples containing TP in excess of  $0.8 \text{ mg l}^{-1}$  should be diluted. Preliminary experiments with runoff samples in the author's laboratory have suggested that TP values are underestimated also in samples containing less than this concentration of TP. Although peroxodisulphate digestion would probably extract all biologically available P, appreciable deviation from the real value must be considered undesirable in the calculation of geochemical mass balances.

To separate PP and DP, water samples are filtered. PP is usually determined as the content of TP in material retained on  $0.2\text{--}0.45 \text{ }\mu\text{m}$  filters (Broberg and Persson 1988). Alternatively, it can be calculated as the difference between concentrations of TP and DP (NS 1984b, SS 1984b, DS 1985b, SFS 1986b). The operational definition of PP partly neglects the smallest particles and colloids (Menzies *et al.* 1991), although these have been identified as important P carriers in water (Rigler 1964, Van Eck 1982). Since colloids, usually defined as particles smaller than  $0.1\text{--}1 \text{ }\mu\text{m}$ , are not totally removed in routine filtration, they are present in both the particulate and the dissolved fractions (Broberg and Persson 1988).

For runoff waters containing eroded particulate material, filtration through  $0.45 \text{ }\mu\text{m}$  filters is recommended (NS 1984a, SS 1984a, DS 1985a, Herve and Kauppi 1986) before analysis of  $\text{PO}_4\text{-P}$  by the method of Murphy and Riley (1962). In-

stead of  $0.45 \text{ }\mu\text{m}$  filters,  $0.4$  and  $0.2 \text{ }\mu\text{m}$  filters are also commonly used in the filtration (SFS 1986a, Broberg and Persson 1988). Depending on the filter used, however, varying amounts of colloidal P may pass through. Strong acid used in the measurement of orthophosphate may dissolve orthophosphate from the colloidal P fraction (Logan 1982, Broberg and Pettersson 1988), leading to too high  $\text{PO}_4\text{-P}$  results. During storage, in particular, acidifying the filtrate with sulphuric acid to prevent microbial growth (NS 1984a, SS 1984a, DS 1985a, SFS 1986a) may cause too high  $\text{PO}_4\text{-P}$  results due to the dissolution of P (Rigler 1973, Turtola 1989). Orthophosphate release from the filters may also lead to an overestimation of  $\text{PO}_4\text{-P}$  (Bloesch and Gavrieli 1984). In view of the possible errors in orthophosphate determination, results quoted in the literature are often referred to as molybdate reactive P or dissolved reactive P. However, dissolved orthophosphate P ( $\text{PO}_4\text{-P}$ ) is preferred throughout this paper, as the more appropriate term for an investigation of the inaccuracy.

The present work was undertaken to study the shortcomings of some commonly used standard methods for determination of the various P-fractions in water samples containing suspended soil particles. The completeness of the P extraction was studied through comparison with results of a HF digestion. The effects of sample dilution before peroxodisulphate digestion and of different amounts of potassium peroxodisulphate ( $\text{K}_2\text{S}_2\text{O}_8$ ) and sulphuric acid ( $\text{H}_2\text{SO}_4$ ) on the TP result were investigated. The magnitude of the errors associated with  $\text{PO}_4\text{-P}$  determinations was investigated by removing different amounts of particulate material from the samples with filters and by centrifugation. The filters were of various types and pore sizes to determine whether this affected the result. Evaluation of the inaccuracies in TP and  $\text{PO}_4\text{-P}$  determinations allowed an estimate of the error in the PP value.

## Material and methods

### Water sampling

The water samples were collected from a drainage and runoff collection system on heavy clay soil in Jokioinen, southwestern Finland (for de-

tails see Jaakkola 1984, Turtola and Paajanen 1995) during autumn and spring runoff. Half of the samples were taken from drainflow and the other half from surface runoff. The samples represented water flow from the same drainage and surface runoff plots during consecutive time intervals. The samples were collected in polyethylene bottles washed with  $2.0 \text{ mol l}^{-1}$  hydrochloric acid, and stored in dark at  $4^\circ\text{C}$ . No preservative agent (e.g.  $\text{H}_2\text{SO}_4$ ) was added to the samples. The content of suspended solids in the water samples (residue of evaporation  $0.1\text{--}2.3 \text{ g l}^{-1}$ ) was typical for runoff of the particular clay soil.

## Measurement of total phosphorus

### Digestions

**HF digestion.** The HF digestion was modified from that developed for soil samples (Bowman 1988). Depending on the amount of suspended solids in the water sample, 100 to 400 ml of the unfiltered sample was slowly evaporated to dryness on a hot plate. Thereafter the procedure was identical to that for soil samples, with sequential additions of concentrated  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}_2$  and HF. The additions were followed by 10 min heating on a  $150^\circ\text{C}$  plate to eliminate excess peroxide, and by dilution of the sample with deionized water. After the digestion the extract was filtered through Nuclepore polycarbonate filter, pore size  $0.2 \text{ }\mu\text{m}$ , and analysed for orthophosphate as described below (Determination of orthophosphate).

**Peroxodisulphate digestion.** The unfiltered water samples were analysed for TP with five variations of the peroxodisulphate digestion, differing in respect of reagent concentrations and dilution of the sample (Table 1). Variations 1, 4 and 5 cor-

respond to the Finnish standard recommendation (SFS 1986b) for determination of TP with no sample dilution and dilution to 50% (twofold) and 25% (fourfold) of the original concentration, respectively. In variation 2 the concentration of sulphuric acid was higher, and in variation 3, in addition, the amount of peroxodisulphate was doubled. For the digestion, the other Scandinavian standards (NS 1984b, SS 1984b, DS 1985b) recommend the same amount of  $\text{K}_2\text{S}_2\text{O}_8$  as the Finnish standard (SFS 1986b) but slightly higher concentration of  $\text{H}_2\text{SO}_4$  ( $0.04$  vs  $0.033 \text{ mol l}^{-1}$  in variation 1). After addition of the reagents, the samples were digested in an autoclave for 30 min ( $120^\circ\text{C}$ ,  $100 \text{ kPa}$ ). The digested samples were filtered through Nuclepore polycarbonate  $0.2 \text{ }\mu\text{m}$  filters and analysed for orthophosphate as described below.

### Experiment

On the basis of a preliminary analysis, the water samples were divided into three classes according to the amount of suspended particles, and hence TP. The concentration of TP in the classes was  $< 0.2$  (low P),  $0.2\text{--}0.8$  (moderate P) and  $> 0.8 \text{ mg l}^{-1}$  (high P), and the respective mean residue of evaporation was  $0.20$ ,  $0.59$  and  $1.46 \text{ g l}^{-1}$  ( $n = 16$ ,  $19$  and  $7$ , respectively). To obtain a reliable estimate of the P, the unfiltered samples were analysed for TP with the HF digestion method. After that, the same samples were analysed with variations of the peroxodisulphate digestion method.

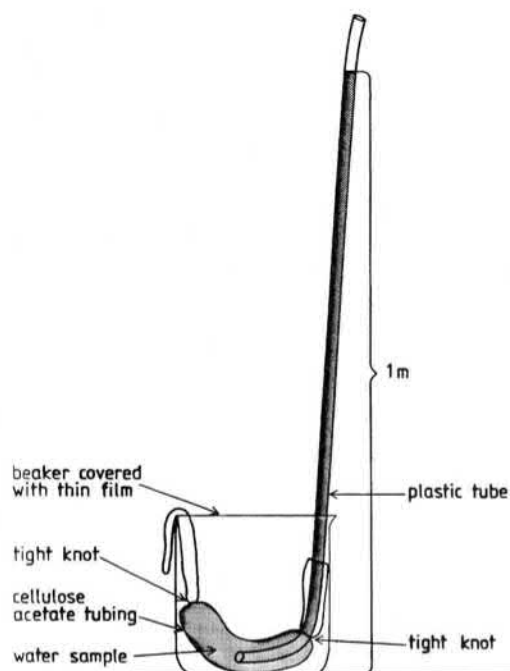
## Measurement of dissolved phosphorus

### Pretreatment for removing particles

**Cellulose acetate tubing.** Colloid-size particles were separated by filtering water samples through cellulose acetate dialysis tubing, pore size  $0.0024 \text{ }\mu\text{m}$  (T 0.0024). The sample ( $100 \text{ ml}$ ) was placed inside a piece of tubing, tied at one end with thread (Fig. 1). To enhance liquid transfer through the pores of the tubing, a 1-m hydrostatic pressure head was developed by tying a 1.3 m long plastic tube, filled with the sample, inside the other end of the tube and hanging the tube vertically (Fig. 1). The water sample was allowed to pass through the pores of the tubing for 20 hours. By that time the amount

**Table 1.** Amounts of water sample, deionized water used for dilution and digestion reagents in five variations of the peroxodisulphate digestion.

	Variation no.				
	1	2	3	4	5
Sample, ml	25	25	25	12.5	6.25
Deionized $\text{H}_2\text{O}$ , ml	0	0	0	12.5	18.75
$\text{K}_2\text{S}_2\text{O}_8$ , g	0.25	0.25	0.50	0.25	0.25
$\text{H}_2\text{SO}_4$ , $\text{mol l}^{-1}$	0.033	0.057	0.057	0.033	0.033



**Fig. 1.** Experimental system used to separate particulate and colloidal phosphorus from a water sample by cellulose acetate dialysis tubing, pore size  $0.0024\ \mu\text{m}$ .

of the filtrate was large enough (10–15 ml) for the  $\text{PO}_4\text{-P}$  analysis which followed immediately. To determine the release of orthophosphate from the tubing, the procedure was repeated with deionized water.

**Filtration.** Filtrations were done with Millipore vacuum glass filtration equipment. The filters were: (1) Nuclepore polycarbonate filter, pore size  $0.2\ \mu\text{m}$  (N 0.2), (2) Nuclepore polycarbonate filter,  $0.4\ \mu\text{m}$  (N 0.4), (3) Sartorius cellulose nitrate membrane filter, PFN phosphate free,  $0.45\ \mu\text{m}$  (PFN 0.45), (4) Sartorius cellulose nitrate membrane filter, ACN,  $0.45\ \mu\text{m}$  (ACN 0.45). The first 20 ml of filtrate was discarded, and filtration continued until the amount of filtrate was 40 ml. The filters were not washed before use but taken directly from the manufacturer's package. The filtration lasted 10–45 min per water sample, depending on the amount of particulate matter in the sample and the pore size of the filter. The filtration time tended to be longer with the Nuclepore than the Sartorius filters. The filtering procedure was repeated with deionized water. After filtration, the samples were analysed for  $\text{PO}_4\text{-P}$  and DP.

**Centrifugation.** Centrifugation was done with a Heraeus Varifuge K 4 500 centrifuge and 150 ml tubes (inside diameter 4.6 cm, height 11 cm). A volume of 130 ml of sample was measured into each of four tubes and centrifuged for 8 min with angular velocity of  $523.6\ \text{s}^{-1}$  (5 000 rpm) to remove particles larger than  $0.2\ \mu\text{m}$  (equivalent diameter) from the suspension (C 0.2). The appropriate centrifugation time was calculated according to the formula of Loveland and Whalley (1991) with an assumption that the density of the suspended particles was  $2.65\ \text{g cm}^{-3}$ . Immediately after the centrifugation, 20 ml of the sample was pipetted from each of the four tubes to form one 80-ml sample for the measurement of  $\text{PO}_4\text{-P}$  and DP. To avoid resuspension from the bottom of the centrifuge tube, the pipetting was done from 2 cm depth and care was taken not to mix the suspension.

### Determination of dissolved phosphorus

For determining the concentration of DP after the filtrations or centrifugation, the samples were digested with peroxodisulphate according to the standard method and analysed for orthophosphate as described below.

### Determination of orthophosphate

After the digestions for TP and pretreatments for DP and  $\text{PO}_4\text{-P}$  measurements, orthophosphate phosphorus was determined colorimetrically by the method of Murphy and Riley (1962), with ascorbic acid used as reducing agent. The analysis was performed with a Lachat Quick Chem autoanalyser. After addition of the reagents to the water sample the pH was about 1. The reaction time per sample before colour measurement was less than one minute.

### Experiments

To study the effect of the pretreatments on the  $\text{PO}_4\text{-P}$  and DP values, three experiments with different water samples were carried out: (1) Pretreatments T 0.0024 and N 0.2; mean residue of evaporation in the unfiltered water samples  $0.70\ \text{g l}^{-1}$ ;  $n = 14$ . (2) Pretreatments N 0.2, N 0.4, PFN 0.45



and C 0.2; mean residue of evaporation in the unfiltered water samples 0.29 g l<sup>-1</sup>, n = 40. (3) Pre-treatments N 0.2, PFN 0.45 and ACN 0.45; mean residue of evaporation in the unfiltered water samples 0.39 g l<sup>-1</sup>, n = 40.

Statistical analysis

Each data set was analysed as a repeated-measures design with one within-subject factor (method) or two within-subject factors (method, sampling time). In the latter case the analyses were based in the following mixed model:

$$y_{ijk} = \mu + s_i + M_j + e_{ij} + T_k + f_{ik} + MT_{jk} + g_{ijk}$$

where  $y_{ijk}$  is the response for the sample  $i$  on method  $j$  at sampling time  $k$ ,  $\mu$  is a constant,  $s$  is the random effect of the sample,  $M$ ,  $T$  and  $MT$  are the fixed effects of method, sampling time and their interaction, and  $e_{ij}$ ,  $f_{ik}$  and  $g_{ijk}$  are the interactions between the random sample effect  $s$  and the fixed effects  $M$ ,  $T$  and  $MT$ , respectively. In the case of one within-subject factor (method), the equation of the mixed model included only the four first terms.

The random variables  $s_i$ ,  $e_{ij}$ ,  $f_{ik}$  and  $g_{ijk}$  were assumed to be independent and normally distributed with zero means and constant variances. All models were fitted by using the residual maximum

likelihood (REML) estimation method. Moreover, 95% t-type confidence intervals (95% CI) were calculated for the differences between the means of the different analytical methods (SAS Institute Inc. 1996). If zero is included in a calculated confidence interval, the difference is not statistically significant at 5% risk level. The confidence intervals were preferred to p values since, in addition to the statistical test result, they provide information about the accuracy of the data. The analyses were performed by means of the SAS/MIXED software (SAS Institute Inc. 1996).

Results and discussion

Total phosphorus (TP)

The TP values obtained with the HF digestion were taken as a reference for the values obtained with the other methods. For soil samples, the HF method gives almost the same amounts of P as the Na<sub>2</sub>CO<sub>3</sub> fusion method (Bowman 1988), which is considered a reliable method for determining total phosphorus in soils (Syers *et al.* 1968). In general, the TP values obtained with HF digestion were the highest, while the values obtained with peroxodisulphate digestion increased in the order of the number of the variation (Table 2). For all samples, the values

**Table 2.** Total phosphorus (TP), mg l<sup>-1</sup>, determined with variations of peroxodisulphate digestion (Table 1), and with HF digestion, in water samples with low (n = 16), moderate (n = 19) and high (n = 7) concentration of P. Confidence intervals (95% CI) refer to the differences (diff.) listed, which were obtained by subtracting the TP value of the previous variation on the left from the TP value in the column in question.

		Variation no.					HF digestion	SEM <sup>a</sup>
		1	2	3	4	5		
LOW P								
TP, mg l <sup>-1</sup>	0.130		0.132	0.133	0.142	0.142	0.012	
Diff., mg l <sup>-1</sup>			0.002	0.001	0.009	0.000		
95% CI			-0.006, 0.009	-0.006, 0.008	0.002, 0.017	-0.008, 0.007		
MODERATE P								
TP, mg l <sup>-1</sup>	0.401	0.414	0.420	0.421	0.438	0.469	0.035	
Diff., mg l <sup>-1</sup>		0.013	0.006	0.001	0.017	0.031		
95% CI		0.001, 0.024	-0.006, 0.018	-0.011, 0.013	0.004, 0.029	0.019, 0.044		
HIGH P								
TP, mg l <sup>-1</sup>	0.979	1.094	1.130	1.138	1.219	1.368	0.143	
Diff., mg l <sup>-1</sup>		0.115	0.036	0.008	0.081	0.149		
95% CI		0.022, 0.208	-0.057, 0.129	-0.085, 0.101	-0.012, 0.174	0.056, 0.242		

<sup>a</sup> Standard error of means

obtained were significantly higher with the HF digestion than with the recommended peroxodisulphate digestion (variation 1 for low and moderate P samples, variation 4 for high P samples).

In peroxodisulphate digestion, the amount of  $\text{H}_2\text{SO}_4$  relative to the amount of particulate material was critical for the release of P from particulate material. This is evident from the higher values obtained with variation 2 than with variation 1 in moderate and high P samples (Table 2). Probably the amount of  $\text{H}_2\text{SO}_4$  was most critical for the release of inorganic particulate phosphorus. The  $\text{H}_2\text{SO}_4$  concentration recommended by the U.S. Environmental Protection Agency (EPA 1971) is considerably higher ( $0.11 \text{ mol l}^{-1}$ ) than that recommended by the Finnish standard (SFS 1986b) ( $0.033 \text{ mol l}^{-1}$ ) or the other Scandinavian standards (NS 1984b, SS 1984b, DS 1985b) ( $0.04 \text{ mol l}^{-1}$ ).

The higher concentration of  $\text{K}_2\text{S}_2\text{O}_8$  in variation 3 than in variation 2 did not cause statistically significant increases in the TP results (Table 2). In high P samples, however, the 95% CI indicates that the data are not sufficiently accurate to show whether there is a difference that is of practical importance.

Differences between variations 3 and 4 (two-fold dilution of the sample in variation 4) were small in all samples (Table 2). Since the amount of  $\text{H}_2\text{SO}_4$  relative to the amount of P was about the same in both variations, the result indicates that again the effect of dilution was determined by the amount of acid relative to the mass of the particulate material.

According to the standard for the determination of TP (NS 1984b, SS 1984b, DS 1985b, SFS 1986b), only samples containing P in excess of  $0.8 \text{ mg l}^{-1}$  should be diluted before the analysis. The present study shows, however, that dilution would also improve the results below this limit. For complete extraction of P, moreover, a very large dilution ratio is necessary, as even the low P samples required fourfold dilution before P was completely released from the particulate material (Table 2).

O'Connor and Syers (1975) found that, compared with  $\text{Na}_2\text{CO}_3$  fusion, peroxodisulphate digestion gave fairly good TP result, when concentrations of PP were low and suspended particles were smaller than  $2 \mu\text{m}$ . However, the peroxodisulphate method gave only low recovery of P for samples with high content of particulate matter

and particles larger than  $0.2 \mu\text{m}$ . According to O'Connor and Syers (1975), the reason for this was the incomplete extraction of P occluded within hydrous oxides of iron, and they concluded that peroxodisulphate digestion cannot be recommended for the determination of P in waters containing particulate inorganic materials of soil origin. Logan *et al.* (1979) observed that peroxodisulphate digestion extracted 17–20% less P than was recovered by perchloric acid digestion (Sommers and Nelson 1972).

### Dissolved orthophosphate phosphorus ( $\text{PO}_4\text{-P}$ )

To obtain  $\text{PO}_4\text{-P}$  values unaffected by all disturbance of colloids, a set of samples was filtered through cellulose acetate tubing before the analysis (Table 3). The mean orthophosphate P concentration of deionized water which similarly passed through the tubing ( $0.005 \text{ mg l}^{-1}$ ,  $n = 5$ ) was subtracted from the result.

Even after the filtering through cellulose acetate tubing, the  $\text{PO}_4\text{-P}$  result may have been too high, due to the hydrolysis of dissolved organic phosphorus during the analysis. Nevertheless, according to Van Eck (1982), hydrolysis during analysis has only a minor effect on the  $\text{PO}_4\text{-P}$  values in natural waters, owing to the small amount of dissolved hydrolysable organic P. In the present experiment the amount of liquid after filtering through the tubing was too small for reliable analysis of DP, and hence for the estimation of dissolved organic P.

Although the number of samples analysed was small, the result suggests that Nuclepore  $0.2 \mu\text{m}$  filtrates slightly overestimate the concentration of orthophosphate.

**Table 3.** Dissolved orthophosphate phosphorus ( $\text{PO}_4\text{-P}$ ),  $\text{mg l}^{-1}$ , determined after filtering through dialysis tubing ( $0.0024 \mu\text{m}$ ) and Nuclepore polycarbonate filter ( $0.2 \mu\text{m}$ ). Confidence interval (95% CI) refers to the difference (diff.) between the results of different filtrates.  $n = 14$ .

	Tubing	Nuclepore	SEM <sup>a</sup>
$\text{PO}_4\text{-P}$ , $\text{mg l}^{-1}$	0.050	0.056	0.010
Diff., $\text{mg l}^{-1}$		0.006	
95% CI		0.002, 0.010	

<sup>a</sup> Standard error of means

The PO<sub>4</sub>-P values obtained with the Nuclepore 0.2 µm and Nuclepore 0.4 µm filters were the same, but those obtained with the Sartorius PFN 0.45 µm filters were slightly higher (Tables 4 and 5). However, the difference was not statistically significant. The difference might have been due to phos-

phate release from the Sartorius PFN filters, indicated by the orthophosphate value in Sartorius PFN filtrates of deionized water (Table 6).

The PO<sub>4</sub>-P values obtained with Sartorius ACN 0.45 µm filters were significantly higher than those obtained with Nuclepore 0.2 µm filters (Table 5).

**Table 4.** Dissolved orthophosphate (PO<sub>4</sub>-P) and dissolved phosphorus (DP), mg l<sup>-1</sup>, determined after filtration through Nuclepore 0.2 µm (N 0.2), Nuclepore 0.4 µm (N 0.4), Sartorius PFN 0.45 µm (PFN 0.45) filters and after centrifugation (C 0.2). Confidence intervals (95% CI) refer to the differences (diff.) listed, which were obtained by subtracting the N 0.2 result from the result in the column in question. n = 40.

	N 0.2	N 0.4	PFN 0.45	C 0.2	SEM <sup>a</sup>	No pretreatment
PO <sub>4</sub> -P, mg l <sup>-1</sup>	0.022	0.022	0.024	0.034	0.001	
Diff., mg l <sup>-1</sup>		0.000	0.002	0.012		
95% CI		- 0.002, 0.002	- 0.0001, 0.004	0.010, 0.014		
DP, mg l <sup>-1</sup>	0.029	0.029	0.041	0.082	0.003	0.205 <sup>b</sup>
Diff., mg l <sup>-1</sup>		0.000	0.012	0.053		
95% CI		- 0.007, 0.007	0.005, 0.019	0.043, 0.063		

<sup>a</sup>Standard error of means

<sup>b</sup>Total phosphorus (TP)

**Table 5.** Dissolved orthophosphate (PO<sub>4</sub>-P) and dissolved phosphorus (DP), mg l<sup>-1</sup>, determined after filtration through Nuclepore 0.2 µm (N 0.2), Sartorius PFN 0.45 µm (PFN 0.45) and Sartorius ACN 0.45 µm (ACN 0.45) filters. Confidence intervals (95% CI) refer to the differences (diff.) listed, which were obtained by subtracting the N 0.2 result from the result in the column in question. n = 40.

	N 0.2	PFN 0.45	ACN 0.45	SEM <sup>a</sup>	No pretreatment
PO <sub>4</sub> -P, mg l <sup>-1</sup>	0.030	0.032	0.048	0.001	
Diff., mg l <sup>-1</sup>		0.002	0.018		
95% CI		0.000, 0.005	0.016, 0.021		
DP, mg l <sup>-1</sup>	0.036	0.040	0.091	0.003	0.376 <sup>b</sup>
Diff., mg l <sup>-1</sup>		0.004	0.055		
95% CI		- 0.005, 0.013	0.046, 0.064		

<sup>a</sup>Standard error of means

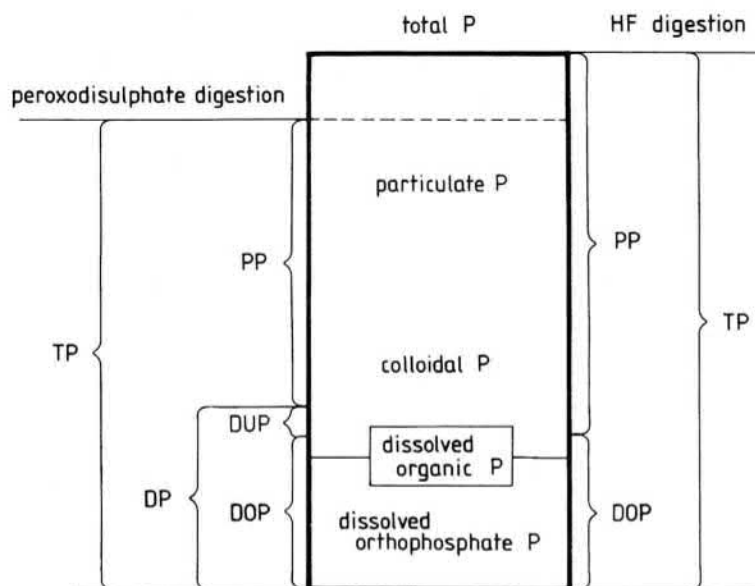
<sup>b</sup>Total phosphorus (TP)

**Table 6.** Dissolved orthophosphate (PO<sub>4</sub>-P) and dissolved phosphorus (DP), mg l<sup>-1</sup>, determined in deionized water after filtration through Nuclepore 0.2 µm (N 0.2), Sartorius PFN 0.45 µm (PFN 0.45) and Sartorius ACN 0.45 µm (ACN 0.45) filters. Confidence intervals (95% CI) refer to the differences (diff.) listed, which were obtained by subtracting the N 0.2 result from the result in the column in question. n = 10.

	N 0.2	PFN 0.45	ACN 0.45	SEM <sup>a</sup>
PO <sub>4</sub> -P, mg l <sup>-1</sup>	0.000	0.002	0.006	0.001
Diff., mg l <sup>-1</sup>		0.002	0.006	
95% CI		- 0.0002, 0.004	0.004, 0.007	
DP, mg l <sup>-1</sup>	0.001	0.000	0.024	0.001
Diff., mg l <sup>-1</sup>		- 0.001	0.023	
95% CI		- 0.005, 0.002	0.019, 0.026	

<sup>a</sup>Standard error of means

SFS 3026



**Fig. 2.** Definition of the various fractions of phosphorus in water according to the Finnish standard SFS 3026 (1986b) (on the left) and modified according to suggestions in this study (on the right).

Bloesch and Gavrieli (1984) observed that Sartorius cellulose nitrate ACN filters released small amounts of phosphate to the filtrate. In the present experiment, the higher  $\text{PO}_4\text{-P}$  value in the Sartorius ACN 0.45  $\mu\text{m}$  filtrates was only partly due to orthophosphate release from the filters, as is evident in the value for orthophosphate after filtering of deionized water (Table 6). The higher value was probably attributable in part to the release of orthophosphate from colloidal P passing through the ACN filters. The presence of more colloidal P in the ACN than in the Nuclepore 0.2  $\mu\text{m}$  filtrates is indicated by the large statistically significant difference in DP results between the two filtrates (Table 5).

Rigler (1964) obtained higher values for  $\text{PO}_4\text{-P}$  with 0.45  $\mu\text{m}$  than with 0.1 and 0.22  $\mu\text{m}$  filters, and he attributed this to desorption of P associated with particles not retained on the 0.45  $\mu\text{m}$  filters. However, the absolute amount of this P was small. In runoff waters from an area dominated by clay soils, Pietiläinen and Rekolainen (1991) observed higher  $\text{PO}_4\text{-P}$  values when Millipore membrane HA (0.45  $\mu\text{m}$ ) filters were used instead of Nuclepore 0.4  $\mu\text{m}$  filters. According to Stainton (1980), the overestimation of orthophosphate due to release of P from colloids will be greater for waters containing a small amount of orthophosphate and large amount of colloidal P, as in the samples used

in the present study.

$\text{PO}_4\text{-P}$  values were higher after centrifugation than in the filtrates (Table 4). After the centrifugation, there was more colloidal P in the samples, as the differences between the DP and  $\text{PO}_4\text{-P}$  results indicate (Table 4). In part, this may have been due to incomplete separation of the larger than 0.2  $\mu\text{m}$  particles during the centrifugation. The possible sources of errors arising from the centrifugation are briefly discussed by Broberg and Persson (1988). However, a more probable explanation of the higher value is that, due to clogging, the filters removed smaller particles from the suspension than would be suggested merely by their pore size. The clogging was especially apparent with the most turbid samples.

The difference between DP and  $\text{PO}_4\text{-P}$  in the Nuclepore and Sartorius PFN filtrates was 0.006–0.017  $\text{mg l}^{-1}$  (Tables 4 and 5). This P fraction, which is mainly colloidal inorganic P (Rigler 1973, Broberg and Persson 1988), and not directly available to algae (Ekholm 1994), is operationally defined as dissolved unreactive P (Broberg and Persson 1988) (DUP, Fig. 2). The characterization is inappropriate, however, since the amount of colloidal P in the filtrate varies with the filter. The same inexactness holds for the use of DP for monitoring purposes.

## Particulate phosphorus (PP)

The concentration of PP is often calculated as the difference between TP values measured in unfiltered water and in the filtrate (TP-DP, see Fig. 2 on the left). However, this leads to underestimation of PP, especially when filters like Sartorius ACN 0.45  $\mu\text{m}$  are used, which may allow a relatively large amount of colloidal P to pass to the filtrate. In this experiment (Table 5), the underestimation, relative to calculation based on the results of Nuclepore 0.2  $\mu\text{m}$  filtrates, would be 16%. An alternative and less laborious way to estimate PP might be to calculate the difference between TP in unfiltered water and  $\text{PO}_4\text{-P}$  in the filtrate (TP- $\text{PO}_4\text{-P}$ , see Fig. 2 on the right). This would have the effect of including most of the colloidal P with PP. In this case the true amount of PP might be overestimated, since dissolved organic P would be considered as particulate. In the present experiments the overestimation would be negligible.

Indirect determination of PP causes errors in TP determination to affect the PP values. Peroxodisulphate digestion gives too low concentrations of TP, especially in water samples with high amounts of suspended material. Runoff waters tend to be most turbid during peak flows in autumn and spring, and these peak flows will often be decisive for the annual P loss from agricultural land to watercourses. In the clay soil field of this study, TP concentration in autumn and spring flow often exceeds 0.5  $\text{mg l}^{-1}$ . On the basis of the results of peroxodisulphate digestion presented in Table 2, the P load may be underestimated by as much as 10–20%.

## Conclusions

Determinations of different phosphorus fractions in water samples containing suspended soil particles are prone to inaccuracies. The concentration of total phosphorus may be underestimated owing to the incomplete extraction of phosphorus from suspended particles. On the other hand, the release of phosphorus from colloidal material may lead to an overestimation of the true amount of dissolved orthophosphate. The following conclusions can be drawn:

1. The peroxodisulphate digestion does not ex-

tract all phosphorus from water samples if they contain appreciable amounts of soil material. This may result in too low estimates of the total and particulate phosphorus losses. Increasing the concentration of sulphuric acid or diluting the sample before digestion will improve the result.

2. Because the fraction of dissolved phosphorus contains variable amounts of colloidal phosphorus, depending on the filter, measurement of this fraction cannot be recommended. The colloidal phosphorus should rather be completely included into the particulate phosphorus fraction.
3. The pore size of filters for dissolved orthophosphate measurement should be as small as possible. Sartorius ACN 0.45  $\mu\text{m}$  filters are not suitable for orthophosphate determination due to impurities in the filter and insufficient restraining of the suspended particles. For later reference, the filtering procedure should be precisely reported.

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## EFFECT OF STORAGE AND SULPHURIC ACID ADDITION ON ANALYTICAL RESULTS OF NITROGEN AND PHOSPHORUS IN WATER SAMPLES CONTAINING ERODED MATERIAL

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Drainage and surface water samples containing eroded material were analyzed for total nitrogen, nitrate nitrogen, ammonium nitrogen, total phosphorus and soluble phosphate phosphorus contents. Effect of storage was examined by analyzing the water samples immediately after sampling and after storing them for two and twelve weeks at +4 °C. The influence of sulphuric acid addition and filtering immediately after sampling were also studied. The analytical results for total nitrogen and ammonium nitrogen changed most during storage. Total phosphorus and soluble phosphate phosphorus results changed insignificantly in two weeks, and the addition of acid could not maintain original concentrations any better. The results show that in case of phosphate filtering before acid addition is necessary. The smallest changes in phosphate concentrations during storage were observed, however, in samples without any pretreatment.

Index words: water analyses, total nitrogen, nitrate nitrogen, ammonium nitrogen, total phosphorus, soluble phosphate phosphorus, storage, acid addition.

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### INTRODUCTION

During a long sample storage period, microbiological and chemical reactions can remarkably influence the concentrations of nitrogen and phosphorus in water. Particularly, the analysis of ammonium nitrogen and soluble phosphate phosphorus is recommended immediately after water sampling (Nat. Board of Waters 1984). During storage, the presence of a large amount of eroded material in the water can also influence sorption processes and thus also nutrient concentrations. For practical reasons, however, immediate analysis of samples are sometimes difficult to carry out.

The primary aim of this work was to find out the magnitude of changes, that occur in nitrogen and phosphorus concentrations during the storage of water samples containing eroded material. Further, the ability of sulphuric acid addition to prevent such

changes was studied. Sulphuric acid addition is recommended for preservation of phosphorus if samples cannot be analyzed immediately (Nat. Board of Waters 1984, Anon. 1986b). Also the possibility to prevent changes from taking place in soluble phosphate phosphorus results by means of immediate filtering and sulphuric acid addition was studied. Filtering was used to diminish the effect of eroded material on the changes in water quality following acid addition. Such a procedure is recommended for soluble phosphate, if samples cannot be analyzed immediately (Anon. 1986a). Herve and Kauppi (1986) noticed that in immediate analyses the results of soluble phosphate phosphorus were higher without filtration than if filtration was used, but they didn't examine the effect of acid addition on phosphate concentrations during storage.

## MATERIALS AND METHODS

Drainage and surface runoff water samples were collected in April–May 1985 and September–October 1987. Sampling was carried out twelve times in all, and the total number of water samples was 124, half of them being drainage waters and the other half surface runoff ones. In 1985, water samples were taken every second day and in 1987 at slightly longer intervals. Samples were collected into polyethylene bottles washed with hydrochloric acid ( $1.5 \text{ mol l}^{-1}$ ) and deionized water. Particularly, in surface runoff water samples the content of eroded material was high, and the residual of evaporation varied from 0.10 to  $1.25 \text{ g l}^{-1}$ .

During sampling a particular water sample was collected in at least three bottles, and one of these was taken for immediate analysis. The other samples were stored before analyses for two and twelve weeks in darkness at a temperature of  $+4^\circ\text{C}$ . The concentrations of total nitrogen and total phosphorus were analyzed in unfiltered water samples. For the other determinations, samples were filtered before analysis through a membrane filter (pore size  $0.45 \mu\text{m}$ ). The effect of sulphuric acid addition was studied by adding sulphuric acid to unfiltered water samples, and to water samples which had been filtered through a membrane filter (pore size  $0.45 \mu\text{m}$ ). The amount of acid added was  $1 \text{ ml } 4 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4/100 \text{ ml}$  of sample.

Total nitrogen was analyzed by oxidizing inorganic and organic nitrogen compounds to nitrate in alkaline solution. The oxidation was done by potassium peroxodisulphate under pressure ( $200 \text{ kPa}$ ,  $120^\circ\text{C}$ ) for 0.5 h. The analyses were done according to Finnish recommendation for the standard method of total nitrogen (Anon. 1975a). After oxidation nitrate nitrogen was analyzed by AKEA auto-analyzer (manufacturer Dtex, Finland).

Nitrate nitrogen was reduced in copper-cadmium column into nitrite and measured colorimetrically ( $\lambda = 520 \text{ nm}$ ) by using sulfanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride as reagents. Nitrite reacts in very acid solution ( $\text{pH } 1.5-2$ ) with sulfanilamide and forms a diazo compound which with N-(1-naphthyl)-ethylenediamine forms an azo colour compound. Nitrate nitrogen was analyzed according to Finnish recommendation for the standard method of nitrate nitrogen (Anon. 1975b).

Ammonium nitrogen, total phosphorus and soluble phosphate phosphorus were analyzed according to the standard methods SFS 3032 (Anon. 1976), SFS 3026 (Anon. 1986b) and SFS 3025 (Anon. 1986a). The analyses were carried out by AKEA autoanalyzer.

Ammonium nitrogen was analyzed colorimetrically ( $\lambda = 630 \text{ nm}$ ) at a temperature of  $60^\circ\text{C}$ . In a slightly alkaline solution ( $\text{pH } 10.8-11.4$ ) together with hypochloride ammonium ion forms monochloramine, which in the presence of phenol and additional hypochloride forms indophenol blue. Pentacyanonitrosylferrate is used as a catalyzer.

In total phosphorus analyses, inorganic phosphate complex compounds and organic phosphorus compounds were converted into orthophosphates by oxidizing with peroxodisulphate in acid solution. Oxidation was done under pressure ( $200 \text{ kPa}$ ,  $120^\circ\text{C}$ ) for 0.5 h.

Orthophosphate forms with molybdate and antimony (valence +3) antimony-12-phosphorus molybdenum acid in  $0.2 \text{ mol l}^{-1}$  sulphuric acid solution. Ascorbic acid reduces it into blue colloidal complex compound, the absorbance of which is measured ( $\lambda = 880 \text{ nm}$ ).

Analysis of variance and Tukey's test (Honestly Significant Difference) were used to find statistically significant differences between group means (Steel and Torrie 1960, pp. 109–110, 132–139).

## RESULTS

### Effect of storage

After storing the water samples for two weeks, the results for total nitrogen analyses increased 10 % and those for nitrate nitrogen about 4 % (Tables 1 and 2). These changes were not statistically significant, however. The results for total phosphorus and soluble phosphate phosphorus did not change during two weeks' storage. After twelve weeks the concentrations of total nitrogen and nitrate nitrogen had increased 13 % and 12 % respectively, and the concentrations of total phosphorus and soluble phosphate phosphorus had decreased 6 % and 3 % (Table 2). The changes were statistically significant for nitrate at a risk level of 5 % and for total phosphorus at a risk level of 0.1 %. The amount of ammonium nitrogen had decreased statistically significantly (0.1 %) already after two weeks of storage (Tables 1 and 2).

### Effect of filtering and sulphuric acid addition

The addition of sulphuric acid into an unfiltered water sample decreased the results for total phosphorus statistically significantly (0.1 %) during two and twelve weeks of storage, and the concentrations of soluble phosphate increased statistically significantly (0.1 %) immediately after the acid addition

Table 1. Effect of storage on the analytical results for total nitrogen, nitrate nitrogen, ammonium nitrogen, total phosphorus and soluble phosphate phosphorus ( $\text{mg l}^{-1}$ ) in water samples. Storage periods 0 and 2 weeks.

Storage period, weeks	Number of samples	Total N	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$	Total P	$\text{H}_2\text{PO}_4\text{-P}$
0	117	3.2	2.8	0.20	0.32	0.048
2	117	3.5	2.9	0.16	0.31	0.049

Table 2. Effect of storage on the analytical results for total nitrogen, nitrate nitrogen, ammonium nitrogen, total phosphorus and soluble phosphate phosphorus ( $\text{mg l}^{-1}$ ) in water samples. Storage periods 0, 2 and 12 weeks.

Storage period, weeks	Number of samples	Total N	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$	Total P	$\text{H}_2\text{PO}_4\text{-P}$
0	59	3.1	2.6	0.22	0.32	0.036
2	59	3.4	2.7	0.15	0.32	0.035
12	59	3.5	2.9	0.12	0.30	0.035

Table 3. Effect of sulphuric acid addition on the analytical results for total nitrogen, total phosphorus and soluble phosphate phosphorus ( $\text{mg l}^{-1}$ ) in water samples. Storage periods 0, 2 and 12 weeks.

Storage periods, weeks	Addition of $\text{H}_2\text{SO}_4$	Number of samples	Total N	Number of samples	Total P	$\text{H}_2\text{PO}_4\text{-P}$
0	no	27	3.4	32	0.33	0.032
0	yes	27	3.5	32	0.33	0.111
2	no	27	3.2	32	0.32	0.034
2	yes	27	3.3	32	0.29	0.150
12	no	27	3.5	32	0.32	0.034
12	yes			32	0.28	0.159

Table 4. Effect of filtering and sulphuric acid addition on the analytical results for soluble phosphate phosphorus ( $\text{mg l}^{-1}$ ). Storage periods 0 and 2 weeks.

Storage periods, weeks	Filtering before storage	Addition of $\text{H}_2\text{SO}_4$	Number of samples	$\text{H}_2\text{PO}_4\text{-P}$
0	no	no	20	0.030
2	no	no	20	0.027
2	yes	yes	20	0.053

(Table 3). Acid addition did not influence statistically significantly the concentrations of total nitrogen. After filtering, sulphuric acid addition and two weeks of storage, the concentrations of phosphate phosphorus were statistically significantly (0.1 %) higher than the original results (Table 4).

## DISCUSSION

Delay in the analysis of water samples containing eroded material had the greatest influence on total

nitrogen and ammonium nitrogen concentrations. Particularly, ammonium concentrations decreased during storage very much. The reason might be the nitrification of ammonium to nitrate by bacteria. Thus the storage of runoff water samples would result in underestimation of ammonium nitrogen leaching. This implies that ammonium nitrogen should always be analyzed immediately after sampling in case of runoff samples.

Also total nitrogen should be analyzed as soon as possible. During a long storage period the concentrations of total nitrogen can increase, e.g. due to ammonia penetration through the plastic bottle wall

and solution of ammonia in a slightly acid water. The concentrations of nitrate nitrogen, total phosphorus and soluble phosphate phosphorus changed insignificantly during two weeks' storage. The results show that storage for twelve weeks is not advisable for any nitrogen and phosphorus determinations.

The addition of sulphuric acid into the water samples containing eroded material seemed unnecessary in total phosphorus determinations. If acid is added into unfiltered water samples, it can considerably increase the analytical results for soluble phosphate phosphorus. This is probably due to the desorption of phosphate from the adsorption surfaces of eroded soil material in acid solution. However, filtering before the acid addition could not maintain the original phosphate concentrations either. Obviously, filtering was not effective for removing all of the phosphate adsorbing material from the water samples. The smallest changes in phosphate phosphorus concentrations were observed in samples without any pretreatment.

## TIIVISTELMÄ

Vesinäytteet on suositeltu analysoitavaksi välittömästi näytteenoton jälkeen, sillä pitkän säilytyksen aikana veden laadussa saattaa tapahtua muutoksia mikrobiologisten ja kemiallisten reaktioiden seurauksena. Vesinäytteen suuri eroosioaineksen määrä voi vaikuttaa huomattavasti sorptioprosesseihin.

Tämän tutkimuksen tavoitteena oli selvittää, kuinka suuria muutoksia ravinnepitoisuuksissa tapahtuu säilytyksen aikana. Lisäksi tutkittiin, voidaanko näitä muutoksia ehkäistä kestäväimällä näyte rikkihapolla. Vesinäytteiden rikkihappokestävävointia suositellaan kokonaisfosforin ja liuenneen fosfaattifosforin määrittämisessä, jos näytettä ei voida analysoida välittömästi.

Tutkittavia vesinäytteitä otettiin keväällä 1985 ja syksyllä 1987 yhteensä 124 kpl, joista puolet oli salaojavesiä ja puolet pintavesiä. Näytteet olivat peräisin savimaan huuhtoutumiskentältä Jokioisista. Etenkin pintavesinäytteet sisälsivät runsaasti eroosioainesta.

Tutkituissa vesinäytteissä typpi yhdisteiden pitoisuudet muuttuivat säilytyksen kuluessa enemmän kuin fosforin määrittä tulokset.

Kahden viikon säilytyksen jälkeen ammonium-

tyypin määrittä tulokset olivat pienentyneet huomattavasti alkuperäisestä. Tähän oli luultavasti syynä ammoniumin nitrifikaatio nitraatiksi. Ammonium- tulokset muuttuivat säilytyksen kuluessa niin paljon, että ammonium tulisin määrittää välittömästi näytteenoton jälkeen. Kokonaistyyppitulokset kasvoivat kahden viikon säilytyksen aikana 10 % ja nitraattitulokset 4 %. Kokonaistypen lisääntymisen syynä saattoi osittain olla ammoniumin tunkeutuminen muovipullon seinämän läpi ja liukeneminen lievästi happamaan näyteveteen. Nitraattityypimäärä kasvoi ilmeisesti ammoniumin nitrifikaation seurauksena.

Muutokset kokonaisfosforin ja liuenneen fosfaattifosforin määrittä tuloksissa olivat säilytyksen kuluessa hyvin pieniä eikä rikkihappokestävävointi parantanut pitoisuuksien säilymistä. Kun rikkihappo lisättiin suodattamattomaan eroosioainesta sisältävään veteen, fosfaattifosforin tulokset vääristyivät fosfaatin liuetessa adsorptiopinnoilta näyteveden pH:n alentumisen seurauksena. Suodatuskaan ei pystynyt täysin poistamaan tästä aiheutuvaa virhettä. Parhaiten fosfaattifosfori säilyi ilman kestävointia.

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# Influence of improved subsurface drainage on phosphorus losses and nitrogen leaching from a heavy clay soil

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## Abstract

Without proper subsurface drainage of heavy clay soil, water logging due to low hydraulic conductivity of the surface soil and especially the subsoil will lead to abundant surface runoff. The abundant runoff will induce soil erosion and phosphorus losses. To determine the influence of improved subsurface drainage (IMP) on soil erosion, phosphorus losses and nitrogen leaching, a heavy clay soil with a 29 year old subdrainage system was fitted with new drains, with topsoil or wood chips used as backfill in the drain trenches. Before IMP, drainage water constituted only 10–40% of the total runoff (drainage + surface runoff) but after IMP 50–90%. Where topsoil was used as backfill, the estimated soil erosion and particulate P and dissolved orthophosphate P losses from ploughed soil during winter were lower after IMP than before (1168 vs. 1408 kg ha<sup>-1</sup>, 0.58 vs. 0.69 kg ha<sup>-1</sup>, 0.09 vs. 0.12 kg ha<sup>-1</sup>, respectively). Where wood chips were used as backfill, soil erosion and particulate P losses were not reduced. Owing to the increased drainage discharge, nitrogen leaching during barley cultivation was much higher after IMP (14 vs. 7 kg ha<sup>-1</sup>a<sup>-1</sup>).

**Keywords:** Subsurface drainage; Leaching; Erosion; Particulate phosphorus; Dissolved phosphorus; Nitrogen

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## 1. Introduction

Problems of water logging and heavy surface runoff are endemic to the heavy clay soils of southwest Finland owing to low water conductivity of the clay layers. In dry clay soil, water tends to pass quickly through cracks and macropores as preferential flow (Talsma and Van der Lelij, 1976, German and Bewen, 1981), but after wetting, and swelling and

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closure of the cracks, the infiltration slows dramatically (Bouma and Wösten, 1979). Moreover, during snowmelt, the macropores of frozen soil may be blocked by ice, reducing water conductivity and water percolation (Bottcher et al., 1981). As a result of low conductivity in topsoil and especially in subsoil, snowmelt and rainwater are easily channelled to surface runoff, particularly on sloping fields.

The route of the runoff water, whether along the surface or through the soil to a subsurface drainage system, would be expected to influence phosphorus and nitrogen leaching from the field. On clay soils, surface runoff induces erosion of soil aggregates and clay particles by mechanical action (Bottcher et al., 1980), while the smallest particles may also become suspended through diffusion. Suspended particles carry phosphorus bonded to iron, aluminium and calcium. Phosphorus fertilizer applied to the surface soil gradually tends to saturate the fixing sites at the surface and locally to raise the concentration of dissolved P in the soil solution (Biggar and Corey, 1969). During runoff, water presumably interacts with a thin layer of surface soil and the concentration of dissolved phosphorus in this layer approaches a maximum value, which is a function of desorbable phosphorus in the soil, the water-to-soil ratio and contact time (Sharpley, 1981; Yli-Halla et al., 1995). In the case of deep infiltration, however, the slow movement of water through the subsoil, where the equilibrium concentration tends to be lower, may allow sorption of dissolved P from the percolating waters (Sharpley and Syers, 1979).

By contrast, nitrate nitrogen, which is highly soluble, is easily carried downward by water infiltrating the soil. If not taken up by plant roots or soil microbes, nitrate ions will progressively move downwards, eventually to drainage and ground water. Little nitrate will be left at the surface to be carried away with surface runoff (Biggar and Corey, 1969; Schwab et al., 1985).

Since 1950, 80% of clay soils in southern Finland have been drained with subsurface drains placed at a depth of 1 m, to lower the ground-water level especially during sowing in spring and harvest-plowing in autumn. After 10–20 years of cultivation, however, many of the drains are no longer functioning well (Puustinen and Pehkonen, 1986). To determine the influence of subsurface drainage improvement on nutrient leaching, an experiment was conducted in 1987–1993 on a poorly drained, heavy clay soil in Jokioinen, southwest Finland. The objective of the study was to evaluate the effects of improved subsurface drainage on soil erosion, particulate and dissolved P losses, N leaching and the distribution of total runoff between surface runoff and subsurface drainage discharge.

## 2. Materials and methods

### 2.1. Soil properties of the experimental field

The texture of the soil on the experimental field was measured by pipette method (Elonen, 1971). The soil was classified as silty or heavy clay according to the Finnish classification (Table 1) and as cambisol according to the FAO classification. The mean content of organic carbon (Table 2) was determined by the wet combustion method. The soil was poor in plant available phosphorus, as reflected by the measurements of acid ammonium acetate (AAAc, pH 4.65) soluble P (Vuorinen and Mäkitie, 1955) (Table 2).



Table 1

Particle size fractions (%) of the soil of the drainage field with the range in parenthesis

Depth (cm)	Particle size fractions (%)		
	< 0.002 (mm)	0.002–0.02 (mm)	> 0.02 (mm)
0–20	61 (43–79)	16 (9–21)	23
20–40	83 (62–93)	8 (3–6)	9
40–80	90 (73–94)	6 (2–14)	4

Table 2

Soil properties of the drainage field. Values in parenthesis indicate the range

Depth (cm)	pH (water)	Org. C (%)	Tot. N (%)	P (AAAc; mg l <sup>-1</sup> )
0–25	5.8 (5.6–6.1)	2.6 (1.9–3.2)	0.19 (0.12–0.39)	3.2 (2.4–5.3)
25–60	6.3 (5.9–6.6)	0.6 (0.4–0.9)	0.05 (0.04–0.06)	0.4 (0.1–0.8)
60–90	6.7 (6.2–6.9)	0.5 (0.3–0.6)	0.04 (0.02–0.06)	0.3 (0.2–0.5)

Table 3

Saturated water conductivity (K, cm h<sup>-1</sup>) and volume of macropores (Vm, %) of the drainage field. Values in parenthesis indicate the range

Depth (cm)	K (cm h <sup>-1</sup> )	Vm (%)	
		30–300 $\mu$ m	> 300 $\mu$ m
0–20	62 (0.1–252)	2.6 (1.5–6.2)	5.8 (2.6–11.1)
20–35	0.63 (0–17)	1.1 (0.1–2.0)	0.4 (0.0–0.6)
35–60	0.0046 (0.0001–0.0400)	0.4 (0.0–1.3)	0.0 (0.0–0.1)

The saturated water conductivity and the volume of macropores (Table 3) were measured in the laboratory in undisturbed soil profiles (diameter 15 cm), three replicates per drainage plot, by the method of Aura (1990). The profiles were taken before the subsurface drainage improvement, in autumn 1989. The mean water conductivity in the surface soil (62 cm h<sup>-1</sup>) was in the normal range for Finnish clay soils (50–200 cm h<sup>-1</sup>, Aura, 1990). The variation was wide, however, and very low K values were measured in some profiles (Table 3). The conductivity was slightly higher at the upper than the lower edge of the field, 66 vs. 58 cm h<sup>-1</sup>. Within a given profile it fell off sharply in the deeper layers. Actual K values during autumn and spring, after prolonged wetting, were probably smaller than the values reported in Table 3, for reasons given by Bouma and Wösten (1979).

## 2.2. Design of the subsurface drainage

Tile drainage pipes had been laid in the experimental field in 1962. The pipes had an inside diameter of 40 mm and were laid parallel, 16.5 m apart and at a depth of about 1 m. In autumn 1975, the drains were cut into 33 m lengths and connected to long plastic cross pipes. Thereby 16 plots were formed, each with two drains 33 m in length (Fig. 1) (Jaak-

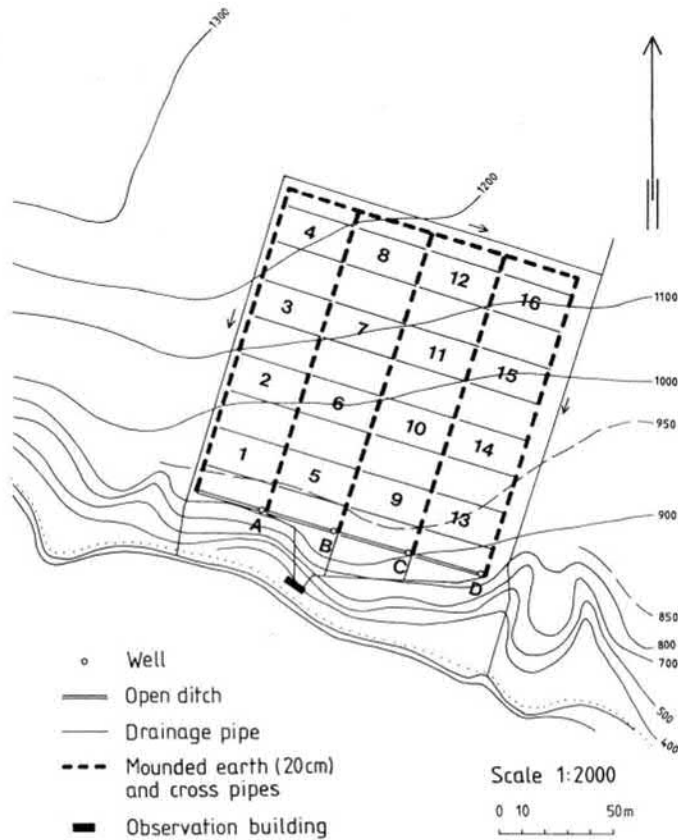


Fig. 1. Map of the drainage field.

kola, 1984). The size of each drainage plot was 0.11 ha. The plastic pipes carried the drainage water to an observation well where the volume was measured with tipping buckets. The flow-weighted water samples were collected with funnels conducting 0.1% of the total discharge to plastic containers. The surface runoff water, in turn, was collected from four long surface runoff areas (A–D), each consisting of four drainage plots, into an open ditch at the lower edge of the field. From there the water was conducted via wells for measurement and analysis.

After 29 years of cropping since installation of the subsurface drainage system, the drains had ceased to function well; surface runoff was abundant and crop yield reduced. To improve the drainage, new plastic drainage pipes were laid in summer 1991. The new pipes were laid at the same depth but 0.3 m from the old ones, and were connected to the same plastic cross pipes. To improve the water conductivity above the drains, the trenches were filled with a layer of gravel 15 cm thick, and additionally with five short, 40–60 cm thick gravel deposits per 33 m of drain. In the upper part of the field the trench above the gravel was

backfilled with topsoil. In the lower part, owing to poor surface soil structure and heavy rain occurring during the filling, wood chips were used instead of the topsoil.

### 2.3. Water analysis

The water samples were collected into polythene bottles washed with hydrochloric acid ( $1.5 \text{ mol l}^{-1}$ ) and deionized water, and stored in darkness at  $+4^\circ\text{C}$ . The samples were analysed for total solids (TS), total phosphorus (TP), dissolved orthophosphate phosphorus (DP), total nitrogen (TN) and nitrate nitrogen (NN). Total solids and the concentrations of TP and TN were measured in unfiltered water samples. Total solids were determined as evaporated residue after drying at  $105^\circ\text{C}$ , and used as a measurement of soil erosion. In TP analyses, inorganic phosphate complex compounds and organic phosphorus compounds were converted into orthophosphate by oxidizing with peroxodisulfate in acid solution. The oxidation was carried out under pressure (200 kPa,  $120^\circ\text{C}$ ) for 0.5 h. The concentration of orthophosphate was determined with an AKEA autoanalyser or, after 1991, with a Lachat Quick Chem autoanalyser, by the method of Murphy and Riley (1962). For DP analysis, the water was passed through a filter. Before 1992, the pore size of the filters was  $0.45 \mu\text{m}$  (Sartorius 11306-PFN), and after 1992 it was  $0.2 \mu\text{m}$  (Nucleopore 111106-PC). The orthophosphate concentration was then measured as described above. The amount of particulate phosphorus (PP) was calculated as the difference between TP and DP, including, thus, particle-bound as well as colloidal P. Determining PP as the difference between TP and DP might have led to an overestimation of PP, as dissolved organic P was attributed to PP. According to a TP analysis of the filtrate, however, the overestimation was only about 3%.

For the determination of TN, inorganic and organic nitrogen compounds were oxidized to nitrate in alkaline solution. The oxidation was carried out under pressure (200 kPa,  $120^\circ\text{C}$ ) for 0.5 h. The concentration of nitrate was determined by reducing the nitrate to nitrite in a copper-cadmium column according to the Finnish recommendation for the standard method for nitrate nitrogen. The determination was done with a SKALAR autoanalyser, and after 1991 with the Lachat Quick Chem autoanalyser. For NN analysis, the water was passed through a filter, as noted above for phosphorus, and the nitrate concentration was measured as just described.

### 2.4. Experimental system

To determine the effect of subsurface drainage improvement (IMP) on nutrient leaching, water discharge and nutrient concentrations in drainage water and surface runoff were compared using the paired *T*-test (comparison of sample means; meaningfully paired observation, Steel and Torrie, 1980). The comparison was made for winter periods preceding and following IMP, for plots under similar cropping and soil cover. The first test was done for the winter periods 1990–1991 (11 October 1990 to 21 May 1991) and 1991–1992 (17 September 1991 to 21 May 1992), when the soil on all four surface runoff areas (16 drainage plots) had been ploughed after barley cultivation in the preceding summer (Table 4). The winter of 1991–1992 was slightly more rainy (392 vs. 284 mm) and much warmer, resulting in thinner snow cover and less water in the snow at the beginning of the

Table 4

Cropping in preceding summer (in parenthesis) and soil cover in winter on surface runoff (A–D) and drainage plots (1–16) before and after the subsurface drainage improvement (IMP). Test 1 between winter periods 1990–1991 and 1991–1992, Test 2 between winter periods 1987–1988 and 1992–1993

	Surface drainage, plot			
	A 1–4	B 5–8	C 9–12	D 13–16
<i>Winter period</i>				
	(fallow)	(fallow)	(ryegrass)	(timothy)
1987–1988	ploughed	ploughed	ploughed	timothy (2)
	(fallow)	(barley)	(barley)	(timothy)
1988–1989	ploughed	ploughed	ploughed	timothy
	(fallow)	(fallow)	(ryegrass)	(timothy)
1989–1990	ploughed	ploughed	ploughed	ploughed
	(barley)	(barley)	(barley)	(barley)
1990–1991	ploughed (1)	ploughed (1)	ploughed (1)	ploughed (1)
<i>IMP</i>				
	(barley)	(barley)	(barley)	(barley)
1991–1992	ploughed (1)	ploughed (1)	ploughed (1)	ploughed (1)
	(timothy)	(timothy)	(timothy)	(timothy)
1992–1993	timothy	timothy	timothy	timothy (2)

main snowmelt (30 vs. 80 mm) and thus larger runoff on bare soil. Otherwise the winter periods were similar, with runoff ceasing in January–February.

The second test was done for the winter periods 1987–1988 (28 August 1987 to 5 May 1988) and 1992–1993 (2 September 1992 to 7 May 1993), when one surface runoff area (four drainage plots) was under grass ley sown the preceding spring. In winter 1987–1988 the grass was a mixture of timothy (*Phleum pratense*) and meadow fescue (*Festuca pratense*), whereas in 1992–1993 it was a mixture of timothy and red clover (*Trifolium pratense*). The second winter was less rainy (346 vs. 447 mm) but slightly warmer, resulting in more runoff on bare soil during winter and especially at the snowmelt in the spring.

### 3. Results and discussion

#### 3.1. Runoff

From 1975 onwards, the relative amount of subsurface drainage from the experimental field had been declining, until just before the subsurface drainage improvement (IMP) it was only about 20% of the total runoff (Table 5). The decline had been most marked in the lower part of the field, where most of the water was discharged to the open ditches either as lateral flow on the soil surface or in the upper more permeable zones. Most of the subsoil was almost impermeable (Table 3), and the negligible water movement to the drains was along cracks and old root channels situated near the trench (Fig. 2). As the macroporosity of the surface soil was only a few percent (Table 3), even a 5–10 mm rain was able to fill the pores, so that subsequent discharge was through surface runoff. Surface runoff was particularly heavy in spring during and just after snowmelt (Fig. 3).

Table 5

Precipitation, drainage water (D), surface runoff (S) and total runoff (T; mm) and loss of total solids (TS), particulate phosphorus (PP), dissolved orthophosphate phosphorus (DP), total nitrogen (TN) and nitrate nitrogen (NN; kg ha<sup>-1</sup>) in 1987–1993

	Surface drainage, plot											
	A 1–4			B 5–8			C 9–12			D 13–16		
	D	S	T	D	S	T	D	S	T	D	S	T
<i>1987, Precip. 572</i>												
Runoff	92	133	225	70	181	251	71	151	222	43	199	242
TS	377	585	962	180	825	1005	225	664	889	110	1069	1179
PP	0.25	0.37	0.62	0.13	0.57	0.70	0.17	0.47	0.64	0.06	0.64	0.70
DP	0.03	0.05	0.08	0.02	0.07	0.09	0.02	0.04	0.06	0.01	0.10	0.11
TN	9.0	5.3	14.3	5.0	5.0	10.0	2.0	2.9	4.9	1.3	3.3	4.6
NN	8.5	5.1	13.6	4.7	4.8	9.5	1.5	2.9	4.4	1.2	2.6	3.8
<i>1988, Precip. 704</i>												
Runoff	124	158	282	65	264	329	69	239	308	51	238	289
TS	568	1965	2533	174	1664	1838	146	1108	1254	143	939	1082
PP	0.44	1.11	1.55	0.10	1.06	1.16	0.10	0.76	0.86	0.10	0.54	0.64
DP	0.05	0.04	0.09	0.01	0.07	0.08	0.02	0.06	0.08	0.02	0.06	0.08
TN	14.8	6.6	21.4	4.5	10.7	15.2	1.7	5.1	6.8	0.5	3.2	3.7
NN	13.9	4.2	18.1	4.2	8.1	12.3	1.3	3.2	4.5	0.2	1.3	1.5
<i>1989, Precip. 637</i>												
Runoff	103	228	331	86	262	348	81	237	318	51	336	387
TS	493	2536	3029	266	2554	2820	305	1409	1714	228	2238	2466
PP	0.39	1.28	1.67	0.21	1.43	1.64	0.24	1.16	1.40	0.15	1.35	1.50
DP	0.04	0.06	0.10	0.03	0.06	0.09	0.03	0.06	0.09	0.02	0.16	0.18
TN	14.8	8.9	23.7	5.7	10.2	15.9	2.3	6.1	8.4	0.6	6.0	6.6
NN	14.2	6.6	20.8	5.1	7.7	12.8	2.2	4.6	6.8	0.2	2.9	3.1
<i>1990, Precip. 668</i>												
Runoff	105	205	310	68	225	293	48	272	320	32	296	328
TS	532	1699	2231	293	1636	1929	148	1940	2088	120	2158	2278
PP	0.46	1.10	1.56	0.25	1.04	1.29	0.09	1.49	1.58	0.09	1.62	1.71
DP	0.05	0.07	0.12	0.02	0.07	0.09	0.02	0.07	0.09	0.01	0.09	0.10
TN	8.8	6.8	15.6	5.0	6.4	11.4	1.4	4.5	5.9	1.1	4.3	5.4
NN	7.8	5.1	12.9	4.1	4.6	8.7	1.1	1.9	3.0	0.9	1.9	2.8
<i>1991, Precip. 612</i>												
Runoff	224	111	335	203	147	350	209	142	351	218	169	387
TS	1302	591	1893	1159	735	1894	861	721	1582	1259	885	2144
PP	0.83	0.36	1.19	0.72	0.42	1.14	0.55	0.38	0.93	0.87	0.51	1.38
DP	0.09	0.05	0.14	0.07	0.06	0.13	0.06	0.05	0.11	0.06	0.07	0.13
TN	17.7	4.4	22.1	13.4	4.2	17.6	16.9	4.1	21.0	11.8	3.9	15.7
NN	15.2	3.8	19.0	11.3	3.2	14.5	14.7	3.4	18.1	10.1	3.0	13.1
<i>1992, Precip. 577</i>												
Runoff	295	55	350	298	55	353	309	36	354	295	68	363
TS	928	148	1076	808	115	923	726	99	825	1198	138	1336
PP	0.50	0.09	0.59	0.45	0.09	0.54	0.40	0.05	0.54	0.45	0.14	0.59
DP	0.08	0.03	0.11	0.07	0.03	0.10	0.07	0.02	0.09	0.07	0.03	0.10
TN	15.9	0.9	16.8	11.8	0.9	12.7	14.5	0.8	15.3	11.4	1.2	12.6
NN	13.5	0.5	14.0	10.1	0.5	10.6	12.2	0.6	12.8	9.7	0.7	10.4
<i>1993, Precip. 558</i>												
Runoff	140	81	221	132	119	251	161	68	229	122	133	255
TS	877	465	1342	701	449	1150	807	308	1115	648	502	1150
PP	0.56	0.28	0.84	0.40	0.31	0.71	0.51	0.19	0.70	0.38	0.37	0.75
DP	0.05	0.08	0.13	0.05	0.16	0.21	0.05	0.08	0.13	0.04	0.18	0.22
TN	10.6	2.1	12.7	9.6	2.7	12.3	9.9	2.0	11.9	8.4	2.7	11.1
NN	8.8	0.4	9.2	8.1	0.7	8.8	8.1	0.4	8.5	7.0	0.7	7.7

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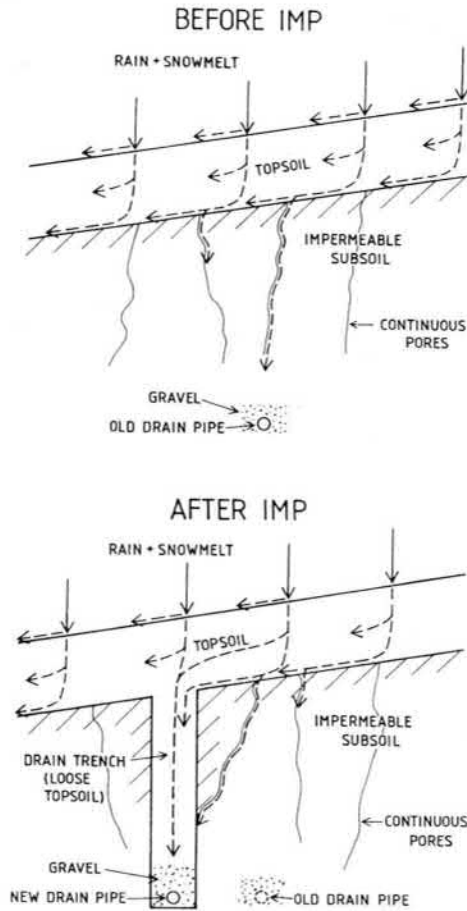


Fig. 2. Schematic representation of the flow medium for surface runoff and drainage water in the drainage field before and after subsurface drainage improvement (IMP).

After IMP, however, as water running in the upper layers or along the soil surface reached the site of a new drain, it infiltrated and passed to the drain through the permeable backfill (Fig. 2). The shift towards more subsurface drainage discharge during peak flows in spring is shown in Fig. 3. After IMP, the hydraulic response of the drains to rain and snowmelt water was rapid, as can be seen in the sharpness of the leading edges of the hydrographs. As a consequence, drainage flow increased drastically, to 80–90% of the total runoff (Table 5). Two years after IMP the proportion of drainage flow diminished to 50–60% of the total, probably partly due to the new grass cover on the soil, which reduced infiltration. The proportion of surface runoff during ley cultivation was observed to increase in an earlier experiment in the same field (Turtola and Jaakkola, 1995). It should be noted that both before and after IMP the major water movement occurred in topsoil and macropores. After



Table 6

Precipitation, total runoff, drainage water and surface runoff (mm) during the winter period before and after the subsurface drainage improvement (IMP). Total runoff, drainage water discharge and surface runoff as percentage (%) of precipitation in ploughed soil, Test 1, and ley, Test 2

	Ploughed (Test 1)		Ley (Test 2)	
	Before IMP	After IMP	Before IMP	After IMP
Precipitation (mm)	284	392	447	346
Total runoff (mm)	229	360	280	273
Drainage (mm)	55	328	44	159
Surface runoff (mm)	174	32	236	114
Total runoff (%)	80.6**	91.8 <i>n</i> = 4	62.6	78.9 <i>n</i> = 1
Drainage (%)	19.4***	83.7 <i>n</i> = 16	9.8*	46.0 <i>n</i> = 4
Surface runoff (%)	61.3***	8.2 <i>n</i> = 4	52.8	32.9 <i>n</i> = 1

\*\*\*Significantly different at the 0.1% level. \*\*Significantly different at the 1% level. \*Significantly different at the 5% level.

IMP, in accordance with the observations of Bewen (1980), the drain trench merely provided more outlets for the water, allowing it to drain more quickly.

On ploughed soil (Test 1), immediately after IMP, more than 80% of the precipitation water was evacuated by subsurface drainage, and less than 10% by surface runoff (Table 6). On ley (Test 2), almost half of the precipitation ended up in the drainage flow (Table 6). Moreover, during the winter periods, IMP appeared to increase the sum of subsurface drainage discharge and surface runoff expressed as proportion of precipitation. This is in accordance with the findings of Seuna and Kauppi (1981) and Bengtson et al. (1988). Seuna and Kauppi explained the increase in terms of reduced evaporation and percolation to the ground water layer.

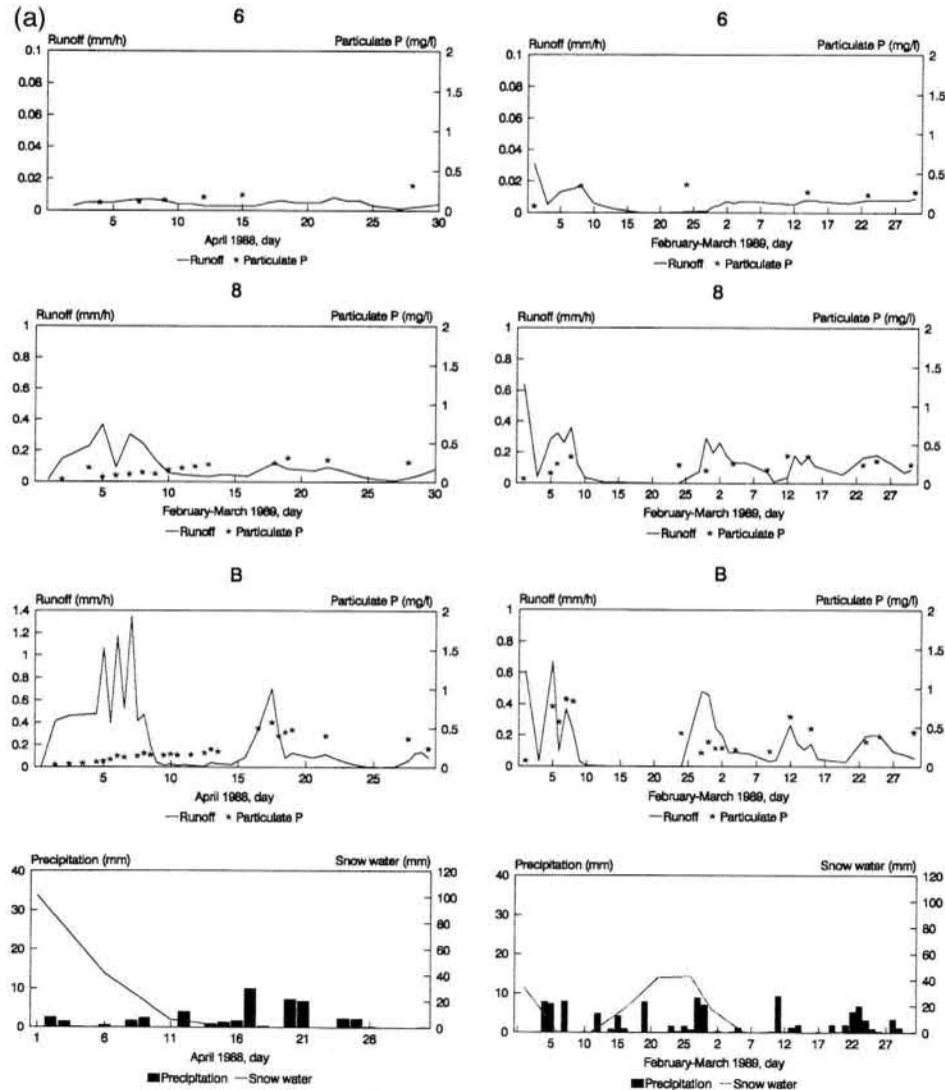
### 3.2. Concentrations and losses of total solids, phosphorus and nitrogen in subsurface drainage water and surface runoff

Before IMP, in both ploughed soil and ley, the concentrations of total solids (TS) and particulate phosphorus (PP) in winter periods were higher in surface runoff than in subsurface drainage water (Table 7), and soil and phosphorus losses were large. PP concentrations in surface runoff usually were higher at the end of a snowmelt when the soil was no longer covered with snow or ice (Fig. 3). Losses of phosphorus thus tended to be large when there were several melting periods in spring. After IMP, however, the TS concentration of surface runoff decreased to the level of drainage water.

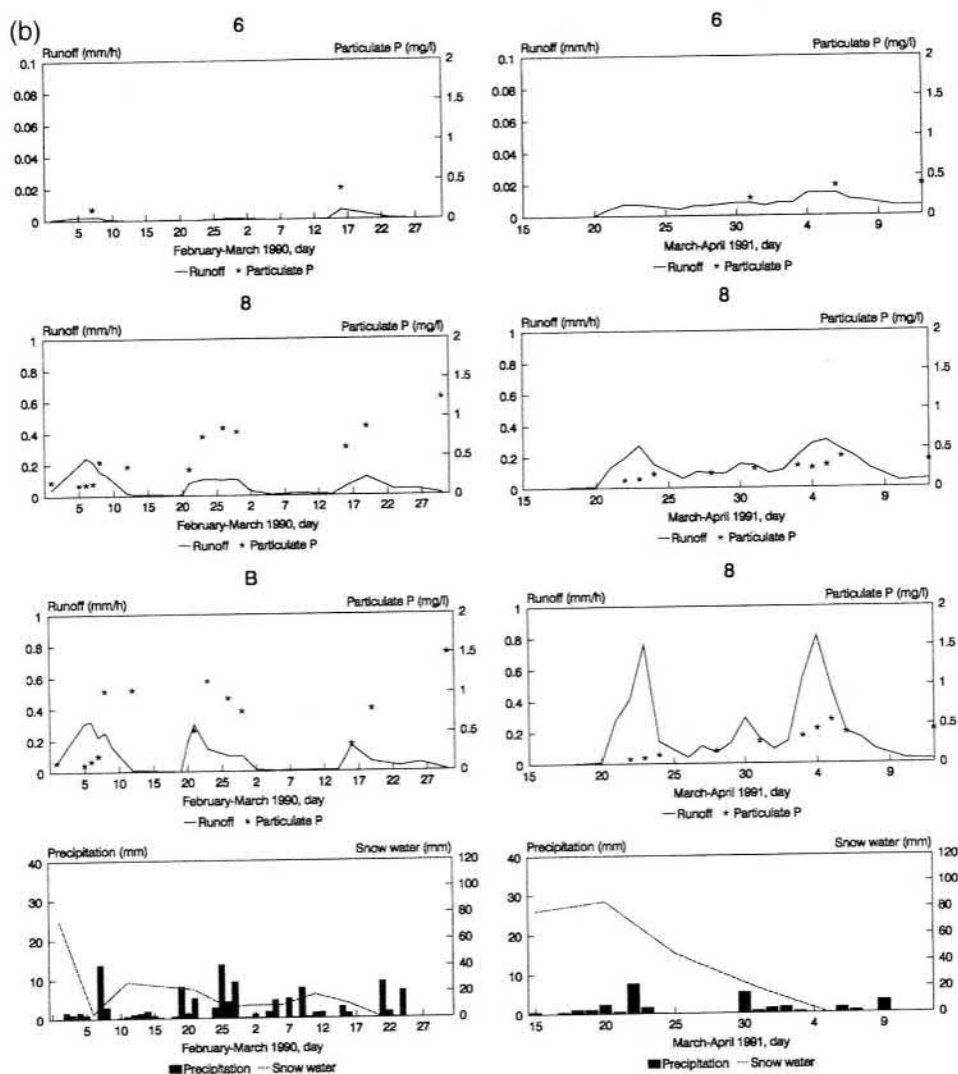
In drainage flow from ploughed soil, where topsoil was used as backfill, the concentrations of TS and PP decreased after IMP (Table 7). This was probably due to a sieving action, as postulated by Sharpley and Syers (1979). In drainage water from a clay soil, Culley et al. (1983) found smaller TS and PP concentrations when drains were installed at greater depth (1.0 vs. 0.6 m). In the present study, the trenches filled with wood chips in the lower part of the field were not effective in reducing the PP concentrations of the infiltrating surface runoff. Instead, they seemed to release soil particles to the penetrating water. This might

have been due to particle detachment from the cut edges of the trench, where the structure of the soil was poor.

Subsurface drainage water contained relatively large amounts of TS and PP both before and after IMP (Tables 5 and 7). Schwab et al. (1977) and Schwab et al. (1980) reported high fine sediment losses in drainage water from silty clay soil, with the possible explanation that once suspended in water at the soil surface, fine sediment remained in suspension as it moved through the soil and the drain backfill. Bottcher et al. (1981) reported the average



(Fig. 3 - cont.)



(Fig. 3 - cont.)

PP concentration in drainage water to vary from 0.15 to 0.22 mg l<sup>-1</sup> in silty clay soil, a magnitude similar to that we measured. Direct channelling of the water from the surface through cracks was considered the most probable cause of the high sediment and PP concentrations. After heavy rain, Thomas and Phillips (1979) observed high sediment concentration in spring water. The response to the rain was quick because of preferential flow through macropores in dry soil. Likewise, the relatively high TS (results not shown) and PP concentrations in the drainage water in our study probably were of surface origin,

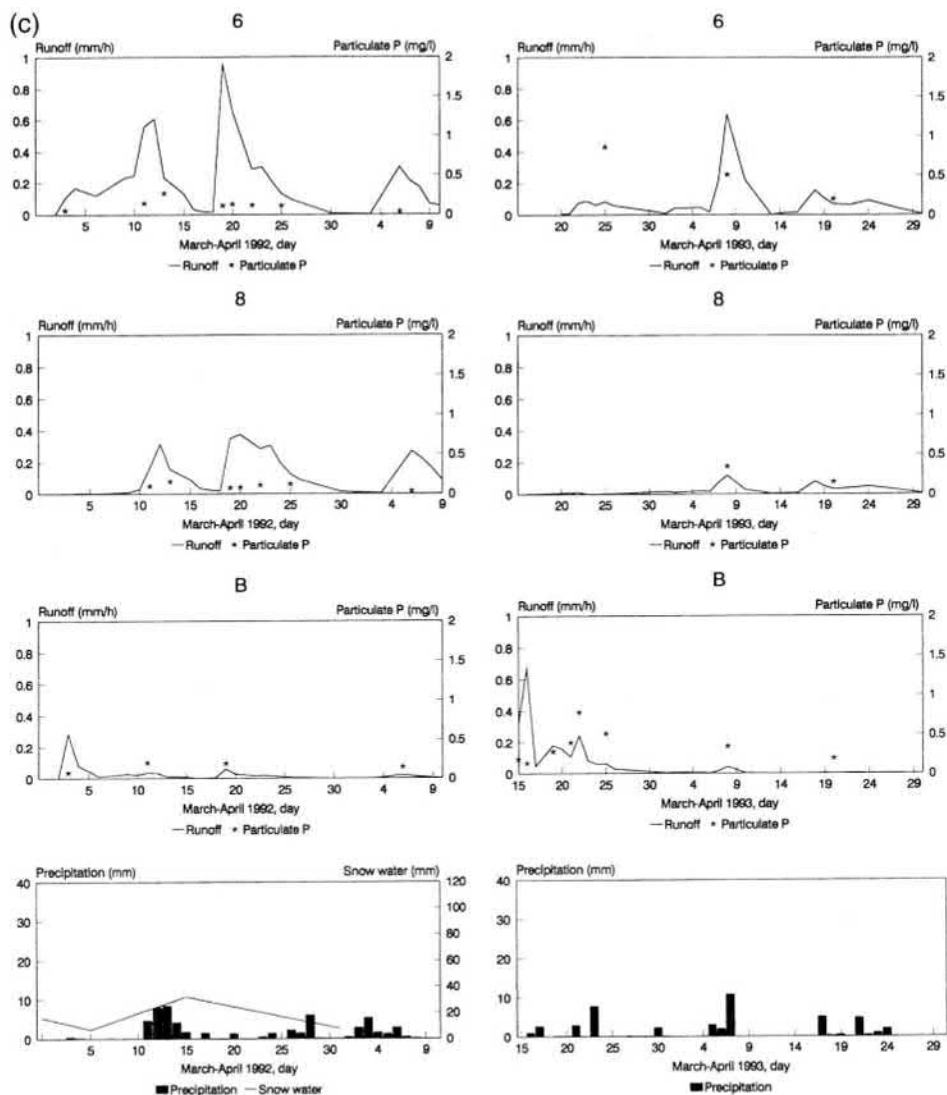


Fig. 3. Subsurface drainage water and particulate P concentration from drainage plots 6 and 8 and surface runoff and particulate P concentration from surface runoff area B in response to snowmelt and rainfall during spring; (a), (b) before and (c) after subsurface drainage improvement.

as they followed fairly closely the concentrations of surface runoff both before and after IMP (Fig. 3).

Irrespective of the backfill, IMP resulted in a decrease in dissolved orthophosphate phosphorus (DP) concentrations in drainage water (Table 7). After IMP, DP concentrations were lower in drainage water than in surface runoff in both ploughed soil and ley, indicating adsorption of orthophosphate in the trenches. Sharpley and Syers (1979) likewise found

Table 7

Concentrations of total solids (TS;  $\text{g l}^{-1}$ ), particulate phosphorus (PP), dissolved orthophosphate phosphorus (DP), total nitrogen (TN) and nitrate nitrogen (NN;  $\text{mg l}^{-1}$ ), in drainage water and surface runoff during the winter period before and after the subsurface drainage improvement (IMP), from ploughed soil, Test 1, and ley, Test 2. Backfill: gravel and topsoil in the upper part, gravel and wood chips in the lower part of the field

Backfill	Ploughed (Test 1)					
	Drainage				Surface runoff ( $n=4$ )	
	Topsoil, $n=8$		Wood chips, $n=8$			
	Before IMP	After IMP	Before IMP	After IMP	Before IMP	After IMP
TS ( $\text{g l}^{-1}$ )	0.41*	0.36	0.46	0.49	0.52**	0.39
PP ( $\text{mg l}^{-1}$ )	0.20**	0.17	0.13**	0.29	0.27	0.27
DP ( $\text{mg l}^{-1}$ )	0.040*	0.028	0.037 <sup>a</sup>	0.026	0.036	0.039
TN ( $\text{mg l}^{-1}$ )	6.1	7.9	2.9	3.3	3.23	2.03
NN ( $\text{mg l}^{-1}$ )	5.5	6.8	2.6	2.7	2.71	1.61
Backfill	Ley (Test 2)					
	Drainage				Surface runoff	
	Topsoil, $n=2$		Wood chips, $n=2$		$n=1$	
	Before IMP	After IMP	Before IMP	After IMP	Before IMP	After IMP
TS ( $\text{g l}^{-1}$ )	0.35	0.40	0.30	0.36	0.47	0.40
PP ( $\text{mg l}^{-1}$ )	0.20	0.20	0.12	0.25	0.25	0.26
DP ( $\text{mg l}^{-1}$ )	0.034	0.027	0.027	0.018	0.034	0.077
TN ( $\text{mg l}^{-1}$ )	1.8	6.2	1.5	1.8	1.25	2.24
NN ( $\text{mg l}^{-1}$ )	1.3	5.2	1.1	1.2	0.57	0.60

\*\*Significantly different at the 1% level. \*Significantly different at the 5% level. <sup>a</sup>Different at the 10% level.

lower DP concentrations in drainage water than surface runoff and attributed this to the extensive sorption of DP by soil components. On a clay soil, Culley et al. (1983) measured lower concentrations in water from deeper drains (1.0 vs. 0.6 m). In the present study, the high DP loss and concentration in surface runoff in ley after IMP (Tables 5 and 7) was not due to IMP, but probably to a higher phosphate release from plant material during winter 1992–1993.

Irrespective of the backfill, total nitrogen (TN) and nitrate nitrogen (NN) concentrations in drainage water were higher after than before IMP (Table 7), resulting in larger absolute losses of nitrogen after IMP (Table 5). The most probable reason for the higher concentrations was nitrification, which was slow in waterlogged soil and accelerated in the more aerobic conditions after drainage. In the case of ley, the increase in the nitrogen concentrations after IMP with topsoil as backfill might partly be due to nitrogen release from the red clover stand, which was more abundant at the upper than the lower edge of the field.

### 3.3. Estimated influence of IMP on soil and nutrient losses

To estimate the immediate effect of IMP on soil erosion and nutrient losses from a poorly drained clay soil, hypothetical 'before IMP' and 'after IMP' winter periods with precipitation

Table 8

Runoff (mm) and losses of total solids (TS), particulate (PP) and dissolved orthophosphate phosphorus (DP), total (TN) and nitrate nitrogen (NN; kg ha<sup>-1</sup>), from ploughed clay soil during hypothetical winter periods with 350 mm precipitation before and after subsurface drainage improvement (IMP)

	Drainage		Surface		Total	
	Before IMP	After IMP	Before IMP	After IMP	Before IMP	After IMP
Runoff (mm)	68	293	215	29	283	322
TS (kg ha <sup>-1</sup> )	292	1056	1116	112	1408	1168
PP (kg ha <sup>-1</sup> )	0.11	0.50	0.58	0.08	0.69	0.58
DP (kg ha <sup>-1</sup> )	0.03	0.09	0.09	0.01	0.12	0.09
TN (kg ha <sup>-1</sup> )	3.1	16.4	6.9	0.58	10.0	17.0
NN (kg ha <sup>-1</sup> )	2.8	13.9	5.8	0.46	8.6	14.4

of 350 mm were constructed on the basis of the data from ploughed soil. Hypothetical total runoff was calculated by assuming that 80.6% and 91.8% of the 350 mm precipitation were evacuated by drainage and surface runoff before and after IMP, respectively. Further, the amounts of drainage discharge and surface runoff were calculated using the percentages given in Table 6. Concentrations of TS, PP, DP, TN and NN in Table 7 were used to compute losses before and after IMP. In view of the much better values obtained with the topsoil than wood chip backfill, the 'topsoil' data were used in estimating the 'after IMP' TS, PP and DP losses.

As a consequence of drastically increased drainage flow and higher nitrogen concentrations in the discharge, IMP enhanced nitrogen leaching by 70% immediately after the operation (Table 8). This is in accordance with the results of Seuna and Kauppi (1981), who found subsurface drainage to increase nitrogen leaching by 52–410% compared with open ditches. Harris et al. (1984) measured 5–10 fold NN leaching from subdrained plots compared with control plots.

The figures in Table 8 show the TS, PP and DP losses to have decreased by 17%, 16% and 25%, respectively. Topsoil backfill would thus seem to slightly reduce soil and phosphorus losses. Seuna and Kauppi (1981) did not find reduced phosphorus losses after subsurface drainage. However, Bengtson et al. (1988) found that, after subsurface drainage, sediment and TP losses decreased by 30% and 36%, respectively, relative to losses through surface drains only. The corresponding reductions in Schwab et al. (1980) were 40% and 45%.

It should be noted that the above estimate describes only the immediate effect of IMP. The permeability of the plough layer above the drainage trenches decreases over time, resulting in increased surface runoff, as can be seen in Fig. 1 and as was found by Seuna and Kauppi (1981). However, after IMP, the macroporosity and water conductivity of the soil between trenches may gradually increase, as a lowered ground-water table enhances soil cracking and root penetration, and also earthworm activity. The higher crop biomass after subsurface drainage, resulting in better soil cover, may also reduce soil and particulate phosphorus losses.

#### 4. Conclusions

On poorly drained heavy clay soil, the leaching of dissolved orthophosphate phosphorus will diminish slightly if the amount of surface runoff is reduced by improving the subsurface



drainage. The amounts of suspended soil particles and particulate phosphorus seem to be reduced much less, although topsoil used as backfill material in the drain trenches evidently has some sieving effect on infiltrating water. Wood chips used as backfill do not efficiently reduce soil and phosphorus losses. The greater drainage discharge, together with the enhanced mineralization after subsurface drainage improvement, will lead to increased nitrogen leaching.

At present, subsurface drainage improvement is done to serve agronomic needs. The environmental benefits or disadvantages of the operation need to be evaluated as well, in terms of the nutrient balances of recipient water. If the load of dissolved orthophosphate phosphorus is critical for algae growth, improving the subsurface drainage might be a cost effective means of reducing eutrophication. Where nitrogen is the growth limiting nutrient, drainage could not be recommended for this purpose.

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# Loss of Phosphorus by Surface Runoff and Leaching from a Heavy Clay Soil under Barley and Grass Ley in Finland

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Phosphorus losses by surface runoff and leaching were studied for three years in a 16-plot field on a heavy clay soil in south-west Finland to compare losses of total phosphorus (TP), particulate phosphorus (PP) and dissolved orthophosphate phosphorus (DP) from barley and grass ley plots. Barley was fertilized with 21 and 42 kg ha<sup>-1</sup> y<sup>-1</sup> P by placement technique. Ley was given P 42 and 84 kg ha<sup>-1</sup> y<sup>-1</sup>, but split into two equal portions, by broadcasting. The mean losses of TP from the barley and ley were 1.2 and 1.6 kg ha<sup>-1</sup> y<sup>-1</sup>, respectively. The PP losses (calculated as the difference between TP and DP) constituted 69% of the TP loss from barley, but only 35% of that from ley. In the case of barley, a considerable amount of PP was carried by drainage water. The mean DP losses were 0.4 kg ha<sup>-1</sup> y<sup>-1</sup> from barley and 1.0 kg ha<sup>-1</sup> y<sup>-1</sup> from ley. The higher DP loss from ley was due to both the higher fertilizer rate and the fertilizer broadcasting technique. During the second and third years of the experiment, fertilizer broadcasting on the ley plots was followed by high DP concentrations in surface runoff and drainage water. The peak DP concentrations in drainage water occurred soon after fertilizer broadcasting followed by only 7–15 mm of flow, indicating fast preferential movement of orthophosphate from the surface through the soil.

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Key words: dissolved orthophosphate phosphorus, fertilizer broadcasting, particulate phosphorus, phosphorus loss.

## Introduction

In Finland, phosphorus losses from agricultural soil by leaching and surface runoff account for 60% of the anthropogenic load of phosphorus to surface waters according to Rekolainen et al. (1993). The load from agriculture is greatest in south-west Finland, which has the highest percentage of agricultural land (10–30%) in the country. There more than 60% of the cultivated area is under cereals and less than 20% is under grass for hay, silage or pasture. The soil is clay

(> 30% clay fraction) in 60% of the field area (Kähäri et al., 1987), and the mean slope of the fields varies between 0.6% and 1.5% (Rekolainen, 1993).

To study the effect of different cultivation practices on phosphorus losses from agricultural soil typical of south-west Finland, an experiment was established on a sloping (2%) heavy clay soil. The experiment lasted three years and was aimed at comparing phosphorus losses during barley and grass ley cultivation with different phosphorus fertilization rates and application practices. The nitrogen leaching losses, studied in

the same experiment, have been reported earlier (Jaakkola, 1984).

In lakes and coastal waters, the effects of phosphorus load on primary production depend largely on the load of dissolved phosphorus (DP), which is directly available for algae (Peters, 1981). Most of the total phosphorus (TP) leached from agricultural land is particulate phosphorus (PP) attached to eroded soil particles and therefore not directly available for algae (Pietiläinen & Rekolainen, 1991). However, PP may become available through desorption, and, especially in shallow lakes, provide a long-term source of phosphorus for primary production (Logan, 1982). In order to evaluate more closely the phosphorus load caused by fertilization, we studied the contributions of DP and PP to TP losses in surface and drainage water from barley and ley cultivations.

## Material and methods

### The drainage field

The experimental field was situated in Jokioinen, south-west Finland. The soil on the field was, according to the Finnish and FAO classification system, silty or heavy clay and cambisol, respectively (Table 1). The mean slope of the field was 2%, varying between 1% and 4%. The soil was poor in plant-available phosphorus, reflected by analyses of phosphorus dissolved in acid ammonium acetate (pH 4.65) (Vuorinen & Mäkitie, 1955) (Table 1).

The field consisted of 16 plots, 33 m × 33 m, each with a separate drainage system to allow measurement and analysis of the drainage water. The drainage pipes (ceramic), two per plot, had an inside diameter of 40 mm and were laid parallel, 16.5 m apart and at a depth of about 1 m. At one end, the drains of each plot were connected to a plastic pipe, which carried the drainage water to an observation building where the volume was measured with a tipping bucket. The water samples, proportional to the water discharge through the buckets, were collected with funnels conducting 0.1% of the total discharge to plastic containers. The surface water, in

turn, was collected from four parallel areas, 33 m × 140 m (each consisting of four drainage plots), into an open ditch at the lower edge of the field, and conducted via wells for measurement and analysis.

During the peak flow periods, the water samples were taken mostly once a day in spring and once a week in autumn, whereas during the base flow in summer and winter the sampling was less frequent. Sampling was always performed before major soil management practices, i.e. seed bed preparation and sowing, fertilization, harvest and autumn ploughing.

### Experimental system

In 1980–82 a factorial experiment, with three factors and two levels in each, was performed on the field:

factor 1, crop: (a) barley, (b) grass ley (timothy + meadow fescue)

factor 2, NPK fertilizer rate: (a) low, (b) high

factor 3, irrigation: (a) not irrigated, (b) irrigated (30 mm in June)

Each treatment had two replicates. The annual amounts of N, P and K applied were (kg ha<sup>-1</sup>):

	Low rate			High rate		
	N	P	K	N	P	K
Barley	50	21	40	100	42	80
Grass ley	100	42	80	200	84	160

On the four surface runoff plots, the experiment had only the crop factor 1, with two replicates, since the experimental system did not allow us to distinguish the effect of fertilizer rate or irrigation on phosphorus losses in runoff.

The barley was sown and fertilized simultaneously with a combination drill that placed the fertilizer between the seed rows at a depth of c. 8 cm. The dates of sowing in consecutive years were May 7, 13 and 10. The barley was harvested at full maturity on

Table 1. Particle size distribution, content of organic carbon, pH (1:2.5 soil:water suspension) and plant-available phosphorus of the soil on the experimental field (range in parentheses).

Depth (cm)	Particle size fractions (%)		Org. C (%)	pH (water)	P (mg/l)
	<0.002 mm	0.002–0.02 mm			
0–20	61 (43–79)	16 (9–21)	2.7	5.9	3.6 (2.7–4.8)
20–40	83 (62–93)	8 (3–6)		6.3	0.2 (0.0–0.5)
40–80	90 (73–94)	6 (2–14)		6.9	0.2 (0.0–0.6)

## Loss of phosphorus by surface runoff and leaching

August 14, September 9 and August 26, respectively. The straw was ploughed in every autumn. The ley had been seeded in 1979 with timothy (*Phleum pratense*) and meadow fescue (*Festuca pratense*). The grass was cut twice a year: June 30, July 10, July 2 and August 29, September 9, September 15 in 1980, 1981 and 1982, respectively. The annual fertilizer dose was split into two equal portions, one broadcast in at the date of sowing barley and the other immediately after the first cutting on July 1, 11 and 3 in the consecutive years.

### Analytical methods

The water samples were collected into polyethene bottles washed with hydrochloric acid (1.5 mol/l) and deionized water, and stored in darkness at +4°C. Often the samples had to be stored 1–2 weeks before analysis, but according to Turtola (1989) this did not affect the analytical results. The samples were analysed for total phosphorus (TP) and dissolved orthophosphate phosphorus (DP). In TP analyses, inorganic phosphate complex compounds and organic phosphorus compounds in the unfiltered water samples were converted to orthophosphate by oxidizing with peroxodisulphate in acid solution. The oxidation was done under pressure (200 kPa, 120°C) for 0.5 h. The concentration of orthophosphate was determined with an AKEA autoanalyser by the method of Murphy & Riley (1962). Before DP analysis, the

water was filtered through a membrane filter (pore size 0.45 µm, Sartorius 13906-ACN) to minimize phosphorus dissolution during analysis. After filtering, the orthophosphate concentration was measured as described above. The amount of particulate phosphorus (PP) was calculated as the difference between TP and DP, including thus true particle-bound phosphorus and colloidal phosphorus. Although dissolved organic phosphorus (DOP) will be included in PP, the inaccuracy probably remains small. Analysis of variance and Tukey's test (hsd = honestly significant difference) were applied to determine whether there were statistically significant differences in phosphorus leaching in drainage water between the fertilizer and irrigation treatments.

## Results and discussion

### Total phosphorus (TP)

Owing to the slope of 2% and low water conductivity of the heavy clay, surface runoff constituted on the average 56% and 65% of the total runoff in barley and ley plots, respectively (Table 2). From barley and ley, surface runoff transported on the average 65% and 79% of the TP. Losses were larger from ley than barley, except in the first year when surface runoff was small (Tables 2 and 3). The difference between ley and barley tended to increase during the experi-

Table 2. Precipitation, surface runoff and drainage (mm) in barley and grass ley plots (surface runoff and drainage during spring (1 Jan.–30 Apr.), summer (1 May–31 Aug.) and autumn (1 Sep.–31 Dec.) periods in parentheses).

Year	Precipitation	Barley		Grass ley	
		Surface runoff	Drainage	Surface runoff	Drainage
1980	645	109 (18, 1, 90)	136 (4, 6, 126)	139 (39, 3, 97)	101 (4, 7, 90)
1981	709	301 (150, 41, 110)	156 (26, 78, 52)	250 (118, 22, 110)	106 (18, 57, 31)
1982	644	183 (99, 16, 68)	165 (63, 20, 82)	225 (89, 16, 120)	122 (39, 16, 67)
Means	666	198	153	205	110

Table 3. Total phosphorus (TP) losses (kg ha<sup>-1</sup> y<sup>-1</sup>) in surface runoff and drainage water from barley and grass ley plots treated with low and high fertilizer rates (percentage of particulate phosphorus (PP) of the total phosphorus (TP) leaching in parentheses).

Year	Barley			Grass ley		
	Surface runoff	Drainage, P rate		Surface runoff	Drainage, P rate	
		21 kg ha <sup>-1</sup>	42 kg ha <sup>-1</sup>		42 kg ha <sup>-1</sup>	84 kg ha <sup>-1</sup>
1980	0.24 (67)	0.24 (71)	0.22 (68)	0.27 (48)	0.11 (50)	0.11 (45)
1981	1.17 (61)	0.49 (67)	0.32 (63)	1.54 (37)	0.28 (46)	0.29 (38)
1982	0.94 (76)	0.75 (81)	0.50 (82)	2.01 (27)	0.56 (55)	0.63 (46)
Means	0.79	0.49	0.35	1.27	0.32	0.34

ment, as will be discussed below. Irrigation had no effect on the phosphorus losses.

The average TP leaching ( $1.2 \text{ kg ha}^{-1} \text{ y}^{-1}$  from barley and  $1.6 \text{ kg ha}^{-1} \text{ y}^{-1}$  from ley) corresponded well to the leaching measured in small hydrological basins influenced by agriculture, and situated in southern Finland (Rekolainen, 1989). For a loam soil in Norway, Uhlen (1978, 1988) has reported annual TP losses between  $0.3$  and  $2.1 \text{ kg ha}^{-1}$  from cereals and  $0.3$  and  $0.8 \text{ kg ha}^{-1}$  from grass. In Sweden, TP losses have been found to vary between  $0.3$  and  $0.4 \text{ kg ha}^{-1}$  (Brink et al., 1987).

#### Particulate phosphorus (PP)

Averaged over the three years, particulate phosphorus (PP) constituted 69% and 35% of the TP losses in barley and ley plots, respectively. PP losses were greatest during spring and autumn runoff (Fig. 1). Contrary to TP, the absolute PP losses were less from ley than from barley, indicating the ability of a grass cover to reduce soil erosion. Smaller losses of PP from grass than other crops have also been reported by Gustafson (1982). In the present experiment, the effect of grass was largest in the rainy autumn of 1981

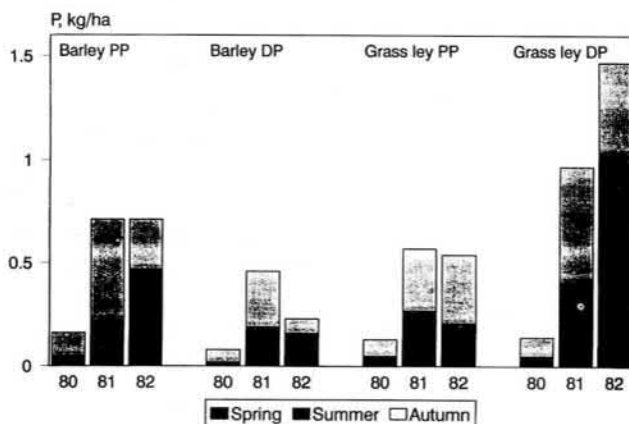


Fig. 1. Loss of particulate (PP) and dissolved orthophosphate phosphorus (DP) in surface runoff during spring (1 Jan.–30 Apr.), summer (1 May–31 Aug.) and autumn (1 Sep.–31 Dec.) from barley and grass ley plots on a clay soil during 1980–82.

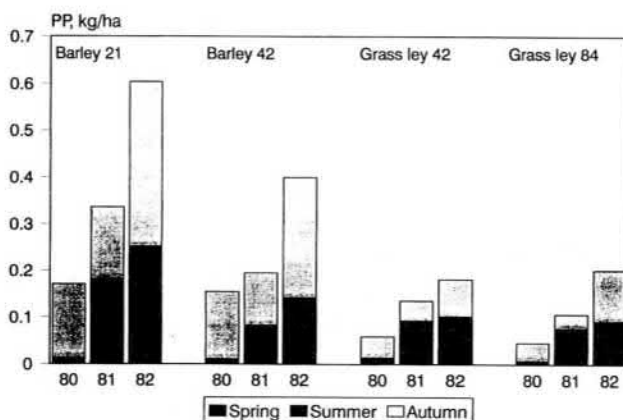


Fig. 2. Loss of particulate phosphorus (PP,  $\text{kg ha}^{-1}$ ) in drainage water during spring (1 Jan.–30 Apr.), summer (1 May–31 Aug.) and autumn (1 Sep.–31 Dec.) from barley and grass ley plots during 1980–82. Phosphorus fertilization rate: barley 21 and  $42 \text{ kg ha}^{-1} \text{ y}^{-1}$ , ley 42 and  $84 \text{ kg ha}^{-1} \text{ y}^{-1}$ .



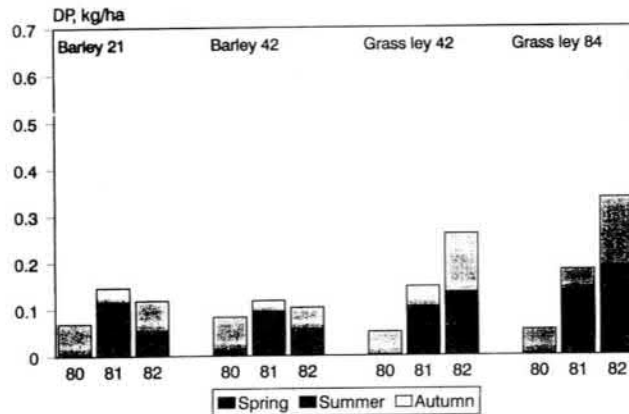


Fig. 3. Loss of dissolved orthophosphate phosphorus (DP,  $\text{kg ha}^{-1}$ ) in drainage water during spring (1 Jan.–30 Apr.), summer (1 May–31 Aug.) and autumn (1 Sep.–31 Dec.) from barley and grass ley plots during 1980–82. Phosphorus fertilization rate: barley 21 and 42  $\text{kg ha}^{-1} \text{y}^{-1}$ , ley 42 and 84  $\text{kg ha}^{-1} \text{y}^{-1}$ .

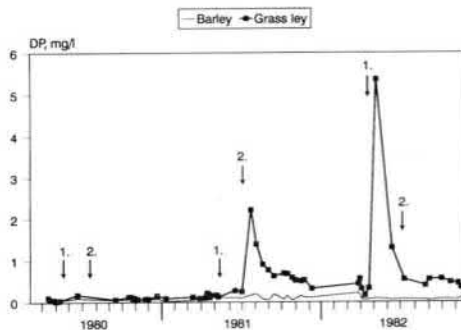


Fig. 4. Concentration of dissolved orthophosphate phosphorus (DP,  $\text{mg l}^{-1}$ ) in surface runoff from barley and grass ley plots during 1980–82. 1. = time of fertilizer placement for barley and of first broadcasting for ley. 2. = time of second broadcasting for ley.

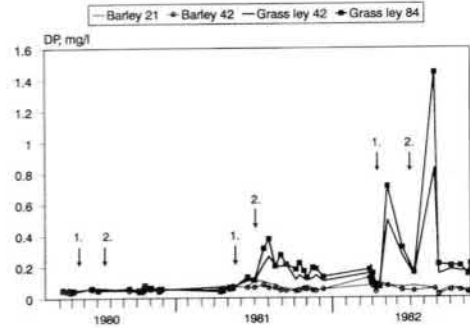


Fig. 5. Concentration of dissolved orthophosphate phosphorus (DP,  $\text{mg l}^{-1}$ ) in drainage water from barley and grass ley plots during 1980–82. Phosphorus fertilization rate: barley 21 and 42  $\text{kg ha}^{-1} \text{y}^{-1}$ , ley 42 and 84  $\text{kg ha}^{-1} \text{y}^{-1}$ . 1. = time of fertilizer placement for barley and of first broadcasting for ley. 2. = time of second broadcasting for ley.

and also in spring 1982 when the soil was not frozen during the heaviest snow melting period in late March–early April. Instead, soil frost seemed efficiently to reduce PP losses in spring 1980 and 1981 from ploughed barley plots.

Although surface runoff transported most of the PP, the amount carried by drainage water was considerable (Table 3, Fig. 2). Also in Norway, Lundekvam (1993) and Oygarden (1994) found PP concentrations similar to surface runoff in drain flow from a levelled silty clay loam soil. In the present experiment, PP losses in drainage water were larger from barley than from ley, and they were slightly higher in plots with the lower fertilizer rate (Fig. 2).

However, the effect of fertilizer rate was not statistically significant.

#### Dissolved orthophosphate phosphorus (DP)

During the years of the experiment, the losses of DP were 0.37 and 1.0  $\text{kg ha}^{-1} \text{y}^{-1}$  from barley and ley plots, respectively. The ratio of DP to TP losses corresponds fairly well to the results of Pietiläinen & Rekolainen (1991), who found dissolved reactive phosphorus to constitute 20–47% of the TP load from agricultural areas, with the proportion highest (47%) in an area influenced by cattle farming and

grass cultivation. Uhlen (1978, 1988) has also reported higher DP losses from ley than from cereal plots. The rate of DP leaching from ley was much higher in our study, however, and each year the rate increased (Figs. 1 and 3).

On average, surface runoff transported 70% and 83% of the DP loss from barley and ley, respectively. DP losses in surface runoff were higher in ley than in barley plots in the rainy summer of 1981 and onwards, with peak concentrations occurring during rainy periods after phosphorus fertilizer broadcasting in July 1981 and May 1982 (Fig. 4). The greater DP loss from the ley might have been due to the higher phosphorus fertilizer rate and to orthophosphate dissolving directly from fertilizer granules. Further, the annually repeated application of 42 and 84 kg P ha<sup>-1</sup> to the ley plots may have enriched the very topmost surface soil with phosphorus. According to Biggar & Corey (1969), this could raise the concentration of orthophosphate in the soil solution and runoff water.

Timmons et al. (1973) observed that deep incorporation of fertilizer by ploughing down gave phosphorus losses by surface runoff about equal to those from unfertilized plots. However, broadcasting the fertilizer on a disced surface resulted in much higher losses. Likewise Sharpley et al. (1992) single out fertilizer broadcasting as a source of large DP losses. Uhlen (1978, 1988) and Sharpley & Syers (1979) measured higher DP losses in surface runoff from grass plots fertilized by broadcasting with 50 kg ha<sup>-1</sup> than from unfertilized plots.

An additional source of DP in the ley plots might have been the release of DP to surface runoff from the vegetation. Grass leaves have been shown to release phosphorus, especially after freezing and drying (Timmons & Holt, 1970; Ulén, 1984). In the present study, this might have caused increased DP leaching from the ley, particularly during the spring periods.

Although DP concentrations in drainage water were less than in surface runoff, they showed a similar pattern (Fig. 5). From summer 1981 onwards, DP concentrations in drainage water were higher for ley than for barley, with the peaks occurring after fertilizer broadcasting followed by only 7–15 mm of drainage flow. For ley, this indicates that orthophosphate may have dissolved from the fertilizer granules spread on the soil surface, and migrated via continuous fissures and macropores to the drainage system, since the drainage flow was too small for uniform movement through the soil. By using packed and undisturbed soil columns in the laboratory, Kanchanasut et al. (1978) observed fast movement of phosphate owing to continuous pores, and pointed out the possibility for pronounced preferential movement of phosphorus also in the field.

With the same fertilizer rate (42 kg ha<sup>-1</sup>), DP leaching in drainage water was significantly higher ( $p < 5\%$ ) from ley than from barley in the summer period of 1982, owing to the peak DP concentrations following fertilizer broadcasting. However, in spite of the larger concentrations also during the rainy summer of 1981, the voluminous drainage from barley plots resulted in similar DP losses from barley and ley. In contrast with barley, the fertilizer rate seemed to have a slight effect on DP leaching from ley (Fig. 3). Our findings agree with those of Sharpley & Syers (1979), who report higher DP concentrations and higher leaching in drainage water from pasture fertilized with 50 kg P ha<sup>-1</sup> than from unfertilized pasture.

The phosphorus load to water courses from Finnish agriculture increased in the period 1981–85 relative to the period 1965–74, owing in part, perhaps, to the large inputs of fertilizer phosphorus and the decline in grass cultivation, especially in southern Finland (Rekolainen, 1989). The present study shows that decrease in the grass area can increase the risk of PP losses. On the other hand, fertilizer broadcasting on the soil surface, as is usual during grass cultivation, will almost certainly result in increased DP leaching, especially during summer, and increase the risk of harmful algal blooms in surface waters.

## Conclusions

On the clay soils typical of south-west Finland, total phosphorus losses depend on the amount of surface runoff. Large surface runoff tends to increase particulate phosphorus loss from fields under cereal cultivation, while from ley cultivations loss of dissolved orthophosphate phosphorus may increase if fertilizer is applied by broadcasting. To minimize these losses during ley cultivation, the bulk of the fertilizer phosphorus needed during the 2–3-year growing period should be mixed with soil in connection with sowing.

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# Nitrogen and phosphorus losses in surface runoff and drainage water after application of slurry and mineral fertilizer to perennial grass ley

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Losses of nitrogen (N) and phosphorus (P) from perennial grass ley on a fine sand soil were studied with five treatments: no fertilizer (1), cow slurry applied in autumn (2), winter (3) or spring (4), and mineral fertilizer applied in spring (5). For N, the total amounts applied (1992–96) were 0, 772, 807, 805 and 510 kg ha<sup>-1</sup> and for P 0, 141, 119, 143 and 107 kg ha<sup>-1</sup>, respectively. In the first year (establishment of the ley, 1992–93), N losses (drainage + surface runoff) were slightly higher after application of slurry in autumn (with immediate ploughing, treatment 2) than in treatments 1, 4 and 5 (21 kg ha<sup>-1</sup> vs. 17 kg ha<sup>-1</sup>), but the respective P losses (0.7–0.9 kg ha<sup>-1</sup>) were not affected. During the ley years (1993–96) the N and P losses were increased by surface application of fertilizers and by abundance of surface runoff (83–100% of the total runoff). Nutrient losses were extremely high after slurry application in autumn and winter, accounting for 11% and 33% of the applied N and 17% and 59% of the applied P, respectively. The N losses during the ley years from treatments 1–5 were 13, 62, 191, 23 and 24 kg ha<sup>-1</sup>, where the proportion of NH<sub>4</sub>-N was 21, 49, 56, 33 and 39%. The respective P losses were 0.73, 16, 54, 4.2 and 4.0 kg ha<sup>-1</sup>, where the proportion of PO<sub>4</sub>-P was 52, 85, 77, 68 and 64%.

*Key words:* ammonium-N, application time, orthophosphate-P, surface application

## Introduction

Fertilizing with slurry is often followed by high losses of nitrogen (N) and phosphorus (P) due to application in excess amounts or unsuitable timing relative to crop requirements (Kemppainen 1995, Oskarsen et al. 1996, Carey et al. 1997,

Paul and Zebarth 1997). Compared with cereals, fields under perennial ley are normally less prone to nutrient losses, and, in spite of the large inputs in manure or slurry, the leaching losses from perennial grass leys are often small (Furrer and Stauffer 1986, Unwin 1986, Eder and Harrod 1996, Cameron et al. 1996). However, several studies have shown high dissolved P losses

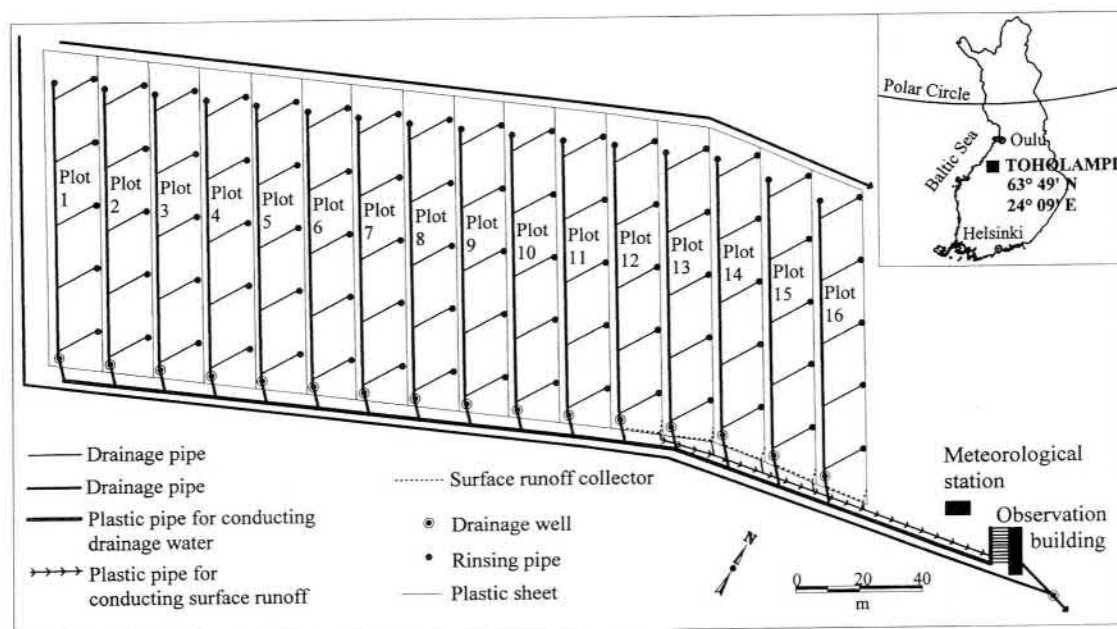


Fig. 1. Map of the experimental field.

in surface runoff from grassland (Uhlen 1978a, Uhlen 1988, Turtola and Jaakkola 1995).

The susceptibility of applied N and phosphorus P to loss via surface runoff or drainage depends on the physical contact with soil, which may or may not render adsorption of  $\text{NH}_4^+$  and  $\text{H}_2\text{PO}_4^-$  possible, on nitrification of  $\text{NH}_4\text{-N}$  or immobilization and crop uptake of  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$ . Surface application of slurry or mineral fertilizers is a common practice during perennial grass cultivation. Surface application leaves the nutrients on the soil surface with little initial contact with adsorbing soil constituents, with the result that the losses in surface runoff are increased (Edwards and Daniel 1993, Misselbrook et al. 1995, Turtola and Jaakkola 1995). Manure and slurry spreading outside the growing season causes high risks of nutrient losses into water-courses (Young and Mutchler 1976, Uhlen 1978b, Braun and Leuenberger 1991, Parkes et al. 1997). The probability of direct losses due to rain or snowmelt water is high especially where the soil is impermeable, e.g. due to frost, or conditions are otherwise favourable to surface run-

off. In Finland, owing to insufficient storage capacity and difficulties associated with spring application, about 30% of manure is spread in autumn (MMM 1998). Previously manure and slurry were also applied in winter on snow-covered or frozen soil but this practice is now to be prohibited by law.

This paper reports the N and P losses in surface runoff and drainage water during a four-year experiment, where slurry was either mixed with the surface soil or surface-applied in autumn, winter or spring. The losses are compared with those from mineral fertilized and non-fertilized soil.

## Material and methods

### The experimental field

The experimental field (2.56 ha) is located on a fine sand soil in Toholampi, western Finland (Fig. 1). Occasional snowmelts during winter,

Table 1. Total precipitation, maximum amount of water in snow in March and dates of snow cover and frost and maximum frost depth during the experimental years 1992–1996 and the average during 1966–96.

Experimental years	Total precip. <sup>1</sup> (mm)	Max. water in snow in March (mm)	Snow cover (date)	Frost (date)	Max. frost depth (cm)
1992–93	594	86	10.10.–5.4. <sup>2</sup>	15.10.–26.5.	62
1993–94	534	150	11.11.–10.4. <sup>3</sup>	16.10.–12.6.	58
1994–95	671	95	8.11.–19.4. <sup>4</sup>	10.11.–3.6.	69
1995–96	486	120	29.10.–20.4.	3.11.–9.6.	66
Average 1966–96	583		18.11.–13.4.	9.11.–30.5.	63

<sup>1</sup> From 1.9. to 31.8.

<sup>2</sup> No snow cover: 16.12.1992 – 5.1.1993

<sup>3</sup> First snow: 10.10.1993

<sup>4</sup> First snow: 3.10.1994; no snow cover: 20.12.1994 – 2.1.1995

Table 2. Characteristics of the experimental soil at the start of the experiment. Values in parenthesis indicate the range.

Depth, cm	pH (water)	Org. C (%)	Al <sub>ox</sub> (g kg <sup>-1</sup> ) <sup>1</sup>	Fe <sub>ox</sub> (g kg <sup>-1</sup> ) <sup>1</sup>	P <sub>Ac</sub> (mg l <sup>-1</sup> ) <sup>2</sup>
0–25	5.7 (5.6 – 5.8)	5.0 (4.8–5.3)	2.6 (2.4 – 2.8)	1.7 (1.0 – 2.6)	6.4 (5.1–7.5)
25–35	5.2 (5.2 – 5.3)	2.6 (2.2–3.1)	3.9 (3.5 – 4.3)	5.2 (4.4 – 6.0)	4.1 (2.8–5.5)
35–60	5.3 (5.2 – 5.3)	0.3 (0.3–0.4)	1.0 (0.9 – 1.1)	4.2 (3.7 – 4.7)	2.7 (1.8–3.9)

<sup>1</sup> Ammonium oxalate (0.5 M, pH 3.3) extractable Al and Fe (Niskanen 1989)

<sup>2</sup> Acetic acid (pH 4.65) extractable P (Vuorinen & Mäkitie 1955)

Table 3. Particle size distribution and saturated hydraulic conductivity ( $K_{sat}$ ) in two plots of the experimental soil.

		Particle size distribution (%) in different size fractions (mm)				$K_{sat}$ (cm/h)
Depth		< 0.002	0.002–0.02	0.02–0.2	0.2–2	
Plot 12	0–25	5	16	76	3	0.38
	25–35	4	22	72	2	0.16
	35–100	9	29	62	0	
Plot 14	0–25	4	18	73	5	0.87
	25–35	5	21	71	3	1.6
	35–100	8	31	61	0	

main snowmelt in March and frost until late May are typical for the study area (Table 1). The soil has been tentatively classified as Haplic Podzol (FAO 1988) and Aquic Haplocryod (Soil Survey Staff 1992). The 25–35 cm horizon is a spodic horizon, characterized by an abundance of oxalate-extractable Fe and Al and a relatively

high amount of organic C (Table 2). Over most of the field, the albic horizon and the upper part of the spodic horizon had been ploughed into the A<sub>p</sub> horizon. The percentage of silt and clay was somewhat higher below 35 cm depth than above (Table 3). The values of saturated hydraulic conductivity were relatively low (Table 3), indicat-



Table 4. N, P and K applications (N,P,K, kg ha<sup>-1</sup>) in fertilizer (f) and slurry (s) and month of treatment during the experimental years 1992–1996.

No	Treatment	1992–93 Ploughed	1993–94 Ley	1994–95 Ley	1995–96 Ley	Total
1	Control	None	None	None	None	None
2	Slurry, Sept.	196,49,136 s, Sept	193,26,163 + 91,11,11 s, Sept + f, July	201,44,154 + 91,11,11 s, Sept + f, June	None	772,141,475
3	Slurry, Dec.	226,28,172 s, Dec	207,32,192 + 91,11,11 s, Jan + f, July	192,37,218 + 91,11,11 s, Jan + f, June	None	807,119,604
4	Slurry, May	211,33,163 s, May	247,61,218 + 91,11,11 s, May + f, July	165,27,171 + 91,11,11 s, May + f, June	None	805,143,574
5	NPK, May	100,35,71 f, May	128,28,52 + 91,11,11 f, May + f, July	100,22,42 + 91,11,11 f, May + f, June	None	510,107,187

ing a tendency for surface runoff instead of deep percolation and drainage flow. The slope varies between 0.30–0.74%, with a mean value of 0.54%. Sideways the mean slope is 1.1%.

Plastic drainage pipes (Ø 44 mm) were laid in the field in 1989, 16 m apart and at a depth of about 1.05 m. The drains were connected to plastic cross pipes (Ø 58 mm) to form 16 separate drainage plots, 16 m x 100 m, i.e. 0.16 ha (Fig. 1). The plots were isolated hydrologically from each other and from the surrounding area with 0.3 m high ridges formed from mounded earth and by a plastic sheet extending to the depth of 1.5 m. The cross pipes carried the drainage water to wells (Ø 300 mm), from where the water was conducted to an observation building for volume measurement with tipping buckets. The flow-weighted water samples were collected with funnels conducting 0.24% of the total discharge to plastic containers for further sampling and chemical analysis. The surface runoff was collected at the lower end of five drainage plots (12, 13, 14, 15 and 16) into 0.2 m deep open ditches strengthened with concrete (Fig. 1). From there the water was conducted through plastic pipes for measurement and analysis.

Water sampling for analysis from the containers was proportional to flow. The drainage water and surface runoff were sampled 17–28 times

per year, each sample representing about 7 mm of surface runoff or drainage water. For the whole experiment (1992–96) the total number of sampling dates was 89 and the average sampling interval 16 days, varying from half a day to four months. Most of the water samples (55%) were taken in winter-spring, while 30% were taken in autumn and only 15% in summer.

## Experimental design

The four-year experiment was performed in 1992–1996 with five fertilization practices (treatments) (Table 4) and three replications, arranged as a randomized complete block design on plots 2–16. Treatment 1 was the control, receiving no fertilizer. The experiment started with the application of cow slurry in September 1992 (treatment 2). Immediately after the slurry was spread on the soil surface, the soil was ploughed to a depth of 22 cm. In December, slurry was applied on the soil surface, covered with snow (treatment 3). (Treatment 3 was included because at the beginning of the experiment slurry spreading on frozen soil was not prohibited but it was only recommended to be avoided.) In May 1993, slurry was applied on the soil surface followed by immediate harrowing of the soil to a depth of 5

cm (treatment 4). For treatment 5, NPK fertilizer was applied in May by placement technique to a depth of 7 cm in connection with sowing. For the establishment of the perennial grass ley, spring barley (*Hordeum vulgare*) was sown in 1993 on all plots, with timothy (*Phleum pratense*) and meadow fescue (*Festuca pratensis*) interseeded. After harvesting of the barley in August, the timothy – meadow fescue ley was grown. The ley was cut twice in 1994 and 1995 and once in 1996.

In autumn 1993 and onwards, cow slurry and mineral fertilizer were applied to the soil surface without any incorporation or mixing with the soil. The application for treatment 3 was again done on snow-covered soil. In 1994–1995, supplemental mineral fertilizer was applied in treatments 2–5 one week after the first cutting of the ley. In treatments 2–4, the target was that the amount of soluble N in slurry (55% of total N) should equal the amount of N applied in mineral fertilizer in treatment 5. For P, the amounts applied in slurry were greater than the amounts applied in the mineral fertilizer (Table 4). No nutrients were applied in 1996 and the ley was ploughed in in autumn 1996.

## Chemical analyses

The water samples were stored and analysed for total nitrogen (TN), nitrate nitrogen ( $\text{NO}_3\text{-N}$ ), ammonium nitrogen ( $\text{NH}_4\text{-N}$ ), total phosphorus (TP), dissolved orthophosphate phosphorus ( $\text{PO}_4\text{-P}$ ) and total solids (TS) as described by Turtola & Paaianen (1995). TN, TP and TS were measured in unfiltered water samples and  $\text{NO}_3\text{-N}$ ,  $\text{NH}_4\text{-N}$  and  $\text{PO}_4\text{-P}$  were measured after filtering of samples through Nuclepore 0.2  $\mu\text{m}$  filter. As the concentration of nitrite nitrogen ( $\text{NO}_2\text{-N}$ ) was not separately determined,  $\text{NO}_3\text{-N}$  represents the sum of  $\text{NO}_3\text{-N}$  and  $\text{NO}_2\text{-N}$ . Organic N was calculated as the difference between TN and  $\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$ . Particulate P (PP), representing the sum of particulate inorganic or organic P and dissolved organic P, was calculated as the difference between TP and  $\text{PO}_4\text{-P}$ .

N and P losses were calculated for autumn (mid-September – December), winter-spring (January – April/May) and summer (May/June – mid-September) periods, where each period started from the day of slurry spreading. For the calculation of the annual losses, the starting point was the autumn period (e.g. for the one-year period marked as 1992–93, the losses of autumn 1992, winter-spring 1993 and summer 1993 were summed).

The amount of mineral nitrogen ( $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$ ) in soil was determined in 0–20, 20–40 and 40–60 cm layers in late May in 1993–95. Sampling, storage and analysis of the soil were carried out as described by Esala (1991). The contents of N, P and K in slurry were determined as described by Kempainen (1989). The crop uptakes of N and P were calculated by multiplying the yield by its nutrient concentrations, which were determined according to Kähäri & Nissinen (1978). N and P balances for the different treatments were calculated by subtracting the total amounts of N and P removed from the amounts applied (input). For the removal, the uptake by the harvested crop was added to the losses in surface runoff and drainage.

## Statistical analyses

The drainage water samples and soil samples represented the five different treatments with three replicates. Statistical analyses were done with one-way analysis of variance and subsequent Tukey's test. Variables were the volumes of drainage water and the losses of  $\text{NO}_3\text{-N}$ ,  $\text{NH}_4\text{-N}$ , TN,  $\text{PO}_4\text{-P}$  and TP in autumn, winter-spring and summer, and the amounts of  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  at the different sampling depths. Owing to the negligible amount of drainage after the first year and the limited movement of N below the surface soil, only some of the test results are presented. There were no replicates in the surface runoff plots, which made it impossible to test the results for surface runoff statistically.

## Results

### Drainage water and surface runoff

In 1992–93, the proportion of autumn and winter-spring total runoff (drainage + surface runoff) was 60–66% and 33–39% of the annual total runoff, respectively. The general pattern for the water flow on ploughed soil and barley was dominance of drainage flow in autumn and surface runoff in spring. Surface runoff averaged 40–52% of the annual total runoff (Table 5), the proportion of surface runoff being in autumn,

winter-spring and summer 11–30%, 95–96% and 73–88%, respectively.

During the ley years 1993–1996, in contrast, the proportion of autumn and winter-spring total runoff was lower in autumn (4–29% and) and higher in winter-spring (67–89%) than it was in the first year. This was due to lower precipitation in autumn (176–217 vs. 270 mm) and more water in snow (maximum amount of water in snow 95–150 vs. 86 mm, Table 1) in the ley years compared with the first year. Surface runoff from the ley averaged as much as 83–100% of the annual total runoff, and water discharge from the field during occasional snowmelt in winter and

Table 5. Drainage water and surface runoff (mm) and losses of total N (TN), ammonium-N ( $\text{NH}_4\text{-N}$ ), nitrate-N ( $\text{NO}_3\text{-N}$ ), total P (TP), orthophosphate P ( $\text{PO}_4\text{-P}$ ) and evaporation residue (TS) ( $\text{kg ha}^{-1}$ ) during the experimental years 1992–1996.

No	Drainage water, n=3							Surface runoff, n=1							
	Treatment	Water	TN	NH <sub>4</sub> -N	NO <sub>3</sub> -N	TP	PO <sub>4</sub> -P	TS	Water	TN	NH <sub>4</sub> -N	NO <sub>3</sub> -N	TP	PO <sub>4</sub> -P	TS
1 Control															
1992-93	130	11		0.058	9.8	0.021	0.007	260	110	6.3	0.57	2.5	0.65	0.028	247
1993-94	32	3.3		0.016	3.1	0.007	0.001	76	161	2.8	1.3	0.49	0.25	0.13	102
1994-95	3.8	0.31		0.002	0.28	0.001	0.000	8.9	261	3.6	1.1	1.0	0.30	0.12	145
1995-96	10	1.4		0.007	1.3	0.003	0.000	22	151	1.6	0.28	0.26	0.17	0.13	145
1992-96	176	16		0.083	14	0.032	0.008	367	683	14	3.3	4.3	1.2	0.41	639
2 Slurry, Sept.															
1992-93	130	16		0.094	15	0.038	0.014	290	98	5.4	0.83	2.1	0.72	0.041	248
1993-94	23	4.3		0.009	3.9	0.004	0.001	72	376	36	22	3.3	9.4	8.2	582
1994-95	0.5	0.070		0.000	0.063	0.001	0.001	1.8	329	16	7.7	1.4	5.2	4.3	293
1995-96	4.0	2.5		0.006	2.2	0.003	0.000	15	135	2.8	0.77	0.38	0.98	0.76	142
1992-96	158	23		0.11	21	0.046	0.016	379	938	60	31	7.2	16	13	1265
3 Slurry, Dec.															
1992-93	115	9.5		0.060	8.7	0.022	0.008	218	78	14	5.4	3.3	2.4	0.47	158
1993-94	24	2.9		0.009	2.8	0.005	0.001	61	234	82	51	0.82	23	19	1220
1994-95	10	1.1		0.002	0.86	0.001	0.000	26	244	100	56	0.92	30	22	1680
1995-96	8.5	2.1		0.006	1.9	0.003	0.000	17	139	2.4	0.54	0.34	0.90	0.52	447
1992-96	158	16		0.077	14	0.031	0.009	322	695	198	113	5.4	56	42	3505
4 Slurry, May															
1992-93	110	9.1		0.094	8.2	0.023	0.005	233	118	8.3	0.64	5.3	0.66	0.050	289
1993-94	18	2.6		0.014	2.4	0.004	0.000	48	316	8.8	4.8	1.1	1.3	0.83	250
1994-95	0.9	0.091		0.000	0.086	0.001	0.001	2.4	327	7.2	2.4	1.4	1.8	1.2	268
1995-96	3.1	2.1		0.004	1.9	0.003	0.000	8.5	140	2.7	0.52	0.34	1.1	0.85	209
1992-96	132	14		0.11	13	0.031	0.006	292	901	27	8.4	8.1	4.9	2.9	1016
5 NPK, May															
1992-93	115	9.4		0.056	8.5	0.023	0.007	243	109	7.1	1.4	2.4	0.86	0.078	333
1993-94	13	1.8		0.004	1.7	0.002	0.001	33	207	6.8	4.0	0.70	0.88	0.52	189
1994-95	0.1	0.016		0.000	0.012	0.000	0.000	0.78	258	11	5.2	1.0	2.0	1.5	205
1995-96	3.5	2.4		0.004	2.1	0.004	0.000	9.3	145	2.1	0.31	0.26	1.1	0.54	648
1992-96	132	14		0.064	12	0.029	0.008	286	719	27	11	4.4	4.9	2.6	1375

the final snowmelt in March was entirely surface runoff. During the ley years, the proportion of surface runoff in autumn, winter-spring and summer was 31–100%, 100% and 49–100%, respectively. Surface runoff was exceptionally high in treatment 2 in 1993–94.

In spite of frost extending to a depth of 20 cm at the end of December 1992, there was altogether 75–88 mm of drainage flow (total runoff 89–116 mm) from the ploughed frozen soil in autumn 1992. In the grass ley, the frozen layer was shallower in autumn, but there was only 8–14 mm of drainage flow (total runoff 26–46 mm) in autumn 1993 and no drainage in autumn 1994 (total runoff 43–77 mm) and 1995 (total runoff 5–7 mm). The amounts of meltwater were about 80, 15, 45 and 5 mm during the frozen periods in autumn 1992, 1993, 1994 and 1995, respectively.

### N and P losses in drainage water

In 1992–93, the loss of  $\text{NO}_3\text{-N}$  in drainage water was statistically significantly higher ( $P < 0.05$ ) from treatment 2 (slurry application in September with immediate ploughing) than from the other treatments. The difference (5–7 kg ha<sup>-1</sup>, Table 5) occurred almost totally in autumn 1992, when the amount of drainage water was much higher than during the rest of the year (107–126 vs. 3–10 mm). For TP and  $\text{PO}_4\text{-P}$ , however, the slightly greater losses from treatment 2 in 1992–93 (Table 5) were not statistically significant. The concentration of P in drainage water was low throughout the experimental period: the annual mean concentration was 0.012–0.068 mg l<sup>-1</sup> for TP and 0.001–0.032 mg l<sup>-1</sup> for  $\text{PO}_4\text{-P}$ .

With the decreasing drainage after the first experimental year, N and P losses in drainage water were reduced and the losses did not vary with the treatment. Statistical analysis of the soil mineral nitrogen data in 1994–95 showed that, although the preceding autumn and winter applications of slurry had increased statistically significantly ( $P < 0.05$ ) the values of soil mineral N in spring in the surface (0–20 cm) and near

surface layers (20–40 cm), the values below 40 cm were not affected (results not shown).

### N and P losses in surface runoff

N losses in surface runoff were low in the control plot and decreased towards the end of the experiment (Table 5). Slurry application and immediate ploughing in September 1992 did not affect the N loss in surface runoff.

From 1993 onwards, N losses varied with the fertilization practice. Compared with spring applications (treatments 4 and 5), TN losses in surface runoff were very much greater after surface application of slurry in autumn (treatment 2) and especially in winter (treatment 3) in 1993–94 and 1994–95. Surface application of slurry in autumn and winter increased the losses of  $\text{NH}_4\text{-N}$  and organic N, while the loss of  $\text{NO}_3\text{-N}$  was little affected (Table 5). The peak concentrations of  $\text{NH}_4\text{-N}$  in surface runoff following the applications were 4–12 mg l<sup>-1</sup> for the autumn and 50–200 mg l<sup>-1</sup> for the winter applications (Fig. 2).

At the start of the experiment, concentrations of TP and  $\text{PO}_4\text{-P}$  in surface runoff from ploughed soil were 0.06–2.2 mg l<sup>-1</sup> and 0.010–0.11 mg l<sup>-1</sup>, respectively. During the experiment, TP losses in the control plot decreased, while  $\text{PO}_4\text{-P}$  concentrations and losses increased slightly relative to the ploughed soil (Fig. 2, Table 5). TP and  $\text{PO}_4\text{-P}$  concentrations and losses in surface runoff were not increased after slurry application and immediate ploughing in September 1992.

In contrast, TP and  $\text{PO}_4\text{-P}$  losses were drastically increased after autumn and winter surface applications of slurry in 1993–94 and 1994–95 (Table 5). In surface runoff samples taken after the surface applications in autumn and winter, concentrations of  $\text{PO}_4\text{-P}$  peaked with highest values of 10–25 mg l<sup>-1</sup> (Fig. 2). Although the increase was smaller than for the autumn and winter applications, TP and  $\text{PO}_4\text{-P}$  losses were also increased after slurry and fertilizer applications in spring.

P losses from plots of winter-applied slurry and mineral fertilizer occurred mainly in winter-spring during the highest runoff, while au-

*Turtola, E. & Kempainen, E. N and P losses after application of fertilizers to grass ley*

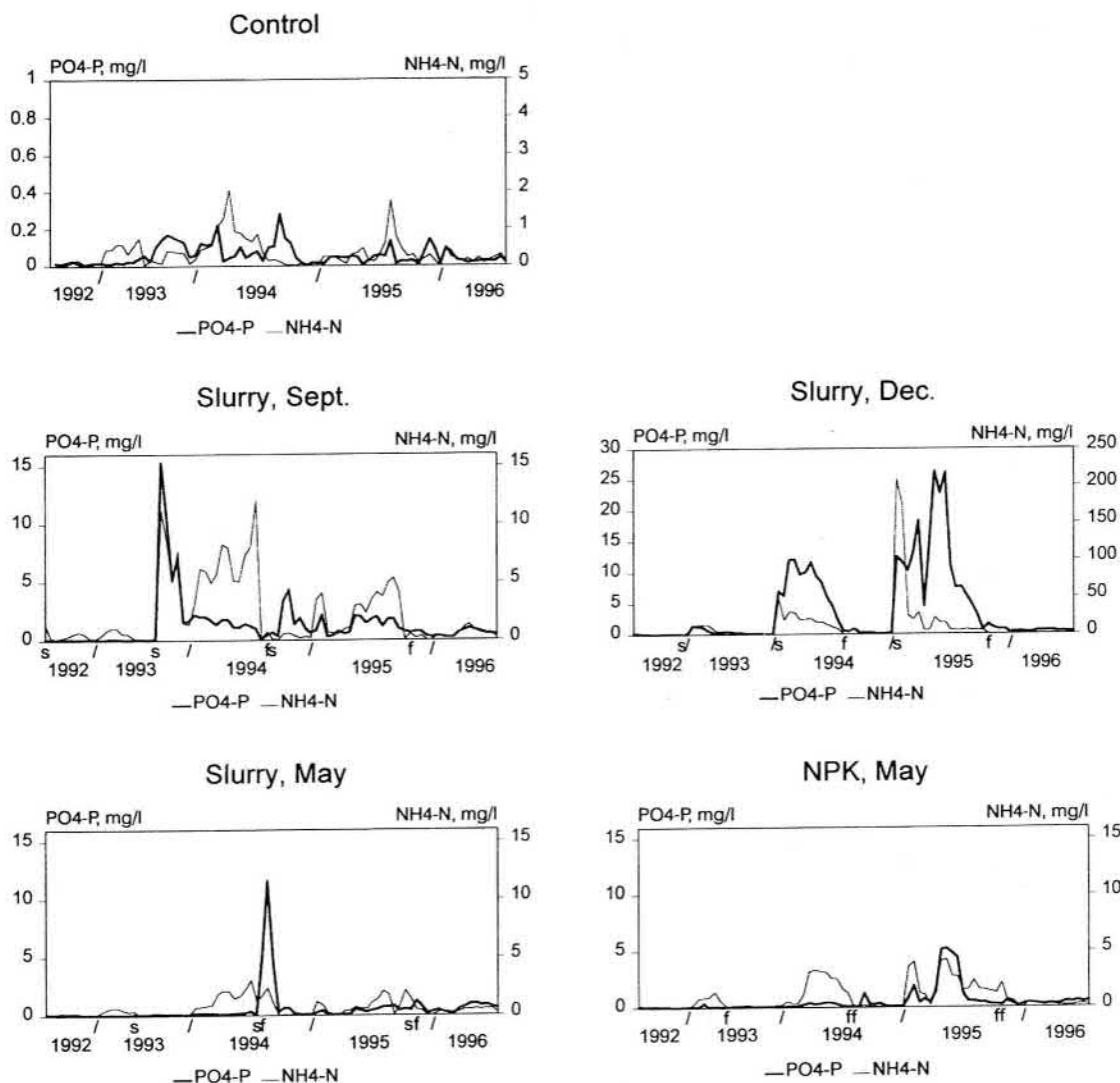


Fig. 2. Concentrations of dissolved orthophosphate phosphorus (PO<sub>4</sub>-P) and ammonium nitrogen (NH<sub>4</sub>-N) (mg l<sup>-1</sup>) in surface runoff in 1992–1996 in the different treatments. Turn of the year denoted by '/' and application times of slurry and mineral fertilizer by 's' and 'f'. Note the different scales on the y-axes.

tumn-applied slurry induced large losses in autumn 1993 and 1994 and spring-applied slurry considerable losses in summer-autumn 1994. Besides showing peaks after surface application of P, the PO<sub>4</sub>-P concentration gradually increased above the base level, to 0.4–0.6 mg l<sup>-1</sup> at the end of the experiment (treatments 2–5). In the con-

trol treatment the concentration remained well below 0.2 mg l<sup>-1</sup> (Fig. 2).

Loss of particulate phosphorus (PP) in surface runoff from ploughed soil and barley in 1992–93 was 0.61–0.78 kg ha<sup>-1</sup> a<sup>-1</sup> (91–95% of TP, treatments 1,2,4 and 5). The growth of ley decreased the loss of PP: loss from the control

Table 6. Dry matter yield ( $\text{kg ha}^{-1}$ ) in 1993–96.

No	Treatment	1993	1994	1995	1996
		Barley	Ley	Ley	Ley
1	Control	1610	1250	1540	— <sup>1</sup>
2	Slurry, Sept.	2750	7530	7980	1950
3	Slurry, Dec.	2790	5150	4730	1370
4	Slurry, May	3310	7320	9250	1040
5	NPK, May	3840	8220	11970	1320

<sup>1</sup> Negligible, not measured

Table 7. Nitrogen and phosphorus input in fertilizer and slurry, removal in harvested crop, surface runoff and drainage water and calculated balance (input-removal) ( $\text{kg ha}^{-1}$ ), with percentage of applied in parenthesis, during 1992–1996.

No	Treatment	Input	Removal				Balance
			Crop		Surface runoff + drainage water		
Nitrogen							
1	Control	0	45		30		−75
2	Slurry, Sept.	772	317	(41)	82	(11)	373
3	Slurry, Dec.	807	213	(26)	216	(27)	378
4	Slurry, May	805	381	(47)	41	(5.1)	383
5	NPK, May	510	531	(104)	41	(8.0)	−62
Phosphorus							
1	Control	0	6.4		1.4		−7.8
2	Slurry, Sept.	141	45	(32)	16	(11)	80 (57)
3	Slurry, Dec.	119	29	(24)	57	(48)	33 (28)
4	Slurry, May	143	52	(36)	4.9	(3.4)	86 (60)
5	NPK, May	107	61	(57)	4.9	(4.6)	41 (38)

plot in 1993–96 was  $0.04\text{--}0.18 \text{ kg ha}^{-1} \text{ a}^{-1}$  (24–60% of TP). For the spring applications of slurry and mineral fertilizer, PP loss was  $0.25\text{--}0.60 \text{ kg ha}^{-1} \text{ a}^{-1}$  (23–51% of TP). The greater losses following autumn and winter applications of slurry on the soil surface ( $0.9\text{--}1.2$  and  $1.9\text{--}8 \text{ kg ha}^{-1} \text{ a}^{-1}$ , respectively) indicated considerable losses of slurry derived PP, which was either in particulate inorganic/organic or in dissolved organic form.

## Calculated N and P balances

The amount of N applied in slurry and mineral fertilizer was the main factor determining the

dry matter yield, and the low N and P uptakes in the control treatment were mostly due to N deficiency. The highest yields were obtained from the mineral fertilizer treatment (Table 6). The N balance indicated a depletion in soil for both the control and the mineral fertilizer treatment (Table 7). Total N input was higher but crop uptake lower for the slurry treatments than the mineral fertilizer treatment, resulting in larger balance values. Slurry applications in autumn and spring resulted in the highest accumulation (balance) of P in soil, partly due to the larger amounts of P applied. Winter application of slurry induced large losses of P in runoff, which reduced the accumulation. P accumulation in soil in the mineral fertilizer treat-



ment was lower compared with slurry application in spring due to the lower applied amount and the higher removal in the harvested crop.

## Discussion

The proportion and amount of surface runoff were increased during the ley years of the study. An increase in the proportion of surface runoff from perennial ley compared with that from barley (soil ploughed in autumn) was also observed on a clay soil in southern Finland (Turtola and Jaakkola 1995, Turtola and Paajanen 1995) and on a loam soil in southern Norway (Uhlen 1978a). Young and Mutchler (1976) measured more surface runoff during spring snowmelt from alfalfa plots compared with ploughed corn plots and explained the difference in terms of smaller depressional storage of water and longer lasting frost on the alfalfa plots.

Besides the larger amount of water in snow, the probable reasons for the abundant surface runoff during cultivation of perennial ley in the present study were the deep and prolonged frost in combination with surface soil compaction. Both factors decreased the water conductivity in the surface layers. After ploughing, the depressional storage to retard surface runoff was larger and the frozen ploughed soil seemed to be more porous due to the recent tillage, enabling water penetration and drainage water flow especially in autumn. During the winter-spring period, however, most of the pores were probably closed by occasional meltwater freezing into the pores thus also increasing the proportion of surface runoff from the ploughed soil.

Low infiltration of water and surface application of slurry proved to be a highly risky combination for N and P losses from ley. N and P compounds were directly lost from the surface-applied slurry in autumn and winter, as shown by the extremely high  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$  concentrations and losses in surface runoff. These concentrations were very similar to those measured

by Edwards & Daniel (1993) in runoff from grass-covered plots exposed to simulated rainfall 24 h after surface application of swine slurry and also to those of Edwards et al. (1996) for pasture fields receiving poultry manure. Likewise, Uhlen (1978b) and Braun and Leuenberger (1991) measured similar  $\text{PO}_4\text{-P}$  concentrations in surface runoff from grassland after off-season manure application without incorporation. Young and Mutchler (1976) reported similar  $\text{NH}_4\text{-N}$  concentrations in surface runoff from alfalfa plots receiving dairy manure and slurry in autumn or winter. N and P losses in the present study attributable to surface application of slurry in autumn and winter were larger than any previously reported losses from cultivated soil in Finland and strongly argue for further restrictions on surface application of slurry on grasslands during autumn.

Although less risky than the applications in autumn and winter, also the spring and summer applications on the soil surface induced much larger  $\text{PO}_4\text{-P}$  losses, with high concentration peaks, than the control treatment or preceding barley. The increase was due to a combination of increased surface runoff from ley, direct loss from surface applied P and accumulation of P in the soil surface. The accumulation of P in the soil surface during the experiment has been separately studied by Turtola and Yli-Halla (1999), who showed that the P not taken up by plants or removed by runoff was accumulated in a shallow layer less than 5 cm thick. Subsequently, the base level of the  $\text{PO}_4\text{-P}$  concentration in surface runoff was increased, from 0.01–0.11  $\text{mg l}^{-1}$  in 1992 up to 0.4–0.6  $\text{mg l}^{-1}$  in spring 1996. Turtola and Jaakkola (1995) found that repeated surface application of mineral fertilizer P on grass ley on a heavy clay soil raised the base level of  $\text{PO}_4\text{-P}$  concentration in surface runoff during three years from less than 0.1 to 0.5  $\text{mg l}^{-1}$ , with concentration peaks (2–5  $\text{mg l}^{-1}$ ) immediately after the application. The peaks and the increase in the base level of  $\text{PO}_4\text{-P}$  concentration demonstrate the environmental risks associated with the surface applications of fertilizers common in perennial ley cultivation.

Compared with surface application, incorporation of the autumn applied slurry by immediate ploughing effectively impeded P losses. The increase in N leaching in drainage water ( $5 \text{ kg ha}^{-1}$ ) relative to the control treatment was small probably because of a slow mineralization of  $\text{NH}_4\text{-N}$  in the prevailing conditions (low soil temperature in autumn, long-lasting frost). In Minnesota, USA, Young and Mutchler (1976) observed that N loss in surface runoff was not significantly increased from manured, fall ploughed plots. In Norway, Uhlen (1978b) found that mixing the manure into the soil efficiently reduced P losses. Data of Niinioja (1993) for a clay soil in eastern Finland suggest no increase in N and P leaching due to autumn incorporation of slurry in comparison with mineral fertilizer treatment. However, considerable increases in nutrient leaching after autumn application of slurry have been measured in warmer climate with high drainage flow during winter or large quantities of applied nutrients (Oskarsen et al. 1996, Carey et al. 1997, Paul and Zebarth 1997).

The lower losses of N and P in surface runoff from winter-applied slurry in the first year were probably partly due to more intensive adsorption of  $\text{NH}_4^+$  and  $\text{H}_2\text{PO}_4^-$  on the ploughed soil surface compared with the ley surface in the later years.

The average  $\text{PO}_4\text{-P}$  concentration in surface runoff from the control plot was slightly higher during the three ley years (0.081, 0.046 and  $0.086 \text{ mg l}^{-1}$ , respectively) compared with the preceding barley cultivation ( $0.025 \text{ mg l}^{-1}$ ). This can probably be attributed to  $\text{PO}_4\text{-P}$  release from the grassy vegetation. In the study of Uhlen (1988), for example,  $\text{PO}_4\text{-P}$  concentration in surface runoff from unfertilized grassland was in the range  $0.1\text{--}0.2 \text{ mg l}^{-1}$  during spring, with even higher concentrations at the outset of snowmelt. In both the present study and that of Uhlen (1988) the resulting  $\text{PO}_4\text{-P}$  losses were 4–5 times as large as losses from ploughed, unfertilized soil. Also McDowell et al. (1989) have reported that  $\text{PO}_4\text{-P}$

P concentrations in almost half of the runoff samples from unfertilized, continuous cotton exceeded  $0.2 \text{ mg l}^{-1}$ , and attributed these, in part, to the release of soluble P from crop residues.

The low level of P found in the drainage water is not surprising as P accumulation was observed only in the 0–5 cm layer (Turtola and Yli-Halla 1999). The low P status and large amounts of oxalate-extractable Fe and Al below the plough layer promoted the adsorption of dissolved P from infiltrating water. After applying slurry in an amount approximately 10 times the grass requirement, Unwin (1980) found no increase of P in soil leachates, although P was accumulated in the 0–30 cm soil layer. Similarly, Dam Kofoed and Søndergaard Klausen (1986), Furrer and Stauffer (1986), Kemppainen (1995) and Cameron et al. (1996) found no increase in P leaching through lysimeters after application of slurry or manure on mineral soils.

A large part of N from the surface-applied slurry was probably lost through ammonia volatilization, which was not measured. Carey et al. (1997) found that in two years following the surface application of pig slurry on a pasture soil ( $\text{N } 200 \text{ kg ha}^{-1} \text{ a}^{-1}$ , comparable to the amount applied in our study), the sum of denitrification and volatilization was 56% of the applied N. Atmospheric losses might thus explain much of the large balance (input-removal) values for N in the slurry treatments.

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## SELOSTUS

### Typen ja fosforin kulkeutuminen pinta- ja salaojavalunnassa lietelannalla ja NPK-lannoitteella lannoitetulta nurmelta

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Typen ja fosforin kulkeutumista heinänurmelta tul-  
leissa valumavesissä tutkittiin Toholammilla hieta-  
maalla kokeessa, jossa oli viisi lannoituskäsittelyä:  
ei lannoitusta (1), naudan lietelannan levitys syksyl-  
lä (2), talvella (3) tai keväällä (4) ja NPK-lannoitus  
keväällä (5). Koejäsenille 1–5 levitettiin kokeen ai-  
kana (1992–96) typpeä yhteensä 0, 772, 807, 805 ja  
510 kg ha<sup>-1</sup> ja fosforia 0, 141, 119, 143 ja 107 kg ha<sup>-1</sup>.  
Nurmen perustamisvuonna 1992–93, kun maa oli  
kynnetty syksyllä 1992, salaojavalunnan osuus koko-  
naisvalunnasta (salaojavalunta + pintavalunta) oli 48–  
60 %. Syksyllä multaamalla tehty lietteen levitys (kä-  
sittely 2) aiheutti hieman suuremman typen kulkeu-  
tumisen (21 kg ha<sup>-1</sup>) kuin käsittelyt 1, 4 ja 5 (17 kg  
ha<sup>-1</sup>), mutta fosforin kulkeutuminen (0.7–0.9 kg ha<sup>-1</sup>)  
ei lisääntynyt. Nurmen viljelyn aikana (1993–96) sa-

laojavalunta väheni ja pintavalunnan osuus kokonais-  
valunnasta oli 83–100 %. Nurmelle pintaan levitetty  
ja käyttämättä jäänyt lannoitefosfori lisäsi ortofos-  
faattikuormitusta pintavalunnassa, minkä lisäksi syk-  
sällä ja talvella levitetystä lietelannasta aiheutui myös  
erittäin korkeita suoria ortofosfaattifosfori- ja ammo-  
niumtyppipäästöjä. Nurmelle syksyllä ja talvella pin-  
taan levitetyn lietteen typpihuuhtoutuma oli 11 % ja  
33 % levitetystä typpimäärästä ja fosforihuuhtoutu-  
ma 17 % ja 59 % levitetystä fosforimäärästä. Typ-  
peä huuhtoutui käsittelyistä 1–5 kolmen nurmivuoden  
aikana yhteensä 13, 62, 191, 23 ja 24 kg ha<sup>-1</sup>, josta  
ammoniumtypen osuus oli 21, 49, 56, 33 ja 39 %.  
Fosforia kulkeutui 0.73, 16, 54, 4.2 ja 4.0 kg ha<sup>-1</sup>,  
josta ortofosfaattifosforin osuus oli 52, 85, 77, 68 ja  
64 %.



## Fate of phosphorus applied in slurry and mineral fertilizer: accumulation in soil and release into surface runoff water

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**Key words:** degree of P saturation, dissolved orthophosphate P, inorganic P fractions, P accumulation, readily extractable P

### Abstract

Phosphorus (P) accumulation on the soil surface and its effect on the concentration of dissolved orthophosphate P ( $\text{PO}_4\text{-P}$ ) in surface runoff water were studied after three years of surface application of slurry and mineral fertilizer to grass ley on a sandy soil, poor in P. The total amount of P applied was  $107\text{--}143\text{ kg ha}^{-1}$ , of which  $72\text{--}119\text{ kg ha}^{-1}$  was applied on the soil surface during two or three years without incorporation or mixing. The addition of slurry and mineral fertilizer resulted in an increase in inorganic P in the  $0\text{--}5\text{ cm}$  but not the  $5\text{--}25\text{ cm}$  soil layer, but organic P was not affected. The measured changes in inorganic P deviated only by  $4\text{--}6\text{ kg ha}^{-1}$  from the values derived from inputs and outputs of P (crop uptake + losses in surface runoff and drainage water). The increase in inorganic-P was accompanied by increases in the degree of P saturation (DPS) and in P extracted with acid ammonium acetate ( $\text{P}_{\text{Ac}}$ ), sodium bicarbonate ( $\text{P}_{\text{Olsen}}$ ) and anion-exchange resin ( $\text{P}_{\text{Resin}}$ ). In surface runoff,  $10\text{--}18$  months after the last surface application of P, the mean flow-weighted concentration of  $\text{PO}_4\text{-P}$  was linearly increased with the values of DPS,  $\text{P}_{\text{Ac}}$ ,  $\text{P}_{\text{Olsen}}$  and  $\text{P}_{\text{Resin}}$  in the  $0\text{--}5\text{ cm}$  soil layer.  $\text{PO}_4\text{-P}$  was lowest ( $0.033\text{ mg l}^{-1}$ ) in the control plots and highest ( $0.62\text{ mg l}^{-1}$ ) in the plot where  $143\text{ kg ha}^{-1}$  P had been applied in slurry and fertilizer. On that plot, the corresponding values of DPS,  $\text{P}_{\text{Ac}}$ ,  $\text{P}_{\text{Olsen}}$  and  $\text{P}_{\text{Resin}}$  were 16%,  $13\text{ mg kg}^{-1}$ ,  $85\text{ mg kg}^{-1}$  and  $71\text{ mg kg}^{-1}$ , respectively. The results showed that on a low P soil, surface applications of slurry and mineral fertilizers may considerably increase the P status at the soil surface, even within a few years, and multiply the P loading to surface runoff from the site. A very shallow soil sampling ( $< 5\text{ cm}$ ) is needed to assess P loading potential in a soil where P has been surface-applied.

### Introduction

Grasses, mostly in rotation with grain crops like barley and oats, occupy  $684\,000\text{ ha}$  (32%) of the arable land in Finland (Statistics Finland, 1997). Nearly half of the grassland is harvested for silage, one third for dry hay, with the rest used as pasture throughout the summer. Particularly in central and northern Finland, dairy farming is by far the most important source of farm income, and in a majority of farms most of the fields are sown with grasses. These farms are not able to apply all manure or slurry to the often very limited area of arable crops and thus slurry application to perennial ley cultivation is common. Because of insufficient storage capacity, slurry is also applied during autumn

and was earlier applied on frozen soil during winter as well. The winter application results in high losses of P in surface runoff (Brink et al., 1983; Turtola and Kemppainen, 1998; Uhlen, 1978), and the practice has been much reduced in the 1990s. Phosphorus (P) in mineral fertilizers is also almost exclusively surface-applied to grasslands. Surface application of fertilizer P has been shown to induce larger losses of dissolved P in surface runoff than does incorporation of fertilizer (Timmons et al., 1973; Turtola and Jaakkola, 1995; Uhlen, 1978).

Besides leading to high direct losses of P due to rain and snowmelt, repeated surface application of P gradually leads to accumulation of P. Heavy applications of P in slurry or manure can even increase the



P saturation of the whole soil profile (De Smet et al., 1996; Holford et al., 1997; Laves and Thum, 1984). Lyngstad and Tveitnes (1996) and Sharpley and Smith (1995) reported that surface application of slurry or manure influenced P status mainly in the 0–5 cm layer. In the acid soils of Finland, residual fertilizer P accumulates in Al- and Fe-bound forms (Hartikainen, 1989). The P sorption capacity of acid soils is dominated by their poorly crystalline Al- and Fe-oxide content (Breeuwsma and Silva, 1992; Lookman et al., 1995). Degree of P saturation (DPS) of poorly crystalline Al and Fe compounds, determined as a molar ratio of oxalate-extractable P and Fe + Al, has been used as an indicator of the residual P sorption capacity of soil and identification of soils from which high loads of P may be expected to enter watercourses. Holford et al. (1997) found, for example, that P leaching began when 17–38% of the sorption capacity of soil horizons had become saturated. In The Netherlands, DPS of 25% is considered the critical value for P movement in surface and subsurface water (Van der Zee et al., 1987).

This paper reports a case study where cow slurry and/or mineral fertilizers were surface-applied to a soil originally poor in P. The accumulation of added P in the topsoil is documented and the influence of this on the dissolved orthophosphate P ( $\text{PO}_4\text{-P}$ ) concentration of surface runoff water is discussed.

## Materials and methods

### *The experimental field*

The experimental field (2.56 ha) was located in Toholampi, western Finland, and had a mean slope of 0.5%. The fine sandy soil was tentatively classified as Haplic Podzol (FAO, 1988) or Aquic Haplocryd (Soil Survey Staff, 1992). The 25–35 cm horizon was the spodic horizon, characterized by the abundance of oxalate-extractable Fe and Al and high organic C content (Table 1). In most of the field, the albic horizon and the upper part of the spodic horizon had been ploughed into the  $A_p$  horizon.

The field constituted of 16 drainage plots (1–16), 16 m  $\times$  100 m, with separate drainage systems to collect the drainage flow from the depth of 1 m for volume measurement with tipping buckets and flow-weighted sampling with funnels conducting 0.24% of the flow to plastic containers. The plots were isolated hydrologically from each other and from the surrounding area with 0.3 m high ridges formed from mounded

earth and by a plastic sheet extending to the depth of 1.5 m. The surface runoff water was collected at the lower end of five drainage plots (plots 12–16) into 0.2 m deep open ditches strengthened with concrete for similar measurement and sampling as the drainage flow. A detailed description of the field can be found in Turtola and Kemppainen (1998).

### *The experimental design*

A four-year experiment comprising five P application practices was carried out in 1992–1995 (Table 2) on plots 2–16. The experiment was arranged as a randomized complete block design with three replications. The first and second blocks were set out on plots 2–11 with drainage water collection only, while the third block comprised plots 12–16 with both drainage and surface runoff collection. In Treatment 1, no slurry or mineral fertilizer was applied. In Treatment 2, slurry was applied at the beginning of the experiment in September 1992 and the soil was immediately ploughed to a depth of 22 cm. For Treatment 3, slurry was surface-applied on a snow-covered soil in December 1992. For Treatment 4, slurry was surface-applied in May 1993 and the soil was immediately harrowed to a depth of 5 cm. For Treatment 5, NPK fertilizer was applied in May 1993 by placement technique to a depth of 8 cm along with sowing. Spring barley was sown on all plots, with timothy and meadow fescue interseeded. Barley was harvested on 31 September 1993. Thereafter timothy-meadow fescue ley was grown, and cut twice a year in 1994–95.

From autumn 1993 onwards, fertilizer and slurry applications were made to the soil surface in September (Treatment 2), in December–January (Treatment 3) and in May (Treatments 4 and 5), with no incorporation or mixing with the soil. During the ley years in 1994–1995, additional P in NPK fertilizer was surface-applied a week after the first cutting in June–July for the Treatments 2–5. The last P applications were made in summer 1995. There were no cuttings and no nutrients applied in 1996 and the ley was ploughed in September 1996.

The amount of soluble N applied (nil in Treatment 1, 75–124 kg ha<sup>-1</sup> a<sup>-1</sup> for barley and 189–228 kg ha<sup>-1</sup> a<sup>-1</sup> for ley in Treatments 2–5; Turtola and Kemppainen, 1998) was the main factor determining the yield, which varied between 2000 and 4500 kg ha<sup>-1</sup> (dry matter DM) for barley and between 1300 and 12 000 kg ha<sup>-1</sup> a<sup>-1</sup> (DM) for ley. The low P up-



Table 1. Characteristics of the experimental soil. Values in parentheses indicate the range

Depth, cm	Texture	pH (water)	Org. C, %	Al <sub>ox</sub> , mmol kg <sup>-1</sup>	Fe <sub>ox</sub> , mmol kg <sup>-1</sup>
0–25	Fine sand	5.7 (5.6–5.8)	5.0 (4.8–5.3)	96 (89–104)	30 (18–47)
25–35	Fine sand	5.2 (5.2–5.3)	2.6 (2.2–3.1)	145 (130–159)	93 (79–107)
35–60	Fine sand	5.3 (5.2–5.3)	0.3 (0.3–0.4)	37 (33–41)	75 (66–84)

Table 2. Treatments and P input in slurry and fertilizer, removal in harvested crop and runoff, calculated balance (input-removal) and measured balance, kg ha<sup>-1</sup>, during 1992–1996

Treatment	Input				Removal			Accumulation in soil		
	Slurry	Fertilizer	Total (of which on surface)		Crop	Runoff	Total	Calculated	Measured	(% of added P)
1) No fertilizers applied	0	0	0	(0)	6.4	1.4	7.8	–7.8	–12	(–)
2) Slurry in September	119	22	141	(92)	45	16	61	80	76	(54%)
3) Slurry in December	97	22	119	(119)	29	57	86	33	29	(24%)
4) Slurry in May	121	22	143	(110)	52	4.9	57	86	82	(57%)
5) NPK fertilizer in May	0	107	107	(72)	61	4.8	66	41	35	(33%)

take in Treatment 1 was strongly associated with the low yields.

#### Analyses of P in soil and water

Soil samples were taken to determine the P status of the soil before the experiment from all plots on 15 May 1991 from depths of 0–25, 25–35 and 35–60 cm. After the experiment, samples were taken from all plots from depths of 0–25, 25–60 and 60–90 cm on 13 November 1995 and from depths 0–5 and 5–25 cm on 13 September 1996. The samples were air-dried, homogenized and stored at room temperature. The findings for samples from the 0–5 and 5–25 cm layers taken in 1996 and from the 25–60 and 60–90 cm layers taken in 1995 were considered to represent the P status of the soil at the end of the experiment. It was assumed that at the beginning of the experiment the whole plough layer (0–25 cm) was homogeneous due to the annual ploughing. Thus the findings for the samples from the 0–25 cm layer were taken to represent the initial P status of both the 0–5 cm and the 5–25 cm layers.

Total P (TP) in soil was determined by wet digestion with concentrated H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub> and HF. Inorganic P reserves were fractionated according to a modified Chang and Jackson method (Hartikainen, 1979), where inorganic P (TIP) was sequentially extracted with NH<sub>4</sub>Cl (P<sub>NH4Cl</sub>), NH<sub>4</sub>F (P<sub>NH4F</sub>), NaOH (P<sub>NaOH</sub>) and H<sub>2</sub>SO<sub>4</sub> (P<sub>H2SO4</sub>). NH<sub>4</sub>Cl was used as an

extractant mainly to remove exchangeable Ca. NH<sub>4</sub>F was assumed to extract P bound by Al-oxide, NaOH to extract P bound by Fe-oxide and H<sub>2</sub>SO<sub>4</sub> to dissolve P contained in apatite. The amount of total organic P (TOP) was calculated as the difference between TP and TIP.

The degree of P saturation (DPS, %) of the hydrous oxides (Breeuwsma and Schoumans, 1986; Lookman et al., 1995) was calculated as a molar ratio of (P<sub>NH4F</sub> + P<sub>NaOH</sub>) / 0.5(Al<sub>ox</sub> + Fe<sub>ox</sub>). The amounts of Al and Fe in hydrous oxides (Al<sub>ox</sub>, Fe<sub>ox</sub>) were estimated by extraction of samples with 0.05 M ammonium oxalate, pH 3.3 (Niskanen, 1989). P bound by the hydrous oxides (P<sub>NH4F</sub> and P<sub>NaOH</sub>) was measured by the modified Chang and Jackson fractionation method referred to above. Despite the lower concentration and higher pH in our oxalate solution (0.05 M, pH 3.3) as compared with the values of Lookman et al. (1995) (0.2 M, pH 3.0), it presumably extracts Al and Fe equally effectively (see Niskanen, 1989), while the NH<sub>4</sub>F and NaOH, which dissolve all secondary P, probably extract P at least as effectively as does the oxalate. On this basis it can be concluded that the DPS values obtained do not differ markedly from those that would have been obtained by the method of Lookman et al. (1995).

Readily extractable P was obtained by extracting soil samples in three ways: with 0.5 M ammonium acetate–0.5 M acetic acid, pH 4.65 (Vuorinen and Mäkitie, 1955) (P<sub>Ac</sub>), which is the method used in

agronomic soil P testing in Finland; with 0.5 M NaHCO<sub>3</sub>, pH 8.5 (Olsen and Sommers, 1982) (P<sub>Olsen</sub>); and with anion-exchange resin (Sibbesen and Rubaek, 1994) (P<sub>Resin</sub>). To estimate P release from soil to runoff water, P was further extracted with water (P<sub>w</sub>) at solution-to-soil ratios of 200:1, 500:1 and 2000:1 (Yli-Halla et al., 1995).

Flow-weighted water samples were collected throughout the experiment in 1992–96 from surface runoff water from plots 12–16, each representing one of the Treatments 1–5. During the time of perennial ley in 1993–96, surface runoff averaged as much as 83–100% of the annual total runoff (surface runoff + drainage) with 67–89% of the total runoff occurring in late winter and spring mostly during snowmelt. The total number of sampling dates in 1992–96 was 89 and the average sampling interval 16 days, varying from half a day to four months. The samples were filtered through Nucleopore 0.2 µm filter and the concentration of dissolved orthophosphate P (PO<sub>4</sub>-P) was determined by the method of Murphy and Riley (1962). The annual losses of total P and dissolved orthophosphate P in surface runoff and drainage water are presented in Turtola and Kempainen (1998).

In the present paper, only the mean concentrations of PO<sub>4</sub>-P in surface runoff are presented for spring 1996 (7 April–13 May), i.e. 10–18 months after the last applications of slurry or fertilizer. The mean concentration of PO<sub>4</sub>-P in surface runoff was calculated by dividing the loss of dissolved orthophosphate in surface runoff during spring 1996 by the surface runoff volume during spring 1996. The number of individual sampling dates in spring 1996 was 13, representing altogether 128–141 mm of surface runoff, mostly from snowmelt in April of a snowcover containing 120 mm of water.

### Statistical analyses

For the response variables tested statistically (TIP, P<sub>NH4F</sub>, P<sub>NaOH</sub>, TOP, DPS and P<sub>Ac</sub>) repeated measurements were made at two depths (0–5 and 5–25 cm). However, there were fairly large inherent differences in the values of the variables between the plots. As a means of eliminating these differences, the values of the variables at the start of the experiment were used as covariates in the models. Consequently, the model used was the following repeated-measures model:

$$y_{ijk} = \mu + \beta x_{ijk} + B_i + T_j + w_{ij} + D_k + (TD)_{jk} + e_{ijk} \quad (1)$$

Table 3. Different forms of P (mg kg<sup>-1</sup>) in 1996 at end of the experiment

Depth	P <sub>NH4F</sub>	P <sub>NaOH</sub>	P <sub>H2SO4</sub>	Total organic P (TOP)	Total P (TP)
0–5 cm	132–255	74	157	479	809–995
5–25 cm	148	61	149	441	799

where  $y_{ijk}$  is the variable response for the block  $i$ , treatment  $j$  and depth  $k$ ;  $\mu$  is a constant;  $x_{ijk}$  is the value of the variable at the start of the experiment for the block  $i$ , treatment  $j$  and depth  $k$ ;  $\beta$  is the regression coefficient for the regression of the value of the variable on the value at the start of the experiment;  $B_i$  is a random block effect;  $T_j$ ,  $D_k$  and  $TD_{jk}$  denote fixed effects of treatment, depth and their interaction;  $w_{ij}$  and  $e_{ijk}$  denote the whole plot error and the subplot error. The random variables  $B_i$ ,  $w_{ij}$  and  $e_{ijk}$  were assumed independent and normally distributed with zero means and constant variances. The model was similar to the split-plot model with a covariate. The model was fitted using the residual maximum likelihood (REML) estimation method.

Where the interaction of treatment and depth was statistically significant (TIP, P<sub>NH4F</sub>, DPS and P<sub>Ac</sub>), analyses were continued at different depths by calculation of 95% t-type confidence intervals (95% CI), where the degrees of freedom were calculated by the Satterthwaite method (SAS Institute Inc., 1996). If zero is not included in a confidence interval, the difference is statistically significant at 5% risk level.

### Results

At the start of the experiment, the mean content of total P (TP) at 0–25 cm was 819 mg kg<sup>-1</sup>, where the proportions of organic (TOP) and inorganic P (TIP) were 455 mg kg<sup>-1</sup> (56%) and 364 mg kg<sup>-1</sup> (44%), respectively. Except for a slight decrease in Treatment 2 in the 5–25 cm soil layer, slurry and fertilizer applications had no statistically significant effect on the amount of TOP in the 0–5 cm or 5–25 cm layers (Table 3, detailed results not presented). The P applications increased TIP significantly, but only in the 0–5 cm layer. The measured changes of TIP deviated only by 4–6 kg ha<sup>-1</sup> from the values derived from the inputs and outputs of P (Table 2).

P forms extracted with NH<sub>4</sub>F (P<sub>NH4F</sub>) and H<sub>2</sub>SO<sub>4</sub> (P<sub>H2SO4</sub>) dominated in the plough layer (0–25 cm)

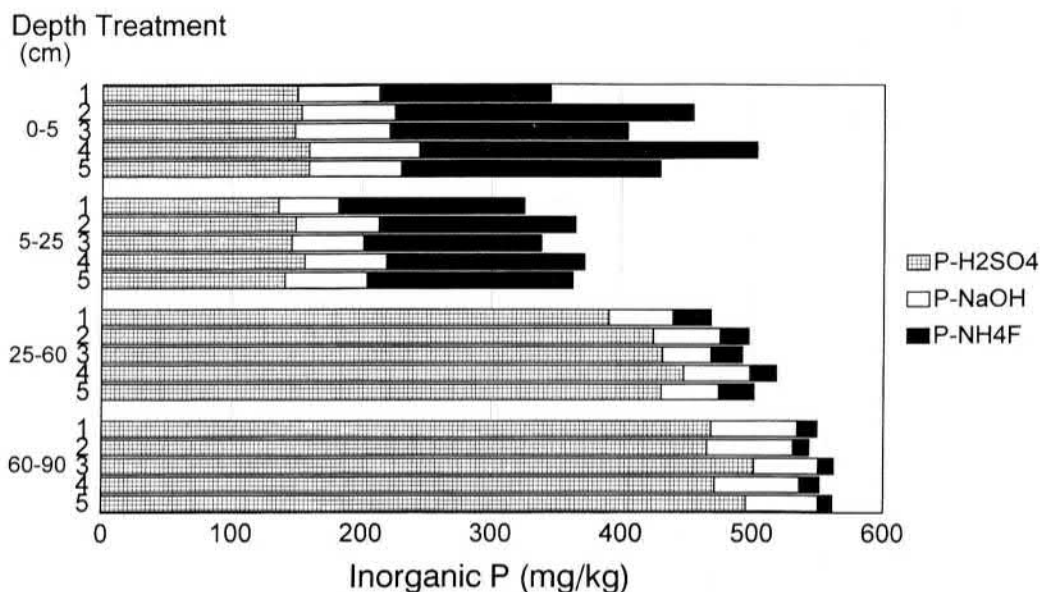


Figure 1. Inorganic P fractions ( $P_{NH_4F}$ ,  $P_{NaOH}$  and  $P_{H_2SO_4}$ ) in 0–5, 5–25, 25–60 and 60–90 cm soil layers at end of the experiment, for the five treatments: 1 = No fertilizers applied, 2 = Slurry in September, 3 = Slurry in December, 4 = Slurry in May, 5 = NPK fertilizer in May.

(Figure 1). Amounts of P extracted with  $NH_4Cl$  ( $P_{NH_4Cl}$ ) were negligible and were therefore summed with  $P_{NH_4F}$ . The  $P_{NH_4F}$  content of the 0–5 cm layer was increased ( $p < 0.05$ ), and the increase was greatest in Treatments 2 and 4 (Table 4), which received the largest amounts of P (Table 2). The slurry application in December induced very high direct losses of P from the slurry in surface runoff during 1993–95 (Turtola and Kemppainen, 1998, Table 2), which reduced the accumulation in soil (Table 4). The P accumulation in the NPK plots was lower compared with slurry application in spring due to the smaller amount applied and the higher yields and removal of P in harvest. In the control (0 P), the calculated P depletion of the soil was slight owing to the low yield (attributable mainly to the lack of N fertilization) and, consequently, the small amount of P removed in the harvested crop.

Relative to  $P_{NH_4F}$  values at the start of the experiment, P applications in Treatments 2, 3, 4 and 5 increased  $P_{NH_4F}$  in the 0–5 cm layer by 75, 25, 88 and 26  $mg\ kg^{-1}$  respectively. In the 0 P treatment,  $P_{NH_4F}$  decreased by 25  $mg\ kg^{-1}$ . Added P was found only to a small extent as  $P_{NaOH}$  and not at all as  $P_{H_2SO_4}$ . Below the plough layer,  $P_{H_2SO_4}$  was the dominant P form (83–89%) (Figure 1), reflecting the low degree of weathering. The low level of  $P_{NH_4F}$  deeper in the pro-

file suggests that transport of inorganic P downwards from the plough layer was minimal.

Before P applications, the DPS was 10% in the plough layer. After surface application of P in Treatments 2–5, the DPS was increased in the 0–5 cm layer but was not significantly affected below that depth (Table 4). Below 25 cm, DPS was 2–4%. In good accord with the changes in DPS during the experiment,  $P_{Ac}$  was slightly lowered in the top layer (0–5 cm) in the 0 P plots, and elevated in the top layer in the Treatments 2–5.

Accumulation of P in the surface layer was also reflected in the amounts of P desorbed from the 0–5 cm soil layer with water at different solution-to-soil ratios (200:1, 500:1, 2000:1) (Figure 2). At the highest solution-to-soil ratio (2000:1), water extraction achieved a recovery of 25–29% of the P added in the slurry amended plots and 48% of that added in mineral fertilizer. The treatments did not influence the P desorption with water from the 5–25 cm soil layer, and the desorption of P from that layer in all treatments (results not shown) was close to the P desorption from the 0–5 cm layer of the unfertilized plots shown in Figure 2.

The changes in DPS and  $P_{Ac}$  in the five plots from where surface runoff water was analysed were in good accord with the changes measured in the other two

Table 4. Total inorganic P (TIP),  $P_{NH4F}$ , degree of P saturation (DPS) and P extracted with acid ammonium acetate ( $P_{Ac}$ ) at soil depths 0–5 and 5–25 cm in 1996 at end of the experiment. Differences (Diff.) and confidence intervals (95% CI) refer to the difference between the mean of the Treatment in question and the mean of Treatment 1

Treatment	$P_{NH4F}$ , mg kg <sup>-1</sup>			DPS, %			$P_{Ac}$ , mg kg <sup>-1</sup>		
	Mean <sup>a</sup>	Diff.	95% CI	Mean <sup>a</sup>	Diff.	95% CI	Mean <sup>a</sup>	Diff.	95% CI
Depth 0–5 cm									
1) No fertilizers applied	132			10.0			6.9		
2) Slurry in September	232	100	78, 123	16.4	6.4	5.0, 7.9	12.2	5.3	4.2, 6.3
3) Slurry in December	185	53	30, 75	13.2	3.2	1.7, 4.6	9.9	3.0	2.0, 4.1
4) Slurry in May	255	123	100, 146	16.4	6.4	5.0, 7.9	13.3	6.4	5.3, 7.4
5) NPK fertilizer in May	195	63	40, 86	14.2	4.2	2.6, 5.8	10.5	3.6	2.5, 4.6
Depth 5–25 cm									
1) No fertilizers applied	145			10.4			7.5		
2) Slurry in September	154	8.6	–14, 31	11.0	0.6	–1.0, 2.2	7.5	0.0	–1.0, 1.1
3) Slurry in December	138	–6.7	–29, 16	9.8	–0.6	–2.1, 0.8	7.1	–0.4	–1.4, 0.7
4) Slurry in May	147	2.4	–21, 25	9.8	–0.6	–2.2, 1.0	7.3	–0.2	–1.2, 0.9
5) NPK fertilizer in May	154	8.5	–14, 32	11.0	0.6	–0.8, 2.1	7.3	–0.2	–1.2, 0.8

<sup>a</sup> Covariate adjusted treatment means. Treatment means at start of the experiment were used as covariate.

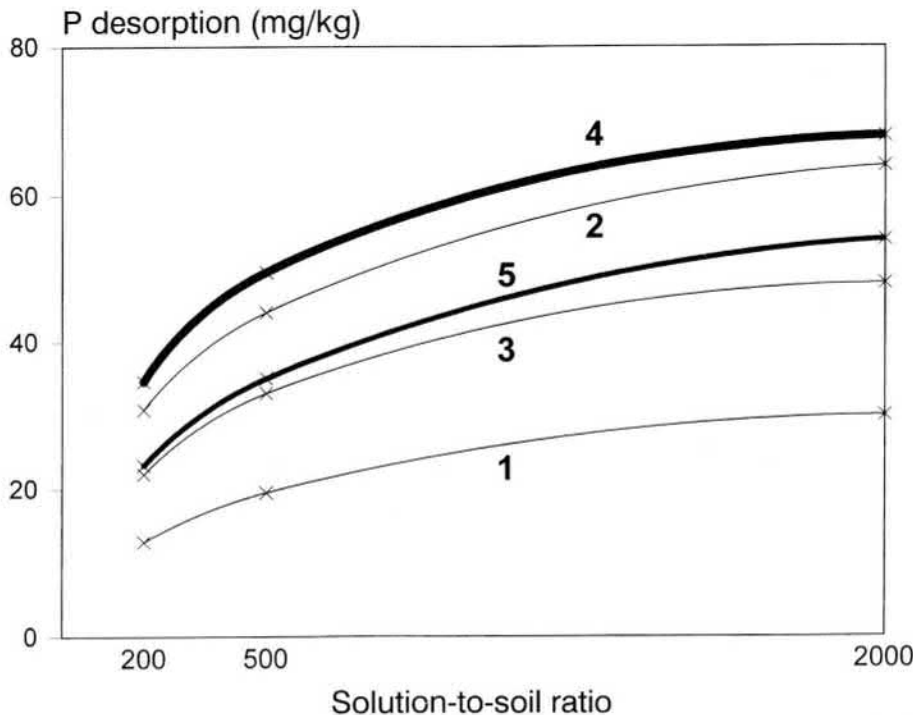


Figure 2. Water soluble P in the 0–5 cm soil layer determined with different solution-to-soil ratios for the five treatments: 1 = No fertilizers applied, 2 = Slurry in September, 3 = Slurry in December, 4 = Slurry in May, 5 = NPK fertilizer in May.

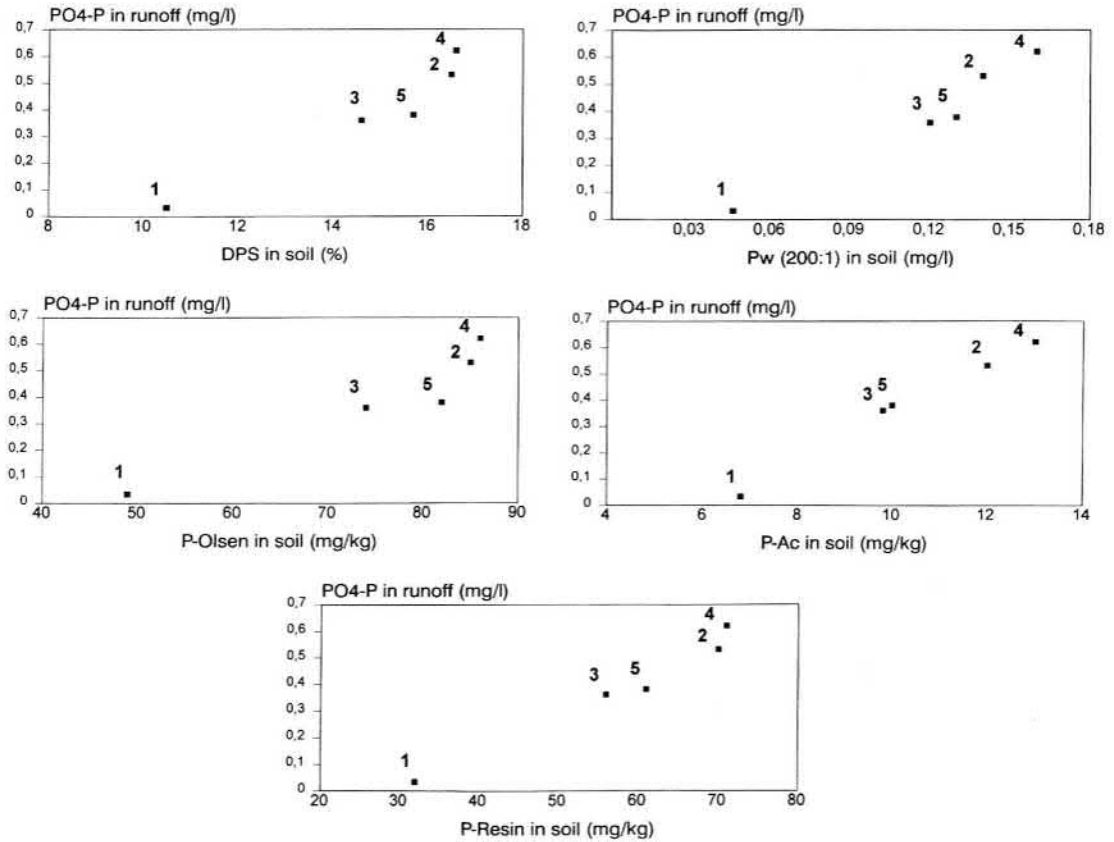


Figure 3. Relationship between mean concentration of dissolved orthophosphate P ( $\text{PO}_4\text{-P}$ ) in surface runoff and degree of P saturation (DPS), P extracted with water ( $P_w$ , solution-to-soil ratio 200:1), sodium bicarbonate (P Olsen), acid ammonium acetate (P Ac) and anion exchange resin (P-Resin) in the 0–5 cm soil layer at end of the experiment, for the five treatments: 1 = No fertilizers applied, 2 = Slurry in September, 3 = Slurry in December, 4 = Slurry in May, 5 = NPK fertilizer in May.

plots with the same treatment where there were no facilities to collect the surface runoff. In the five surface runoff plots, soil P status in the 0–5 cm layer, measured as DPS,  $P_w$ ,  $P_{\text{Olsen}}$ ,  $P_{\text{Ac}}$  and  $P_{\text{Resin}}$ , correlated closely ( $r \geq 0.96$ ) with the mean  $\text{PO}_4\text{-P}$  concentration in the surface runoff water in spring 1996 (Figure 3). The P concentration of the water extracts at the solution-to-soil ratio of 200:1 was strongly influenced by the increased level of P in the surface soil. In the 0 P treatment,  $\text{PO}_4\text{-P}$  in the surface runoff and  $P_w$  (200:1) values were close to each other. Where P was applied, however, the  $\text{PO}_4\text{-P}$  values were higher than the average  $P_w$  (Figure 3).

## Discussion

Under ample P supply, P uptake by the crop is mainly determined by the size of the yield. Higher P supply does not, therefore, result in higher uptake but instead in higher accumulation in soil or leaching. The measured accumulation of inorganic P in the top 5 cm of the soil was close to estimates derived from the P balances for both the slurry amended plots and the plots receiving only mineral fertilizers. According to Van Faassen and Van Dijk (1987), only 5–15% of total P in slurry remained in organic compounds after storage for two months irrespective of the initial distribution between organic and inorganic forms. Although organic P content of slurry was not measured in the present study, some P in the applied slurry

must have been bound in organic compounds. However, during the experimental period this organic P has been mineralized since accumulation of organic P was not observed. Chardon et al. (1997) observed that six years after application of a large amount of pig slurry there was almost no difference in the P composition of soil solution of the slurry amended plots and plots receiving only mineral fertilizers. The present results are consistent with these results and suggest that the sum of Chang and Jackson inorganic P fractions gives a reliable estimate of the accumulation of P after a short-term P application. Moreover, after long-term P application, Sharpley and Smith (1995) found that the increase in P was greater for inorganic than for organic fractions on plots where slurry and manure had been applied up to 35 years; and Rubaek and Sibbesen (1995), in turn, found no difference in the amounts of total organic P between plots receiving NPK fertilizer and plots receiving slurry for 100 years.

The DPS values we recorded in the top 5 cm were low ( $< 17\%$ ), even after the slurry applications, compared with values found in an area of intensive animal production in northern Belgium, where the average DPS in the plough layer was 53% (Lookman et al., 1995). This is probably due to higher Al and Fe contents and smaller amounts of P applied in the past in the soil of the present study. The low DPS in the present soil at the start of the experiment is in agreement with the  $P_{Ac}$  value, which was lower than the median of  $8 \text{ mg l}^{-1}$  in cultivated soils of Finland. According to the results of Saarela et al. (1995), crops growing on this soil required  $30\text{--}60 \text{ kg ha}^{-1} \text{ a}^{-1}$  fertilizer P for optimal growth, confirming that the amounts of P applied in slurry and NPK in the present experiment represented no over-fertilization. Moreover, the average  $\text{PO}_4\text{-P}$  concentration in surface runoff water of the present unmanured plot was as low as  $0.03\text{--}0.04 \text{ mg l}^{-1}$ . However, the present results also show that two to three surface applications of slurry and mineral fertilizers can elevate DPS and readily extractable P at the surface, even on soil with low P status initially. Together with the results showing large direct P losses from surface-applied slurry and mineral fertilizer in surface runoff from the experimental plots (Turtola and Kempainen, 1998), the present results suggest that subsurface placement of P on perennial leys would greatly reduce the P loading potential compared with surface application.

Yli-Halla et al. (1995) found that the  $\text{PO}_4\text{-P}$  concentration of surface runoff water from two clay soils corresponded to the  $P_w$  values obtained at solution-to-

soil ratios of 250:1–100:1. In the present fine-sandy soil,  $\text{PO}_4\text{-P}$  measured in the surface runoff water was close to  $P_w$  (200:1) value ( $0.033$  vs.  $0.046 \text{ mg l}^{-1}$ ) only in the 0 P Treatment. In the other treatments where P was applied on the soil surface,  $\text{PO}_4\text{-P}$  values were much higher than the respective  $P_w$  values ( $0.36\text{--}0.62 \text{ mg l}^{-1}$  vs.  $0.12\text{--}0.16 \text{ mg l}^{-1}$ ). Possible explanations for the higher  $\text{PO}_4\text{-P}$  values include (1) leaching of fertilizer and slurry P not adsorbed by the soil; (2) release of P from the vegetation (McDowell et al., 1989; Uhlen, 1988); (3) difference in the P release characteristics of the present fine sand soil and the clay soils investigated earlier and (4) interaction with the surface runoff not of the whole 0–5 cm layer used in the water extraction but of a shallower layer.

Explanation (1) is unlikely since we monitored the P concentration of the surface runoff water for 10–18 months after the last surface application of P. In our view, explanation (4) offers the most likely reason for the high  $\text{PO}_4\text{-P}$  concentrations. The 0–2 cm layer is the most runoff-sensitive portion of the surface soil (Sharpley and Withers, 1994), especially in perennial leys (Sharpley et al., 1996; Nash and Murdoch, 1997). In the present study, it is very probable that P saturation and  $P_w$  values were in fact much higher in the top 1–2 cm than in the 5 cm layer as a whole. Corroborating this, on a silt loam soil under grass Pote et al. (1996) found a high correlation between the  $\text{PO}_4\text{-P}$  concentration of runoff and the amount of water extractable P of the 0–2 cm soil layer. According to Holford et al. (1997) and Van der Zee et al. (1987), DPS values of 17–38% and 25%, respectively, are required before considerable P leaching will begin. The mean concentrations of  $\text{PO}_4\text{-P}$  in surface runoff in spring 1996 ( $0.53\text{--}0.62 \text{ mg l}^{-1}$ ) in the present plots earlier top-dressed with slurry in autumn or spring were too high for the DPS value of 16.4% measured in the 0–5 cm layer, but rather the  $\text{PO}_4\text{-P}$  concentrations must have been produced by a shallower surface soil with substantially higher DPS.

The thin soil layer enriched with surface-applied P is the same soil layer that interacts closely with surface runoff water, which, in turn, extracts more P at elevated DPS. Routine soil tests, such as  $P_{Ac}$  and  $P_{Olsen}$ , have been developed to estimate plant available P. Our study, in agreement with the work of Sharpley et al. (1977), shows that these tests may also be used to estimate the  $\text{PO}_4\text{-P}$  loading potential. Samples for soil testing are commonly taken from the surface to a depth of 25 cm. For agronomic needs this procedure may be satisfactory, particularly when the soil is ploughed



annually. However, if fertilizers are applied to the soil surface, resulting in a substantially higher P status in a thin surface soil of a few centimetres, the P loading of the soil needs to be estimated with a shallow sampling. For perennial leys where fertilizer or slurry is surface applied, samples should be taken from 0–2 or 0–5 cm layers, for example. Deeper sampling very much underestimates the P loading from top-dressed soils, especially for soils with originally poor or moderate P status.

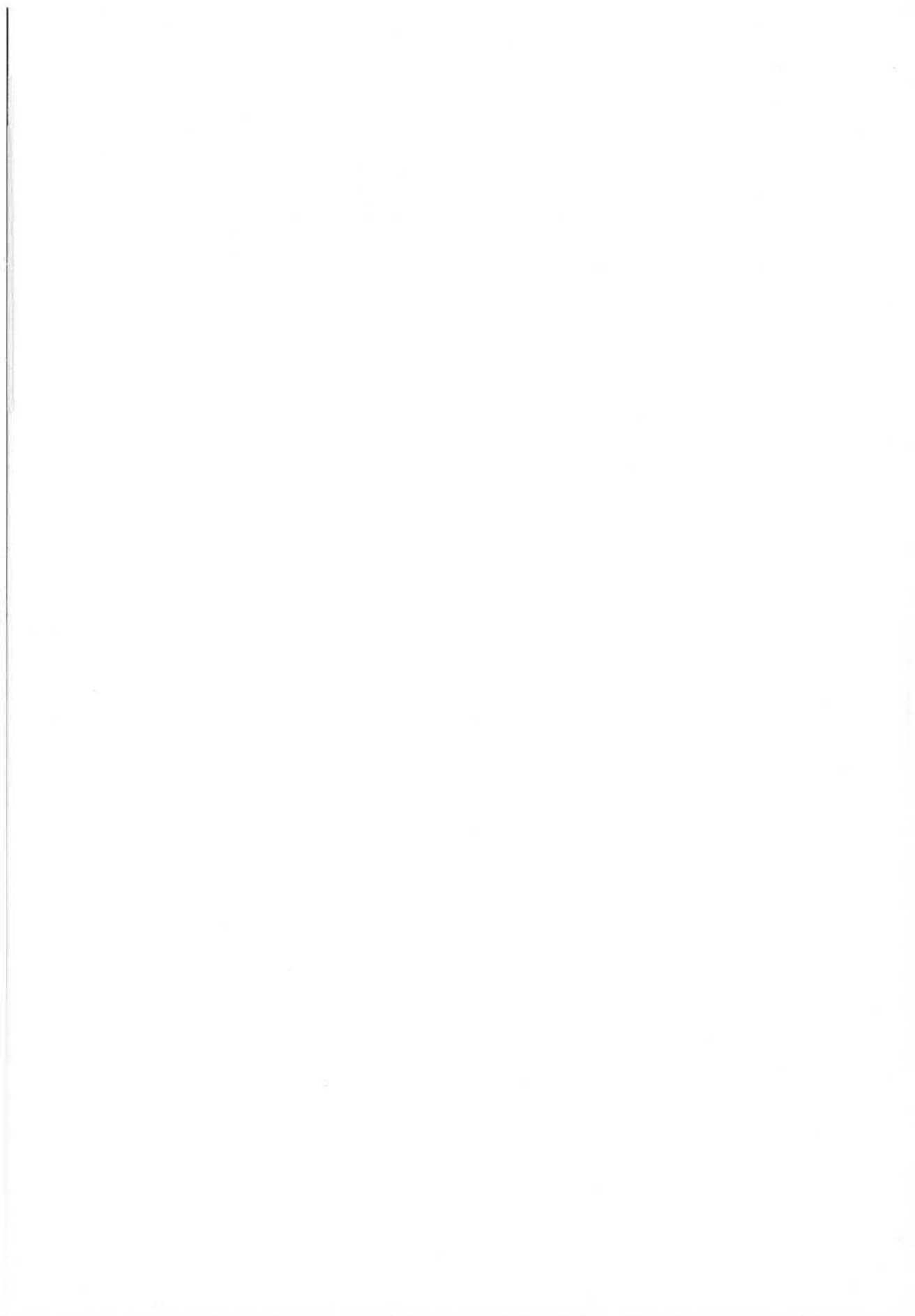
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