



Potential bioavailability of particulate phosphorus in runoff from arable clayey soils

Doctoral Dissertation

Risto Uusitalo



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particulate phosphorus in runoff
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Risto Uusitalo

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Potential bioavailability of particulate phosphorus in runoff from arable clayey soils

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Abstract

Runoff phosphorus (P) associated with eroded soil contributes to eutrophication to some extent. The present work examines two methods for estimating the potential bioavailability of particulate P (PP) in runoff, and studies the concentrations and losses of different P forms in surface and subsurface runoff from arable soils. The potential bioavailability of PP was approximated by extraction with (i) anion exchange resin (AER-PP), giving a measure of desorbable PP under aerobic conditions, and with (ii) bicarbonate-dithionite (BD-PP), which dissolves redox-labile PP. Both methods were applied in runoff analysis without sediment preconcentration. In turbid runoff, AER extracted about 50% of the PP pool utilized by *Selenastrum capricornutum* in 3-week biotests. The AER-PP yields correlated well ($R^2 = 0.94$) with the algal uptake of PP. The BD extraction solubilized 5–6 times the amount of PP extracted by AER. Of the total P of rock phosphates (Ca-P) and P-amended synthetic Al and Fe(III) oxides, BD extracted 0.1% (Ca-P), 7% (Al-P), and 72% (Fe-P), respectively. Concentrations of AER-PP and BD-PP in runoff were closely related to the concentration of sediment-associated P ($R^2 = 0.77$ – 0.96), and the estimates of annual surface runoff losses of BD-PP and AER-PP were derived from the relationships between PP and these P forms. The annual AER-PP losses in surface runoff from three field sites during 4 years ranged from 13 to 270 g ha⁻¹ and the annual BD-PP losses from 94 to 1340 g ha⁻¹. Since DRP losses at the same time equaled 29–510 g ha⁻¹, runoff PP was considered to make at least as marked a contribution to bioavailable P losses as DRP. Soil P status affected the losses of all bioavailable P forms, but major fluctuations in the transport of AER-PP and BD-PP were due to the annual variation in soil losses. Therefore, erosion control was regarded as a necessary part of P loss abatement at all sites of this study. At one of the sites, drainflow P losses were 3–4 times those via the surface pathway, drainflow being the major runoff pathway. The particles carried by surface and subsurface runoff were enriched in clay-sized particles and ¹³⁷Cs by a factor of about 2 as compared to topsoil, and contained about as much total P as did the bulk Ap horizon soil. The great drainflow losses of potentially bioavailable (topsoil-derived) PP show that soil dispersion and subsurface transport may be the major factors contributing to eutrophying P losses from subdrained clayey soils.

Key words: Phosphorus, eutrophication, field runoff, bioavailability, redox, anion exchangers, drainage, environmental risk assessment, ¹³⁷Cs

Peltovalumavesien maa-ainekseen sitoutuneen fosforin biologinen käyttökelpoisuus

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Tiivistelmä

Osa peltovalumavesien maa-ainekseen sitoutuneesta fosforista (P) voi vapautua leville käyttökelpoiseen muotoon maa-aineksen päädyttyä vesistöön. Tässä työssä tutkittiin valumavesien pelloilta kuljettaman maa-aineksen fosforin (PP; partikkelimuotoinen P) vapautumista kahden uuttomenetelmän avulla: uutto anioninvaihtohartsin avulla (AER) ja uutto bikarbonaatilla puskuroidun ditioniitti-pelkistimen avulla (BD). Uuton AER:n avulla oletetaan kuvaavan hapellisissa oloissa vapautuvan PP:n määrää vedessä, kun taas BD-uutto kuvaa hapettomissa oloissa tapahtuvaa P:n vapautumista sedimentoituneesta maa-aineksestä. Menetelmien luotettavuutta tarkasteltiin laboratorionkokein, määritettiin eri olosuhteissa vapautuvan PP:n pitoisuuksia pinta- ja salaojavalunnassa ja arvioitiin P:n eri muotojen kulkeutumista neljältä savimaan koekentältä. Savisameista valumavesistä saatiin 20 tunnin AER-uuton aikana uutettua noin 50 % kolmen viikon aikana levätestissä käyttökelpoiseksi tulevasta PP:sta. Levätestin ja AER-uuton tulokset korreloivat hyvin keskenään ($R^2 = 0.94$) ja AER uutti *Selenastrum capricornutum*-levän kanssa samaa maa-aineksen fosforijaetta. Hapettomia oloja jäljittelevässä BD-uutossa vapautuvan maa-ainesfosforin määrä oli noin 5–6 -kertainen verrattuna AER-uuton tulokseen nähden. Laboratoriossa valmistetuilla oksideilla tehtyjen kokeiden mukaan BD-uutossa vapautuu lähinnä rautaoksidien sitomaa P:a (72 %:n P-saanto), kun P:n saanto oli selvästi pienempi (7 %) alumiinioksidien sitoman ja apatiitin sisältämän P:n (0,1 %:n saanto) osalta. Sekä AER- että BD-uutoissa vapautuvan P:n pitoisuutta valumavesinäytteissä säätelivät näytteen PP-pitoisuus ja maan P-tila ($R^2 = 0,77-0,96$). Eri koepaikoilla tehtyjen valumamittausten ja pitempiaikaisten valumavesien P-pitoisuuksien seurantojen perusteella laskettiin koemailta tulevan rehevöittävän P-kuormituksen määrät. Vuotuisen liuennun P:n kuormituksen määrät (29–510 g ha⁻¹) olivat suurempia kuin AER:lla uutuvan PP:n määrät (13–270 g ha⁻¹), mutta selvästi pienempiä kuin pelkistyneissä oloissa vapautuvan PP:n kuormat (94–1340 g ha⁻¹). Näin ollen tehokas eroosiontorjunta pienentäisi kaikilla koepaikoilla rehevöittävän P:n kuormaa. Koska salaojavalunta saattaa olla hyvin merkittävä pintamaasta peräisin olevan maa-aineksen ja P:n kulkureitti pelloilta vesistöön, pintamaan eroosioherkkyyttä tulisi vähentää koko pellon alalla, ei ainoastaan pellon reunamilla.

Avainsanat: Fosfori, maatalouden valumavedet, rehevöityminen, pelkistyneet olat, anioninvaihtajat, ympäristöriskien arviointi, salaojitus, ¹³⁷Cs

Foreword

The work summarized in this thesis, supervised by Drs. Markku Yli-Halla and Eila Turtola, got under way at MTT Agrifood Research Finland in 1997. My first job was in a research project studying particle and nutrient transport to the subsurface drainage system. This research received funding from the Finnish Drainage Research Foundation and the Ministry of Agriculture and Forestry, whose support I am pleased to acknowledge here. The results of the project are utilized in Papers III and IV. After the project ended in 2000, I was lucky to spend some months working for Professor Erkki Aura, who had a scintillating interest in the characteristics of runoff sediment matter. He made it possible for me to continue my work on the potential bioavailability of particulate phosphorus, and it was at that time that the first tests reported in Paper II were made. When the Ministry of Agriculture and Forestry launched the second evaluation of the Finnish Agri-environmental Programme, I was given the opportunity to work on runoff phosphorus with Dr. Petri Ekholm; the results of our co-operation are partly presented in Paper I.

This work would not have been possible without the invaluable co-operation of Maija Paasonen-Kivekäs of the Helsinki University of Technology and Markku Puustinen of the Finnish Environment Institute. They provided me with samples, and flow and water quality data from the Aurajoki and Sjäkulla fields, and co-authored Paper III. I also owe heartfelt thanks to all of you numerous persons who contributed to this work, whether in the field or in the laboratory. The soils were classified with Tommi Peltovuori (who probably did most of the digging) and the practical work in the laboratory was done for the most part by Helena Merkkiniemi, Raili Tirkkonen, Anja Lehtonen, and Maria Sipponen. Warm thanks are due to the co-authors of the papers summarized here: Petri Ekholm (Finnish Environment Institute), Tommi Kauppila (Geological Survey of Finland, previously University of Turku), and Taina Lilja, Eila Turtola, and Jaana Uusi-Kämppe (MTT Agrifood Research Finland). I am also indebted to my co-workers in other projects in which I have participated. I gratefully thank Dr. Wim Chardon (Alterra, NL) and Professor Emmanuel Frossard (ETH, Switzerland), the official pre-examiners, and Dr. Eila Turtola, Dr. Markku Yli-Halla and Professor Helinä Hartikainen for providing insightful comments on the synopsis of this work. I also warmly thank Gillian Häkli for editing the English.

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List of original articles and participation

The thesis is a summary and discussion of the following articles, which are referred to by their Roman numerals:

I Uusitalo, R. and P. Ekholm. 2003. Phosphorus in runoff assessed by anion exchange resin extraction and an algal assay. *Journal of Environmental Quality* 32: 633–641.

II Uusitalo, R. and E. Turtola. 2003. Determination of redox-sensitive phosphorus in field runoff without sediment preconcentration. *Journal of Environmental Quality* 32: 70–77.

III Uusitalo, R., E. Turtola, M. Puustinen, M. Paasonen-Kivekäs, and J. Uusi-Kämppä. 2003. Contribution of particulate phosphorus to runoff phosphorus bioavailability. *Journal of Environmental Quality* 32: 2007–2016.

IV Uusitalo, R., E. Turtola, T. Kauppila, and T. Lilja. 2001. Particulate phosphorus and sediment in surface runoff and drainflow from clayey soils. *Journal of Environmental Quality* 30: 589–595.

I Paper I was planned by both authors in cooperation. R. Uusitalo was responsible for the experiments on anion exchange resin and Dr. P. Ekholm for the algal assays. The main responsibility for writing the paper lay with R. Uusitalo; both authors took part in the interpretation of results.

II R. Uusitalo was responsible for planning the work, carrying out the experiments, and writing the article. Dr. E. Turtola commented on the work plans and manuscripts at different stages, and took part in interpreting the results.

III This paper was planned and written by R. Uusitalo. The co-authors supplied runoff and water quality data from the experimental fields, and water samples for the additional analyses (AER and BD extractions). The co-authors also commented on the manuscript before its submission for publication and suggested improvements.

IV Paper IV was planned jointly by R. Uusitalo and Dr. E. Turtola, R. Uusitalo being primarily responsible for the data processing and writing the paper. The Jokioinen field ¹³⁷Cs distribution data were obtained from an unpublished work by Dr. E. Turtola and T. Lilja, and Dr. T. Kauppila participated in sediment characterization work in the laboratory. The co-authors also commented on several manuscript drafts.

Permission to reproduce the articles in the journal layout was granted by the publishers of the *Journal of Environmental Quality*: the American Society of Agronomy, the Crop Science Society of America, and the Soil Science Society of America.

Abbreviations

AER	anion exchange resin
BD	bicarbonate-buffered dithionite
DRP	dissolved (<0.2 μm) molybdate-reactive phosphorus
P	phosphorus
PP	particulate phosphorus
TP	total phosphorus

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1 Introduction

1.1 Forms of agricultural runoff P contributing to eutrophication of surface waters

Continued inputs of P to freshwater environments tend to produce undesirable changes in water quality (Schindler, 1977; Correll, 1998), in severe cases leading to toxic blooms of blue-green algae. Sources of P are many, but due to effective P stripping from industrial and municipal wastewaters, more diluted P streams, such as runoff from agricultural fields and other non-point sources, have become relatively more important contributors of P to surface waters in many areas (Carpenter et al., 1998; Foy et al., 2003; Raike et al., 2003). In Finland, agriculture was recently estimated to account for about 60% of anthropogenic P leakage to watercourses (Valpasvuo-Jaatinen et al., 1997).

Depending on factors such as soil management, crops, and rainfall, the amount of P transported annually by runoff from agricultural soils may range from less than 100 g to several kg per hectare (e.g., Burwell et al., 1975; Turtola and Kempainen, 1998; Djodjic et al., 2000). As well as by the variation in P export rates between different sites, P losses are characterized by a relatively high temporal variation (Schoumans and Chardon, 2003). Under Finnish conditions, particulate P (PP) concentrations in runoff from arable soils typically increase after plowing as a result of the increased amount of eroded soil. The dissolved (reactive) P (DRP) concentration in runoff is in turn more directly related to soil P status, fertilization rates, and fertilization methods (Sharpley et al., 1977; Culley et al., 1983; Heckrath et al., 1995). Particulate P often accounts for a higher proportion of total P transport than does DRP (Logan et al., 1979; Pietilainen and Rekolainen, 1991; Vanni et al., 2001).

It is difficult to make a true distinction between dissolved and particle-associated forms of elements (e.g., Hens and Merckx, 2002) but, operationally, runoff P can be subdivided into DRP and PP by passing a water sample through a filter with small openings (often 0.45 μm or less in diameter). This subdivision into DRP and PP facilitates evaluation of the ecological effects of the P load (Logan, 1982; Bailey-Watts and Kirika, 1999): DRP is considered immediately bioavailable, whereas P transported as attached to eroded mineral and organic matter needs to be transformed into a dissolved form before it can be utilized by freshwater algae to any greater extent (Williams et al., 1980; Ekholm, 1994; Reynolds and Davies, 2001). The magnitude of the transformation of land-derived PP depends on the physical and chemical characteristics of the P-containing particles, as well as on the chemistry of the environment in which these particles end up. The

environmental variables influencing the fate of P include pH, p_e (redox state), dissolved ionic species, and ionic strength. According to one estimation, the amount of desorbable (bioavailable) PP transported into the oceans would correspond to 2–5 times the riverine DRP flux (Froelich, 1988).

In fields, rainfall (or other water input) that exceeds the infiltration capacity of the topsoil causes surface runoff, that is, lateral flow on (or near) the soil surface. Raindrop impact and water flowing on the soil surface detach or silt up particles, dissolve soluble matter, and transport particles and solutes downslope. If the infiltration capacity is not exceeded, water percolates into the soil. At depth, however, it may encounter a relatively impermeable soil layer and start to travel laterally. Percolation water may again reach the soil surface at a lower position in the landscape, or be incorporated in ground water. If the soil is artificially drained – the heavy soils of cool and temperate climates tend to need pipe drainage to be workable in spring and autumn – drainage pipes and their backfills conduct subsurface flow off the fields along with solutes and particulate matter.

One of the first scientists to publish studies on water pathway effects on runoff quality was Helmut Kohnke (1941). Working on Indiana Spodosols, soils that have developed on calcareous glacial tills, he summarized his findings thus: *‘Typically surface runoff water, assuming erosion to occur, is high in solid particles, especially clay and organic matter, high in total nitrogen, high in adsorbed phosphorus, but low in soluble salts. Percolation water contains a relatively high concentration of soluble salts, but little or no organic matter, phosphorus, and colloids.’* Later studies have shown, however, that other types of soils, in contrast, may leak appreciable amounts of P and colloid particles via the subsurface pathway (e.g., Øygarden et al., 1997; Hooda et al., 1999; Laubel et al., 1999). In some soils, especially subsurface drainflow has been found to become more highly enriched in particle-associated P than has surface runoff (Turtola and Paajanen, 1995; Simard et al., 2000).

1.2 Reactions of P in soils and sediments

A conceptual model of the reactions of P with soils and sediments might have the following major components: (i) P sorption onto and desorption from Al and Fe oxide surfaces (Hsu, 1964; Harter, 1968; Richardson, 1985); (ii) precipitation, coprecipitation or sorption onto CaCO_3 and dissolution of secondary Ca-P-associations (Brown, 1981; House et al., 1998; House, 2003); (iii) dissolution of Fe(III) oxides and formation of Fe-P precipitates under varying redox conditions (Li et al., 1972; Miller et al., 2001; Gunnars et al., 2002); (iv) weathering of primary P-bearing minerals such as apatite (Höweler and Woodruff, 1968; Chien, 1977; Anderson et al., 1985); and (v)

synthesis and mineralization of organic P-bearing compounds (Chu, 1946; Stewart and Tiessen, 1987; Paytan et al., 2003).

All of the above reactions are possible, and also probable, in certain circumstances, but the P associations listed do not impair water quality at equal rates. For example, even if much of the terrestrially stable organic P were mineralizable by marine algae or bacteria (Chu, 1946; Suzumura and Kamatani, 1995; Huang and Hong, 1999), the organic P in soils and sediments would be a poor P source for growing algae (Williams et al., 1980; Krogstad and Løvstad, 1991). Moreover, in algal assays land-derived (primary) apatite has been classified as a practically unavailable P source, because it tends to release P slowly. Hence, P may accumulate in lake sediments predominantly as (apatitic) Ca-P (Frink, 1969; Hupfer et al., 1995), and the algal-available portion of runoff PP is understood to consist of inorganic non-apatite P (Logan et al., 1979; Williams et al., 1980). Although a rigid separation of PP into available and non-available portions is unwarranted (Frossard et al., 2000), the most relevant runoff PP fractions during sedimentation and early sediment diagenesis are usually those associated with Al and Fe oxides (Hartikainen, 1979; Froelich, 1988).

The oxides of Al and Fe, as well as the broken edges of silicate minerals, act as P exchangers. When manure or fertilizer P is mixed into a soil, these exhibit specific P sorption by a ligand exchange reaction in which HPO_4^{2-} and H_2PO_4^- anions displace $-\text{OH}$ and $-\text{OH}_2$ groups on the oxide surfaces (Hingston et al., 1967; Arai and Sparks, 2001). This is an ecologically important reaction, that restricts nutrient P from leaching out of the rhizosphere. It also acts very efficiently as long as the sorption sites have a low degree of P saturation. When plant P-uptake (or some other process) depletes solution in dissolved P, the oxide surfaces supply P to the solution and buffer the changes in the solution-phase P concentration (Holford and Mattingly, 1976). When eroded soil matter enters an environment with a much lower solution P concentration than it has equilibrated with, large quantities of P may be released to water (Hartikainen, 1991; Torrent and Delgado, 2001). On the other hand, when the eroded particles come into contact with a solution whose P concentration is higher than that with which the soil matter has equilibrated, P may sorb onto particle surfaces (Taylor and Kunishi, 1971; Hartikainen, 1979; Sharpley et al., 1981). In surface waters, soil matter originating from manured or fertilized fields is expected to act as a net source rather than as a sink for dissolved P.

1.3 Estimating algal-available P by laboratory methods

An algal assay (see e.g., Williams et al., 1980; Krogstad and Løvstad, 1991; Ekholm, 1994) would give a sound measure of runoff P bioavailability. However, the expense of biotests restricts their use, even though the term

“algal assay” also includes relatively simple procedures. When the number of samples to be analyzed is high, an alternative approach is to assess the algal-availability of PP by chemical methods with yields known to correlate with the pool of bioavailable PP (e.g., Cowen and Lee, 1976; Dorich et al., 1985; Sharpley, 1993).

In the context of sediment matter studies, chemical methods can be divided into those that employ P sinks and those that use extraction solutions. Many of the solutions used in extractions are familiar from soil tests or P speciation schemes (Römken and Nelson, 1974; Burwell et al., 1975; Dorich et al., 1985). As in soil analyses, solid-phase P is typically extracted at a fixed soil-to-solution ratio to promote uniform reaction conditions from sample to sample. When such extractions are applied in runoff studies, it is more practical to preconcentrate runoff sediment before the extraction than to try to adjust both the extractant concentration and the solid-to-solution ratio of the samples simultaneously. A major drawback is that preconcentration is a time-consuming step that complicates the analysis.

As P sinks, water studies (whether runoff or stream) have employed ion exchangers (Cowen and Lee, 1976; Huettl et al., 1979; Hanna, 1989) or iron oxide (FeO)-impregnated filter paper (Ekholm and Yli-Halla, 1992; Sharpley, 1993; Dils and Heathwaite, 1998). These differ from chemical dissolution in being less destructive, their aim being to utilize the capacity of the sink to withdraw solution-phase P and thus drive the sorption-desorption equilibrium toward exhaustion of desorbable P reserves. This process resembles the condition whereby rapid cell synthesis of primary producers depletes assimilable P from water.

Analyses with P sinks have been conducted on sediment slurries with a fixed TSS concentration (Huettl et al., 1979; Sharpley, 1993) or without sediment preconcentration (Hanna, 1989; Ekholm and Yli-Halla, 1992; Uusitalo et al., 2000). In the FeO paper method, the amount of P sorbed by FeO is determined after dissolution of the FeO coating in acid (see Chardon et al., 1996), which is potentially problematic in runoff analysis. As runoff sediment becomes attached to the FeO strips during extraction, sparsely soluble PP may also dissolve in acid solution, resulting in exaggerated estimates of desorbable PP (Ekholm and Yli-Halla, 1992). To obtain a relatively equal level of error for different samples, it may be appropriate to make FeO extractions of runoff in a constant TSS concentration. Using such premises, Sharpley (1993) showed that extraction with FeO paper and an increase in algal cell numbers in runoff sediment slurries gave excellent correlations ($R^2 = 0.92\text{--}0.96$) with each other.

Without using any sample preconcentration procedures, Hanna (1989) found a good correlation ($R^2 = 0.83$) between algal-P uptake and anion exchange resin-extractable (AER-extractable) P. As the AER procedure can be

performed without acidic extractants, there is little risk of dissolution of sparsely soluble P associations (Uusitalo and Yli-Halla, 1999). However, AER is not capable of extracting all of the PP assimilated by algae during an assay (e.g., Cowen and Lee, 1976; Hanna, 1989; Fabre et al., 1996). Other potential drawbacks of the AER method include unspecificity of sorption for ortho-P over other anions, restricted P sorption capacity (in high P loading of AER), and possible alteration of pH, which is linked to the anion species used in AER saturation (Frossard et al., 2000). These and other uncertainties in runoff analysis by AER are largely undocumented, most studies on the AER method being restricted to comparisons between AER-P yields and algal utilization of P.

1.4 Potential for P release under anoxic conditions

Because the oxides of Al and Fe make a major contribution to P cycling, transformations of these oxides are important in controlling the fate of P in the environment. Under the conditions prevailing in soils and sediments, dissolution of metal oxides is brought about by acid dissolution, chelation onto organic molecules, and redox reactions (e.g., Kohnke and Bradfield, 1935; Afonso et al., 1990; Urrutia et al., 1999). Of the reactions listed, the most important role in modifying solution-phase P concentration is probably played by reductive dissolution of Fe(III) oxides. As a result, the transformations and fate of P at low redox potentials have attracted keen interest by soil scientists (e.g., Mahapatra and Patric, 1969; Lefroy et al., 1993; Scalenghe et al., 2002) and limnologists (e.g., Theis and McCabe, 1978; Gomez et al., 1999; Koski-Vähälä and Hartikainen, 2001).

In natural environments, the reductive dissolution of a number of different Fe(III) oxides (see Ponnampetuma et al., 1967) may occur through biological and chemical pathways (Szilágyi, 1971; Roden et al., 2000; Nevin and Lovley, 2002). Whatever the nature of the reactions at electron transfer to Fe(III) oxides, X-Fe(III) bonds weaken when the oxidation state of Fe changes from +III to +II (e.g., Suter et al., 1991). Dissolution of Fe(III) oxides in a reduced environment is accompanied by increases in the solution P concentration and a clearly lower P retention capacity of sediment matter containing Fe and Mn (Mortimer, 1971; Jensen et al., 1995; House and Denison, 2000). However, dissolution of P-Fe(III) oxide associations has not been experimentally confirmed as the explicit cause of P release from anoxic sediments (Golterman, 2001).

Studies on P solubilization and transformations at low redox potentials are typically conducted with samples retrieved from environments often influenced by redox changes. Fluctuations in the redox state may be due to seasonal waterlogging of soils (Mahapatra and Patrick, 1969; Sah and Mikkelsen, 1986; Young and Ross, 2001), to varying biological activity in ditch sediments (Sallade and Sims, 1997), or to periods of low oxygen supply

to lake and marine sediments (Theis and McCabe, 1978; Jensen et al., 1995). Some authors have also assessed the P release potential of stream sediment with chemical reductants (Logan et al., 1979; Pacini and Gächter, 1999; James et al., 2002), but hardly any studies have quantified the potential for solubilization of redox-labile runoff P in a manner that could be related to the chemical properties of the sediment source.

1.5 The purpose of this study

Phosphorus inputs to water environments tend to accelerate eutrophication, provided P is in a form that can be utilized by primary producers. Comparison of P sources has shown that the amount of algal-available P in turbid field runoff is smaller than that in industrial and municipal wastewaters (Ekholm, 1998). This state of affairs affects the environmental risks posed to surface waters by P from different sources. We know that agriculture accounts for about 60% of the total anthropogenic load of P on Finnish watercourses (Valpasvuo-Jaatinen et al., 1997); thus, the adverse effects of agricultural P sources on surface water quality are likely to be considerable. However, the actual contribution of agriculture to the eutrophication of surface waters is less certain, and is probably much less than 60% of the combined effects of anthropogenic P loading.

In Finland, fine-textured soils are common in the leading agricultural areas, which are located along the coastline. These soils tend to produce turbid runoff in which PP dominates over DRP. Data abound on the effect of different land management options on losses and concentrations of DRP and PP (Puustinen, 1994; Turtola, 1999; Uusi-Kämppe et al., 2000). We also know that management practices designed to curb PP losses often result in higher DRP transport (Culley et al., 1983; Uusi-Kämppe et al., 2000; Bundy et al., 2001). Because of the nonequivalent effects of DRP and PP on eutrophication, the findings of studies on land management practices cannot be fully utilized in cost-effective catchment management. To be able to predict the effects of field management on eutrophying P losses in these areas, we should know the pollution potential of runoff PP.

The present work attempts to characterize the ease with which PP is transformed into a bioavailable form (termed potential bioavailability of PP) running off fine-textured arable soils. For the purpose of PP characterization, two methods that can be applied for large surveys are proposed, and the potential error sources associated with these methods are examined. The two methods seek to describe (i) the desorbable pool of PP that may solubilize in an aerobic water column, and (ii) the reserves of redox-labile PP. Losses of DRP and PP were quantified at four field sites in southern Finland, and the contribution of DRP and PP forms to eutrophying P losses was assessed. At two of the sites, the relative contributions of surface and subsurface pathways to P losses were also evaluated. Soil P and runoff PP characteristics were

PP characteristics were studied, and the origin of surface and subsurface runoff sediment was investigated by comparing the ^{137}Cs activities of soils and sediment.

2 Material and methods

2.1 The study sites

The study was conducted at four experimental fields in southern Finland: Aurajoki, Jokioinen, Lintupaju, and Sjäkulla (Fig. 1). Long-term (1971–2000) average annual precipitation sums at the stations of the Finnish Meteorological Institute nearest to the Aurajoki field (Turku meteorological station) and the Jokioinen and Lintupaju fields (Jokioinen station) were 698 and 607 mm, respectively. At the two meteorological stations (Vihti/Maasoja and Lohja) located some tens of kilometers from the Sjäkulla field, the average annual precipitation sums for 1971–2000 were 626 and 710 mm. Rainfall in southern Finland is fairly evenly distributed within a single year, and the rains are typically gentle. Kuusisto (1980) summarized 24-h precipitation sums during 1961–1975, concluding that the return periods for rainfalls of about 40 mm, 55 mm and 65 mm were 5, 20, and 50 years, respectively. In the south of the country, the probability of rainfall exceeding 30 mm in 24 h is highest between August and October (Kuusisto, 1980).



Fig. 1. Map of Finland showing the location of the four fields of this study; Aj = Aurajoki, Jo = Jokioinen, Lj = Lintupaju, and Sj = Sjäkulla

The soils of the four sites are sedimentary deposits of the ancient Baltic Sea, the clay content (particles less than 2 μm in diameter) typically ranging from 45% to 90% within 1 m depth. All soils are artificially drained and, according to the US Soil Taxonomy (Soil Survey Staff, 1998), are classified as fine or very fine Cryaquepts. Some details of the soil profiles are given in Table 1. Detailed profiles, including the mineralogy, of Jokioinen (Kotkanoja) and Sjökulla have been given by Peltovuori et al. (2002). The Jokioinen and Sjökulla profiles are of particular interest here, because the subsurface drainage quality was studied at these sites.

At Aurajoki, which has 50-m field plots, the degree of slope is about 7–8%, the steepness increasing toward the lower edge (Puustinen, 1994; Puustinen et al., 2004). At Jokioinen, the average degree of slope of the 140-m long field is 2%, with a 1–4% range (Turtola and Paajanen, 1995). At Sjökulla, there is a steeper part in the middle of the two undulating field segments, one 150 m and the other 200 m long. The average degrees of slope of the two Sjökulla field segments are about 3% and 5% (Paasonen-Kivekäs et al., 1999). At Lintupaju, the upper part of the 70-m field is relatively level, but over a distance of 15–20 m at the lower end the degree of slope exceeds 15% in parts (Uusi-Kämpä and Ylärinta, 1992).

Finland's national agronomic standards are based on P extraction with an acidic (pH 4.65) ammonium acetate buffer (P_{AAAc} ; Vuorinen and Mäkitie, 1955) and a 7-step classification system (see e.g., Peltovuori, 1999). According to these standards, the status of the Aurajoki field (with P_{AAAc} 11–23 mg l^{-1} soil) is “good” (class 5), that of Lintupaju and Sjökulla (with P_{AAAc} 6–9 mg l^{-1} soil) is “satisfactory” (class 4), and that of the Jokioinen soil (with P_{AAAc} 4–6 mg l^{-1} soil) “fair” (class 3). The total P concentration of the soils varied between 1150 and 1760 mg kg^{-1} , and 49–64% of it was extractable by the Chang-Jackson P-fractionation scheme (Chang and Jackson, 1956), which was performed as modified by Hartikainen (1979). The major P fractions were those extracted by NaOH and H_2SO_4 , and they made up 43–51% and 32–40% of the extractable P, respectively. The P fractionation results are given in Paper III.

All plots were fertilized with P by band placement at about 5 cm depth in combination with sowing. The P rate was adjusted according to soil P status, crop, and yield expectations, following the guidelines of the national Agri-Environmental Programme discussed by Valpasvuo-Jaatinen et al. (1997). Annual P applications at the four sites during 1997–2001 were between 7 and 20 kg ha^{-1} . Averaged over the study years, the mean annual rates were about 13 kg P ha^{-1} for wheat (*Triticum aestivum*) at the Aurajoki field, 18 kg P ha^{-1} for barley (*Hordeum vulgare*) at the Jokioinen field, about 11 kg P ha^{-1} for oats (*Avena sativa*), barley, and wheat at the Lintupaju field, and about 16 kg ha^{-1} for wheat and barley at Sjökulla.

Table 1. Profile description of the study sites, and some characteristics of the soil profiles.

Horizon	Depth	Texture†	Org. C	pH	Al _{ox}	Fe _{ox}
	cm		%		mmol kg ⁻¹ soil	
Aurajoki, Aeric Cryaquept						
Ap1	0–18	cl	1.4	6.3	49	199
Ap2	18–29	cl	1.5	6.2	49	183
Bw1	29–40	cl	0.6	6.6	59	216
2Bw2	40–80	c	0.6	7.3	67	255
2Bw3	80–130	c	0.7	7.1	66	235
3C	130–	c	1.6	6.7	63	94
Jokioinen, Typic Cryaquept						
Ap	0–24	c	2.5	6.5	103	235
Bw1	24–32	c	0.6	4.8	82	207
2Bw2	32–56	c	0.4	5.3	109	134
2Bw3	56–76	c	0.3	5.6	98	99
3C	76–	c	0.3	5.8	76	72
Lintupaju, Typic Cryaquept‡						
Ap	0–27	cl	2.7	6.2	55	79
2Bw	27–87	c	0.3	5.8	42	28
2C	87–	c	0.2	5.9	32	17
Sjökulla, Aeric Cryaquept						
Ap1	0–20	sic	2.1	4.6	87	146
Ap2	20–29	sic	2.5	5.2	85	142
2Bw	29–46	c	0.7	5.7	104	125
2BC	46–70	c	0.4	6.2	100	104
3C	70–	c	0.2	7.0	87	84

† c = clay, cl = clay loam, sic = silty clay

‡ The Lintupaju profile was not described in the experimental field where runoff was sampled, but in a field nearby.

2.2 Runoff measurement and sampling

At the Aurajoki, Jokioinen and Lintupaju fields, runoff was measured and water samples were collected with a tipping bucket arrangement. At Jokioinen, both surface and subsurface runoff were sampled, but at Aurajoki and Lintupaju only surface runoff. The runoff collectors were equipped with dataloggers to count the times the buckets with known volumes tipped up and emptied. A constant fraction from each tipping of the collector bucket was emptied into polyethene containers, which were sampled for chemical analyses at intervals. Estimates of annual P losses were summed up after multiplying the measured flow volumes by the P concentrations of the corresponding flow fractions.

At Sjökölla, the runoff draining from the two field segments was grab sampled at four v-notch weirs. Two of these were for surface runoff sampling (weirs S1 and S2) and two for drainflow sampling (weirs D3 and D4). Two weirs, one for surface runoff (weir S2) and the other for drainflow (weir D3; these were not draining the same field segment), were equipped with H.F. Jensen (Majestic Electronics Ltd., Oxford, UK) type PSL pressure sensors for the estimation of flow volume. At the drainflow weir (D4) not equipped with a pressure sensor, samples were taken automatically with an EPIC 1011 portable water sampler (Buhler Montec Ltd., Manchester, UK). Drainflow at this weir was calculated from the measurements made at the other drain by assuming that the drainflow per field hectare was similar in both field segments.

In Paper III, annual P loss estimates for Sjökölla were calculated for both drainflow source areas. Surface runoff, however, was neither generated nor sampled in the whole field segment; only in parts of the fields. Thus, P losses were calculated only at the surface runoff weir (S2) where the runoff volume was measured. The other surface runoff weir (S1) was not included because runoff volumes from the source area were not measured. Nor could runoff via the surface pathway be confidently assumed to be equal from the two surface runoff-generating parts of the field segments, differing as they did in topography.

The P losses at Sjökölla were calculated for the sampling dates only by multiplying the daily runoff volumes by the concentrations measured from grab samples or by the daily average concentrations of the samples taken automatically (see Paper III). Here, it was assumed that the measured P concentrations of the samples approximated the daily averages, but further interpolation between the samplings was not done. Hence, the calculated losses of P forms at Sjökölla constituted only part of the annual losses. In Paper IV, the objective of which was to compare concentrations of sediment and P in surface and subsurface runoff, the Sjökölla data included a field segment where the surface runoff volume had not been measured (S1 and

D3). This field segment differed from that sampled in Paper III. A different field segment was chosen for these comparisons because the surface and drainflow source areas were closer in size than were those of the other field segment.

2.3 Chemical analyses in routine runoff monitoring

Dissolved molybdate-reactive P (DRP) was determined after filtration of the samples through 0.2 μm Nuclepore filters (Whatman, Maidstone, UK). An exception to this practice was made for the Aurajoki samples in Paper III, when 0.4 μm Nuclepore filters were used (the analyses were performed in a different laboratory). Total P (TP) was determined after 30-min autoclave-mediated digestion (120°C, 100 kPa) of an unfiltered subsample with $\text{K}_2\text{S}_2\text{O}_8$ and H_2SO_4 . Modification of the molybdenum blue method (Murphy and Riley, 1962) was employed in photometric P analyses at 880 nm. The analyses reported in Papers I, II, and IV were carried out using a LaChat QC Autoanalyzer (LaChat Instruments, Milwaukee, WI, USA), but other instruments, too, were employed in the runoff quality monitoring reported in Paper III. The particulate P (PP) concentration was calculated as the difference between TP and DRP. The concentration of total suspended solids (TSS) was estimated by weighing the evaporation residue of 40-80 ml of runoff for all samples except those from Aurajoki in Paper III; in these the mass of dried matter retained on the 0.4 μm Nuclepore filter was used as a proxy for TSS.

2.4 Extraction of runoff P by anion exchange resin

For the extraction of AER-P from runoff samples, the procedure developed by Sibbesen (1977, 1978) was applied. Nylon nettings (trade names Sefar Nitex and Sefar Fluortex; Sefar Inc., Heiden, Switzerland) with mesh sizes of 0.25 or 0.30 mm were used to make small bags, and 1 g of Dowex 1 \times 8 (Fluka Chemika, Neu-Ulm, Germany) strong basic anion exchange resin (product no. 44324) was enclosed in each bag. It was calculated that each AER bag had a total anion exchange capacity of about 2 mmol_c. Before use in runoff extractions, AER was converted into HCO_3^- form by shaking an AER bag in two 100-ml portions of 0.5 M NaHCO_3 solution; the same procedure was used to regenerate the AER bags after use.

In the AER analysis, an undiluted 40-ml runoff sample was shaken in a plastic test tube with one AER bag overnight (about 20 h) on an end-over-end shaker at 37 rpm. Afterwards, the AER bag was removed from the sample, washed with deionized water, and placed on a clean test tube. To displace P from the AER sorption sites into solution, 40 ml of 0.5 M NaCl was added to the tube, which was then shaken for 4 h. The AER bag was then removed from the NaCl solution (and was at this stage ready to be regenerated by repeated NaHCO_3 baths). The NaCl solution, now containing the P displaced from the AER sorption sites by Cl^- ions, was acidified with 1 ml of 6 M HCl

and allowed to stand overnight to reduce CO₂ evolution during photometric P determination. The concentration of P in the NaCl solution was recorded by a LaChat Autoanalyzer at 880 nm using a modification of the molybdenum blue method (Murphy and Riley, 1962). The amount of PP extracted by AER (i.e., AER-PP) was taken as the difference between AER-P and DRP. All AER extractions were performed in triplicate, the majority within a week of sampling.

Paper I describes a limited method validation, including the experiments and variables listed in Table 2. In addition, the relevance of AER-extractable P in assessing P bioavailability was studied by testing whether AER extracted P from the pool utilized by a green alga, *Selenastrum capricornutum* Prinz, in laboratory assays. Further, the relationships between AER-P yields and algal P uptake were established with samples containing little suspended matter and with turbid field runoff samples. For details of the dual culture algal assay (DCAA) technique used, see Ekholm (1994; 1998).

Table 2. Tests made to study the performance of the anion exchange resin and bicarbonate-dithionite extraction procedures.

Test on	Detailed in
Anion exchange resin extraction	
Limit of detection	Paper I
Linearity and systematic error in P detection	Paper I
Random errors in runoff analysis	Paper I
Effects of competing anions on P recovery	Paper I
Comparison of P yields between AER and an algal assay	Paper I
Extractability of runoff PP from soils with variable P status	Paper III
Bicarbonate-dithionite extraction	
Electron potential (redox) and pH changes in BD extraction	Paper II
Recovery of P from P-spiked synthetic Al and Fe oxides	Paper II
Extractability of rock phosphate Ca-P	Paper II
Short-term storage effects on P, Fe, Al, and Ca extractability	Section 2.6
Long-term storage effects on P extractability	Paper II
Effects of extraction atmosphere	Section 2.6
Limit of detection	Paper II
Random errors in runoff analysis	Paper II
Extractability of runoff PP from soils with variable P status	Paper III

2.5 Extraction of redox-sensitive P by bicarbonate and dithionite

To assess the fraction of runoff PP that has the potential to solubilize in severely reduced environments, a preliminary study was made of a bicarbonate-buffered dithionite (BD) extraction technique in Paper II. The application adopted was yet another modification of the widely used soil and sediment extraction techniques for Fe (McKeague and Day, 1966; Torrent et al., 1987; Kostka and Luther, 1994) and Fe-associated P (Williams et al., 1971; Theis and McCabe, 1978; Psenner et al., 1984) that employ dithionite as a reducing agent. Here, the technique was applied to runoff analysis without sample pretreatment; thus, the sample matrix differed clearly from soils and sediments.

The BD extraction of runoff proceeded as follows: a 40 ml subsample of runoff was pipetted into a 50-ml capacity centrifuge tube, and 1 ml of 0.298 *M* NaHCO₃ (prepared for daily use) and 1 ml of 0.574 *M* Na₂S₂O₄ (dithionite dissolved just before extraction) solutions were added. Immediately after dithionite addition, the centrifuge tube was capped and placed on an orbital shaker adjusted to 120 rpm. After 15 min, the sample was removed from the shaker and passed through a 0.2 μm Nuclepore filter. For colorimetric determination of BD-extractable P, the filtrate was digested as in TP analysis. The amount of P in these digests is referred to as BD-P_t, following the nomenclature used by Psenner et al. (1984). The amount of redox-sensitive particulate P (BD-PP) was calculated by subtracting DRP (or TDP) from BD-P_t.

2.6 Effects of extraction atmosphere and sample storage on P extraction by bicarbonate-buffered dithionite

To make a preliminary assessment of the performance of the BD extraction, changes in the solubility of P, Fe, and Al following the BD additions were monitored. The extractability of P from defined P associations (synthetic Al and Fe oxides and rock phosphates) was recorded, and the effects of long-term sample storage on P yields were studied. These experiments are outlined in Table 2 and described in detail in Paper II. Two additional tests, made after submission of Paper II, on the performance of the BD-P_t extraction are described below. The first of these tests was made to study the influence of oxygen level on the amount of BD-extractable P, and the other to detect any changes in the samples during days to weeks of storage that might affect BD-P_t yields.

A suspected source of error in the BD-P_t analysis was reoxidation of Fe(II) to Fe(III) during extraction, as this might strip P from the solution phase and lower the BD-P_t yields (Paper II). In the experiments presented in Paper II,

the extraction atmosphere was not controlled, but the time from the start of extraction to the mixing with acidic digestion reagent was kept as short as possible. Therefore, an additional test utilizing 15 Aurajoki runoff samples with TSS concentrations between 0.57 and 3.16 g l⁻¹ was performed in a more controlled manner. For this test, each runoff sample studied was split in two; one subsample was extracted under normal atmosphere (as was the practice in Papers II and III), and the other under anoxic atmosphere and thereafter filtered in low O₂ concentration. The anoxic extraction was done inside a glove bag (I²R, Cheltenham, PA, USA) filled with pure (99.999%) N₂ gas (AGA, Sundbyberg, Sweden), and the reagents used were prepared in N₂-bubbled deionized water. After the samples had been shaken for 15 min, they were removed from the glove bag and decanted to 0.2 µm Nuclepore filters secured on Millipore vacuum filtration units. Immediately after the decantation, 3-l plastic bags filled with N₂ gas were secured to the top of the filtration units with rubber bands. The upper part of the units had about 300 ml of air space, which means that O₂ was not totally excluded during filtration but was lowered to about one tenth of the atmospheric concentration. After a 15 ml portion had passed through the filter, filtration was aborted and the filtrate was immediately pipetted into a digestion flask to be digested (see section 2.5). The results of the extractions performed under normal and N₂ atmosphere were paired, and compared by Student's *t*-test with one-tailed distribution.

Changes in BD-P_i yields during 3 weeks of sample storage at +4°C were studied by performing the BD extraction (with triplicates) at intervals. The first extraction was done within 2–8 h of sampling, and the last one after 22–24 days of storage. To detect other signs of transformations of suspended matter besides those in P concentrations, 5-ml subsamples of the filtered BD extracts were diluted with 5 ml of 1.2 M HCl and analysed for dissolved Al, Fe, and Ca by an inductively coupled plasma atomic emission spectrometer (ICP-AES; Thermo Jarrel Ash, Franklin, MA, USA). To compare the concentrations measured on the BD extracts with the concentrations present in original, non-extracted runoff, the above analyses were also made on subsamples of filtrates digested as in TP analysis for P (i.e., total dissolved P, TDP) or diluted to a 1:1 ratio with 1.2 M HCl for ICP-AES measurements of Al, Fe, and Ca. The concentrations in non-extracted runoff are later (e.g., Fig. 8) referred to as time zero concentrations.

2.7 Losses of potentially bioavailable P forms assessed from monitoring data

Annual losses of desorbable PP (AER-PP) and redox-sensitive PP (BD-PP) from the experimental fields were estimated by means of the relationships between the concentrations of PP vs. AER-PP and PP vs. BD-PP (Paper III). Predicted AER-PP and BD-PP concentrations were calculated for all of the individual runoff samples taken from the fields during the study periods and

multiplied by the volume of runoff represented by the sample in question. The results were then converted to annual loss estimates. For these estimates, 95% prediction interval coverage were also calculated (e.g., Johnson, 1994; the calculations are described in detail in Paper III).

For the Aurajoki, Jokioinen, and Lintupaju fields, where sampling was automated, P losses could be estimated reliably for the whole 4-year period, starting in August 1997. The most reliable runoff data were obtained from the Jokioinen and Lintupaju fields. The Aurajoki flow data, as recorded by dataloggers at the field, had to be corrected for some periods due to inflow from outside the field plots selected for this study (see Paper III). At Sjäkulla, flow monitoring by pressure sensors was hampered by freezing of the sensors. Therefore the study reported in Paper III includes only the 1-year period at Sjäkulla when flow monitoring proceeded smoothly.

2.8 Phosphorus and particle transport by surface and subsurface flow

The concentrations (Paper IV) and losses (Paper III) of different P forms via surface and subsurface pathways were recorded at Jokioinen and Sjäkulla. In addition, the origin of runoff sediment was traced by ^{137}Cs gamma spectrometry, and the relative enrichment in fine particles of runoff as compared to topsoil was estimated utilizing measurements made with a laser particle counter (Paper IV). In Paper IV, the quality of surface and subsurface runoff was characterized by determining concentrations of DRP, AER-PP (i.e. AER-P less DRP; in Paper IV inconsistently labeled as PPI), particulate “unavailable” P (PUP; PP less AER-PP), and TSS.

In the study reported in Paper IV, the surface and subsurface runoff samples represented water quality during peak runoff, which was the only period during which simultaneous sampling of surface and subsurface runoff was possible. However, “simultaneous” sampling does not mean the same thing at the two sites studied. At Jokioinen, “simultaneous” samples comprised surface and subsurface flow-weighted runoff fractions collected during a fixed period of some days. Even during peak runoff periods, not every rain shower necessarily resulted in both surface and subsurface runoff. In contrast, for the Sjäkulla grab samples, “simultaneous” means that water running off the field via the two pathways was sampled within minutes. However, the source areas for surface and subsurface runoff did not match each other exactly due to the relatively long slope and undulating topography of the Sjäkulla field. The footslope was then the more important source of surface runoff (and sediment), and the upslope of drainflow. Statistical comparison of the P forms and TSS in these “simultaneously” taken runoff samples was made using the Mann-Whitney U-test.

3 Results and discussion

3.1 Validation for using the anion exchange resin method in runoff P analysis

Anion exchange resins are much used in soil analysis, and a large volume of method validation data and comments on the possible interferences in soil analysis by this method have been published (e.g., Sibbesen, 1978; Somasiri and Edwards, 1992; Skogley and Dobermann, 1996). Fewer such data have been published on the use of AER in analyses of runoff P. Although soil analysis by AER is made on a soil-water suspension, which principally has the same components as runoff, runoff and soil are two different matrices from the analytical point of view. Hence, some method validation is required before AER extraction can be applied to runoff. The factors considered important, especially in the study of desorbable, or algal-available, runoff PP under the conditions prevailing in southern Finland were reported in Paper I, and are summarized here.

All chemical analysis methods have a lower limit of concentration that can confidently be said to differ from the analytical zero concentration. This detection limit (DL) is a critical measure in runoff studies, because low P concentrations are sometimes measured. In the AER analysis applied here, the DL was at about 0.030 mg AER-P l⁻¹ for the AER bags reused in 15–20 extractions. Limiting reuse to 15–20 extractions was advisable, because the DL crept towards higher concentrations with repeated reuse of the AER bags (Paper I). It is clear that a DL of 0.030 mg l⁻¹ restricts use of the AER method at some monitoring sites. As an example, Rekolainen (1989) reported average TP concentrations of less than 0.030 mg l⁻¹ for several forested basins. Likewise, runoff from agricultural soils may periodically have very low concentrations of P (e.g., Haygarth et al., 1998). However, if we look at the sites of the present study, the typical DRP concentration in Jokioinen runoff (0.041 mg DRP l⁻¹) was higher than the DL of the AER method. Considering that sediment-associated P also contributes to AER-P, the lower limit of detection in the AER extraction would probably be exceeded in analyses of turbid runoff. At the other sites of this study, soil test P levels were higher than those at Jokioinen, and runoff AER-P concentrations at least as high as those at Jokioinen were expected.

According to the tests made on standard P solutions (Paper I), the response of AER-P yields to increasing concentrations of dissolved and desorbable runoff P should be linear, at least up to 2.0 mg AER-P l⁻¹. Similar findings are reported in studies of other anion exchangers (Amberlite IRA and Ionics anion exchange membrane; Somasiri and Edwards, 1992; Cooperband and Logan, 1994, respectively). A P concentration of about 2 mg l⁻¹ is similar to the peakflow TP concentrations in runoff from the fields we studied here.

Considering that not all runoff P is algal-available at these sites [see Ekholm (1998) for Aurajoki runoff algal assays], we did not expect the upper limit of the tested linear range to be reached in the field studies. While testing the linear range of the AER method, we recorded a slight systematic underestimation of the P concentration of solutions with 0–2 mg P l⁻¹. Here, a slope value of 0.96 between added P and P recovery was obtained, which differed statistically significantly ($p < 0.001$) from the 1:1 ratio (i.e., slope value of 1.0). However, such constant systematic errors can be corrected in the final calculations (e.g., Doerffel, 1994).

Random errors, which express themselves as scattering of the replicate determinations, were relatively small in AER-P analysis of runoff samples. The higher the AER-P concentration in runoff, the lower was the coefficient of variation (CV) in the replicate AER determinations. At concentrations greater than 0.030 mg AER-P l⁻¹, the CV seldom exceeded 10% (Paper I). Exceptions to this were usually due to leaks in the AER bags, resulting in loss of some of the resin beads during shaking in the sample suspension. If such a loss was observed, the results were naturally discarded.

Type I AER (e.g., Dowex 1×8) would withdraw all types of anions from a solution containing equal molar concentrations of, say, bicarbonate, chloride, nitrate, phosphate, and sulfate, but the amounts of anions sorbed onto the AER would follow the order: NO₃⁻ > Cl⁻ > HCO₃⁻ > SO₄²⁻ > HPO₄²⁻ (Skogley and Dobermann, 1996). Different anions thus have variable sorption affinities for anion exchangers and compete for available sorption sites. This competition affects the choice of counter-anion used to displace the anion of interest from the sorbed phase back to solution. When P is determined by an AER method, any of the anions listed would thus be suitable as a counter-anion. On the other hand, because of their stronger sorption affinity than that of ortho-P, the anions listed above may also reduce P yields by AER. By its nature, anion competition is a source of systematic error, but its magnitude may vary according to variations in the chemical composition of runoff samples and is therefore difficult to control.

In the light of recoveries of P from standard P solutions spiked with different amounts of competing anions (Fig. 2), and considering the water quality measured at several Finnish agricultural basins (see Paper I), anion competition might well result in a reduction of about 10–15% in P yields in runoff analyses. The decrease in AER-P yields due to anion competition in the laboratory test in which competing anions were added to ortho-P solution was obviously linked to the total amount of competing anions, not to the anion species (Fig. 2). The effect of anion competition is noted here, but later in the field studies no attempt was made to adjust the AER-P yields to take account of any such effect. This effect was rather uniform over a wide concentration range of competing anions (Fig. 2), and it was assumed to be

included in the conversion coefficient between AER-P and algal-available P (section 3.2).

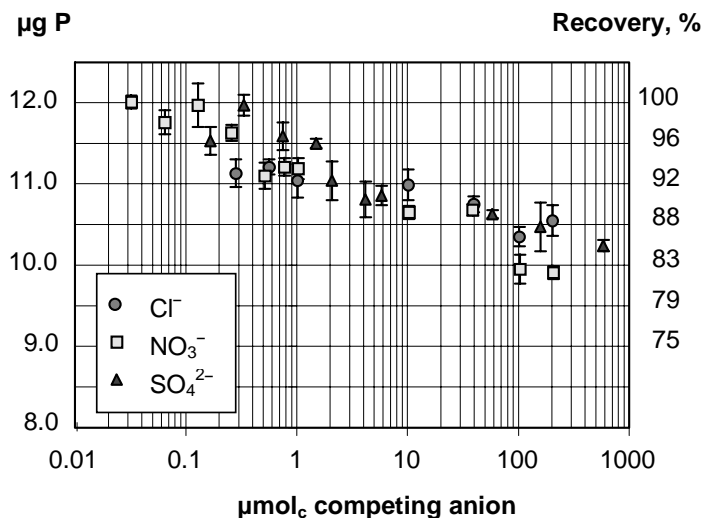


Fig. 2. Phosphorus yields ($\mu\text{g P}$; error bars indicate SD; $n = 6$) and recovery (%) in anion exchange resin extraction when the amount of competing anions (Cl^- , NO_3^- , or SO_4^{2-} ; expressed as molar equivalents of negative charge) increased. All solutions contained $12 \mu\text{g P}$.

3.2 Anion exchange resin-extractable P and P uptake by algae from runoff samples

Comparison of AER-P extraction with an algal bioassay (the DCAA test) showed that the test alga (*Selenastrum capricornutum* Prinz) utilized the same P pool as was exploited during the AER extraction (Paper I). The concentrations of AER-extractable runoff P also correlated well with algal P uptake. However, different relationships were obtained for non-turbid samples (with a low PP concentration and, for some samples, extremely high DRP concentration), on the one hand, and for turbid runoff samples (mainly from agricultural fields, with a relatively high PP concentration), on the other (Paper I). When small amounts of suspended soil were present, the P yields by AER and DCAA were essentially equal, in accordance with the results of Hanna (1989). In contrast, less P was extracted by AER than by DCAA from the runoff samples retrieved from the Aurajoki, Jokioinen, and Sjökkulla fields, which contained abundant suspended soil matter ($0.3\text{--}1.7 \text{ g l}^{-1}$). However, for these samples, too, the correlation between DCAA-P and AER-P was good ($R^2 = 0.92$; $n = 14$; Paper I).

The lower P yields achieved in AER analysis of turbid runoff than in the DCAA tests are probably mainly attributable to the fact that anion

exchangers act as dynamic exchangers (e.g., Barrow and Shaw, 1977; Cooperband and Logan, 1994) but not as infinite sinks. During AER extraction of runoff, AER initially withdraws ortho-P from the solution phase, and is able to do so until the P concentration in solution is at a level of a few $\mu\text{g l}^{-1}$ (DRP concentrations measured after the AER bag was removed from the soil or runoff samples were less than $4 \mu\text{g l}^{-1}$; data not shown). Lowering the solution P concentration triggers P desorption from runoff sediment. At some point, when sufficiently low P saturation is approached, further P desorption from the solid phase is restricted by even a small amount of ortho-P in the solution phase. Here, three-phase equilibrium involving sediment-P, solution P, and AER-P is approached. In contrast, algal P-uptake is a non-equilibrium process and, during the DCAA tests, solution P reached near-zero concentration (Paper I). Under such conditions, during the 3-week algal assays, desorption of sediment-associated P is driven still further from the point at which desorption initially slows down (see Frossard et al., 2000). Slowly desorbable PP reserves are also being exploited in a reaction that is a reversal of the “aging” of added P (see Sillanpää, 1961; Chardon and Blaauw, 1998). Because the ultimate control is the AER sorption process tending to equilibrium, prolonging the extraction time would as such only have a minor effect on P yields by AER (Cowen and Lee, 1976; Paper I).

Desorption of solid-phase P in the DCAA tests was likely also promoted by the practices of diluting the samples and buffering pH to 8 prior to the algal assay. Increased desorption of sediment P when alkalinity increases above neutral is a known phenomenon (e.g., Koski-Vähälä and Hartikainen, 2001), but the extractions of runoff by HCO_3^- -saturated AER do not promote great enough changes in solution pH for pH 8 to be reached (Uusitalo and Yli-Halla, 1999). The dilution tests reported in Paper I further confirmed that the AER-P yields increased when the samples were diluted as in DCAA, possibly as a result of decreased ionic strength in solution and decreased anion competition for AER sorption sites. Because dilution always reduces the actual amount of P withdrawn from a sample during extraction, and random errors increase with declining AER-P yields, dilution was not applied to the field study material.

To permit comparison of the amounts of PP desorbed during AER extraction and utilized by *S. capricornutum*, the data given in Paper I (Table 1 in Paper I) were recalculated. Here, the dissolved fraction, which is almost entirely algal-available and effectively retained by AER, was subtracted from the AER-P and DCAA-P yields. In this calculation, we end up with a relationship showing that in turbid runoff AER extracted slightly more than 50% of the PP that became algal-available during the 3-week DCAA (Fig. 3). The trend was approximately linear, and a high value for the correlation coefficient ($R^2 = 0.94$) was obtained.

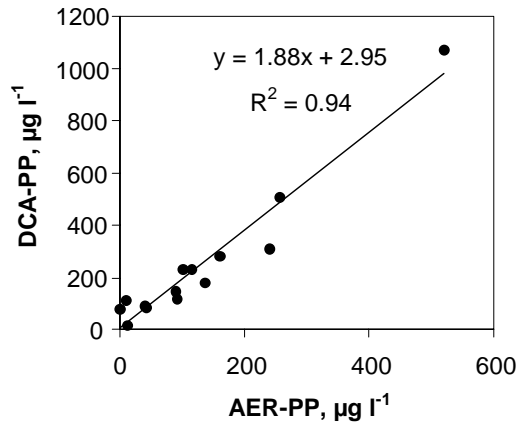


Fig. 3. Relationship between the amount of particulate P obtained in an overnight extraction by anion exchange resin (AER-PP) from undiluted runoff and the amount of particulate P taken up from diluted and pH-buffered runoff by the *Selenastrum* test alga during a 3-week dual culture assay (DCAA-PP).

The leverage by one sample containing high concentrations of AER-PP and DCAA-PP was eliminated when these PP data were further related to the content of suspended solids in the samples (Fig. 4). Then, somewhat less variation was accounted for ($R^2 = 0.71$), but a somewhat higher proportion of the algal-available, sediment-associated P appeared to be extracted by AER: 57% as compared to 53% according to the equation in Fig. 3.

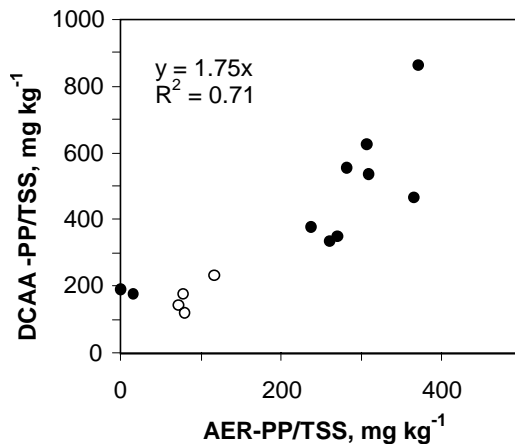


Fig. 4. The suspended solids-normalized amounts of particulate P obtained by anion exchange resin (AER-PP/TSS) tests and dual culture algal assays (DCAA-PP/TSS). The data included 10 Aurajoki runoff samples (black markers) and two each of Jokioinen and Sjököulla runoff samples (white markers). The equation shown is for a linear relationship forced through the origin; see Fig. 5 and text.

The relationship between the AER-PP and DCAA-PP concentrations of suspended solids in Fig. 4 seemed to follow a curvilinear trend. The upward curving of the relationship in Fig. 4 suggests that the higher the concentrations of algal-available PP in sediment, the relatively less PP is desorbed by AER. Provided that a greater proportion of sorbed P is loosely retained in high P saturation (e.g., Muljadi et al., 1966), this is a contradictory result. A closer look at the two Aurajoki samples with very little AER-extractable PP shows that they deviated from the other samples in another respect as well. In Fig. 5, the AER-PP/TSS ratio is related to the total P concentration of runoff sediment (PP/TSS), and the relationship in the two deviating Aurajoki samples clearly differs from the general trend in a larger set of Aurajoki runoff samples (Fig. 5) in that PP in these samples was not desorbable in the AER extraction. The results for these two samples suggest that the AER extraction failed. Unfortunately, the reason for the failure is unknown; the results of the replicate AER analysis also had a standard deviation that did not strongly differ from the usual values (see Fig. 5).

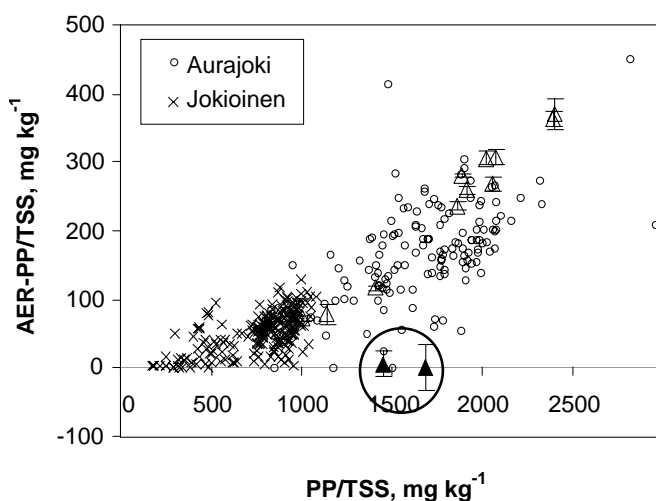


Fig. 5. Extractability of sediment-P by anion exchange resin (AER-PP/TSS) as a function of increasing runoff sediment P concentration (PP/TSS). The samples marked with triangles (with error bars indicating SD, $n = 3$) are those (10 Aurajoki, 2 Jokioinen, and 2 Sjökölla) studied in Paper I; the two samples circled, with black markers, are discussed in the associated text. The smaller markers show results from studies of a larger set ($n = 369$) of Aurajoki and Jokioinen runoff samples.

The comparison of AER-PP and DCAA-PP provided a basis for AER extraction-based estimates for the algal-availability of runoff PP for a larger field study material. Exclusion of the two suspect samples discussed above had only a minor effect on the equation presented in Fig. 3. In the field

studies discussed later, the estimated AER-PP losses were converted to algal-available PP by multiplying them by a constant value of 1.9.

3.3 Target-specificity of bicarbonate-buffered dithionite in extraction of redox-labile runoff P

The basic idea of bicarbonate-dithionite (BD) extraction was to solubilize redox-labile P-bearing compounds. The role of dithionite was to lower the redox potential of a runoff sample, whereas bicarbonate was included in the extraction as a pH buffer. Buffering pH was necessary to reduce the acid dissolution of stable P-bearing minerals (see Paper II). During the BD extractions, only a moderate decrease in pH (typically from around 7 to about 6.5), as opposed to a rapid and dramatic decline in Eh (from more than +200 to -200 mV or less), was observed in bicarbonate-buffered runoff suspensions upon the addition of dithionite. At the same time, P and Fe solubility increased very distinctly, concentrations of soluble P and Fe being much higher in the BD-treated runoff than in unmanipulated runoff samples (Paper II).

The studies on synthetic Fe and Al oxides further suggested that P solubilization in BD extraction was intimately linked to Fe(III) oxide dissolution. Seventy-two percent of the total amount of P sorbed by synthetic Fe oxide-coated quartz sand (Fe-QS) was recovered in BD extraction (Paper II). Judging by the difference between BD-extractable P and (0.298 M) bicarbonate-extractable P, 85% of the P solubilized from Fe-QS was due to a reductive mechanism brought about by dithionite. In contrast, chemical reduction by BD only dissolved 7% of the P sorbed by Al oxide-coated quartz sand (Al-QS). As much as 86% of the small amount of P extracted from Al-QS by BD was also extractable by a pure (0.298 M) bicarbonate solution. Psenner et al. (1984) studied variscite ($\text{AlPO}_4 \cdot \text{H}_2\text{O}$) and strengite-type (FePO_4) condensed P-containing minerals, and found that BD extraction (extraction conditions: 0.11 M dithionite and 0.11 M bicarbonate, at +40°C) solubilized about 5% and 25% of their P, respectively. The clearly lower recovery of P from FePO_4 in their study is probably related to the crystallinity of strengite, which is higher than that of the synthetic P-containing Fe-oxides of the present work (further discussion of this topic follows in section 3.4).

Bicarbonate-dithionite clearly extracted more P from four Ca-P minerals (characterized in Paper II; one of them was apatite mined at Siilinjärvi, eastern Finland) than did water and bicarbonate solution. However, in this case, the more probable cause was the marked decrease in solution pH, not reductive dissolution. In contrast to runoff samples, water suspensions of the Ca-P minerals were initially rather alkaline, and pH values declined in both 0.298 M bicarbonate and BD extractions as compared to the values in water suspensions. For the Siilinjärvi apatite, pH values for suspensions in water, NaHCO_3 , and BD solutions were 9.1, 8.7, and 7.4, respectively. In water

suspension, less than 4 mg P was dissolved from 1 kg of apatite, whereas about 40 mg P was dissolved in 0.298 M bicarbonate, and an additional 50 mg P in BD solution. The amount of P solubilized during BD extraction accounted for less than 0.1% of the total P concentration (106 g P kg⁻¹) in Siilinjärvi apatite. A similar percentage was earlier reported by Psenner et al. (1984), who found that 0.2% of apatite-P was solubilized during BD extraction with higher concentrations of bicarbonate and dithionite.

3.4 How are chemical and bacterial reductions related to each other?

Does BD-P_i actually derive from the pool, mainly Fe(III) oxides, that in natural environments undergoes biological reduction reactions? This study does not answer that question. Moreover, comparisons of chemical and biological reactions appear rarely to have been contemplated, even though the reductive dissolution of natural and synthetic Fe oxides has been studied extensively both with chemical extractions and with experiments involving biological reduction. The findings of the only paper published on this topic are summarized below; otherwise the gap in our knowledge is merely noted.

The published comparison of chemical and bacterial Fe oxide dissolution, authored by Roden (2003), reports initial rates of bacterially catalyzed Fe(III) reduction at pH 6.8 and reductive dissolution by ascorbic acid at pH 3.0. As a rule, owing to the decrease in available surface area with an increase in crystallinity, the higher the degree of order in the crystallinity of minerals, the more slowly both biological and chemical reductions proceed. Therefore, Roden (2003) recalculated the reduction rates on a surface area-normalized basis. Bacterial Fe(III) reduction at a near neutral pH generally occurs at slower initial rates than reductive dissolution in acidic ascorbate solution. Of interest is that Roden (2003) found that the surface area-normalized rates in bacterial reduction were similar for poorly and well-crystallized Fe(III) oxides. In contrast, chemical reduction was affected not only by the available surface area but also by the Fe(III) oxide crystal thermodynamic properties related to the Gibbs free energy of formation. The initial surface area-normalized rates for poorly crystallized ferrihydrite and lepidocrocite were higher in purely chemical dissolution than in bacterial reduction. However, well-ordered goethite and hematite were chemically reduced at initial rates comparable to those of the biological reaction.

As well as reaction kinetics, an interesting subject for comparison would be the extent of bacterial vs. chemical Fe(III) reductive dissolution. However, no published studies appear to have addressed this topic, perhaps due to the difficulty of defining appropriate conditions for biological Fe(III) reduction experiments. For example, Urrutia et al. (1998) concluded that the bacterial Fe(III) oxide reductive dissolution capacity may be grossly underestimated if inferred from the results of batch incubations. In batch experiments, Fe(III)

dissolution rates are substantially slowed down, as solubilized Fe(II) blocks solid surfaces by forming (e.g., siderite, green rust) precipitates on them. In this way, Fe(II) impedes electron transfer onto oxide surfaces. In a laboratory study on the bacterial dissolution of synthetic goethite, Roden et al. (2000) noted that the reduction reaction reached an asymptote in batch cultures when 13% of the total Fe(III) was dissolved. However, when the same oxide was placed in a flow-through column in which Fe(II) was continuously removed from the oxide surfaces, the dissolution proceeded to near completion: about 95% of Fe was recovered in a reduced state. In soils and sediments, at least partial Fe(II) removal from the oxide surface occurs as a result of Fe(II) chelation and sorption onto organic and mineral matter (Urrutia et al., 1999).

3.5 Performance of the bicarbonate-dithionite method in runoff analysis

A close correlation ($R^2 = 0.93\text{--}0.97$) between PP and suspended soil matter at the four sites of this study was reported earlier (Uusitalo et al., 2000). This finding implies that runoff sediment from these soils probably has a reasonably constant chemical composition over a series of runoff events and that an increased PP concentration should also be accompanied by an increasing BD-PP concentration in runoff. The assumption seemed correct: the correlation coefficients (R^2) between BD-PP and PP for the four field sites ranged from 0.89 to 0.96, as shown in Fig. 6. In these soils, the BD-PP concentrations in runoff at a given PP concentration were 5–6 times the AER-PP concentrations (Fig. 6), thus exceeding the estimate of (under oxic conditions) algal-available PP approximated to equal 1.9 times the AER-PP concentration of runoff.

The basic analytical variables in terms of limits of determination (DL and linearity) were found satisfactory with regard to the determination of $BD-P_i$ in runoff from the soils of this study (Paper II). However, a greater tendency to random scattering was apparent in the results of the BD analysis than in those of the AER analysis. This was shown by the test in which only five of the 10 samples extracted with five replicates had a CV of less than 10% (Paper II). A similar scattering in BD-P results has been reported in sediment studies by Psenner et al. (1984) and Farmer et al. (1994). The reasons for the occasionally relatively high variability in $BD-P_i$ might lie in the extraction procedure, perhaps due to reprecipitation of dissolved Fe, or other changes during sample storage. Sample heterogeneity might also play a role. Because distinct redox concentrations (i.e., Fe oxide mottles) were observed in the Ap horizons of the fields (see the cover photo), we can speculate that runoff sediment may also have contained colloidal Fe oxide particles or small aggregates with non-uniform surface coatings by Fe. In the colloid-size particles found in natural water systems, the concentrations of Fe(III) and P have been found to be highly positively correlated (Mayer and Jarrell, 1995; Gunnars et al., 2002). The occurrence of this type of colloidal matter, or its

effects on the homogeneity of runoff sediment, was not studied here. Instead, two other possible sources of variation, namely sample storage and precipitation of P as a result of Fe oxidation due to contact with air during extraction and filtration, were considered in greater detail.

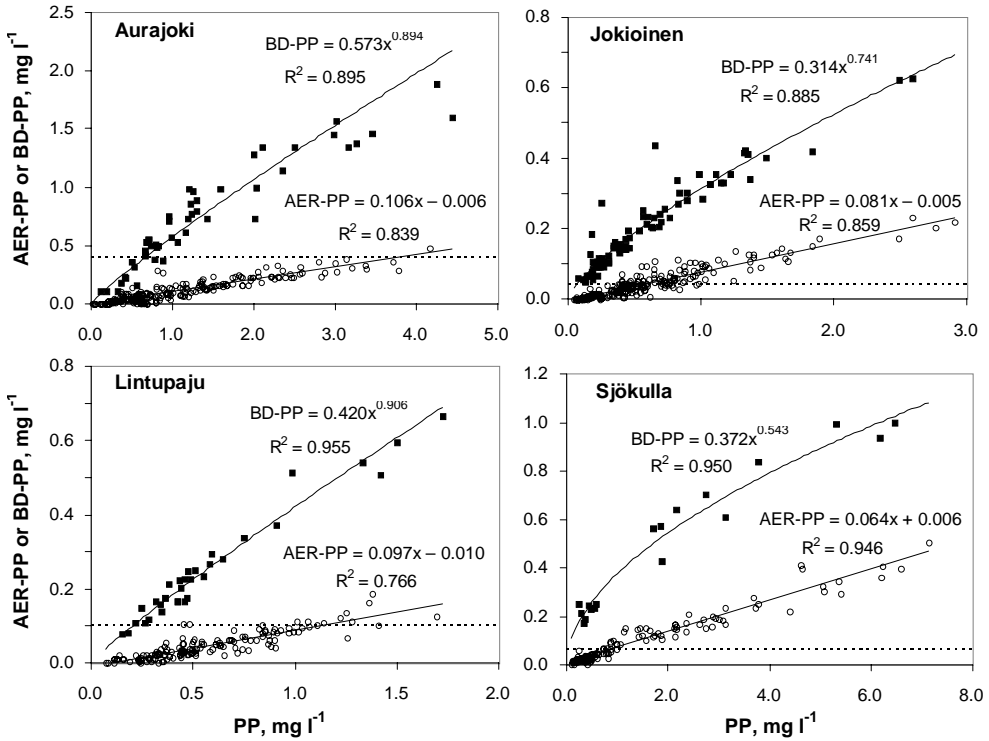


Fig. 6. Relationships between particulate P (PP) vs. bicarbonate-dithionite (BD)-extractable PP (marked with black squares) and anion exchange resin (AER)-extractable PP (white circles) in runoff from the fields studied. The dotted horizontal line indicates the average dissolved molybdate-reactive P concentration in surface runoff.

Contact of runoff samples with air was not found to affect the BD-P_t results. Comparison of the results obtained from two sets of subsamples ($n = 15$) that were either (i) extracted under N₂ atmosphere and filtered in about one tenth of the oxygen level of the normal atmosphere, or (ii) extracted under normal atmosphere showed that the BD-P_t yields were relatively unaffected by the O₂ concentration during extraction (Fig. 7). When there was a measurable difference in the amount of BD-P_t, slightly more P tended to be extracted under normal atmosphere. However, this difference in P yields obtained under different extraction atmospheres was not statistically significant at the 5% risk level.

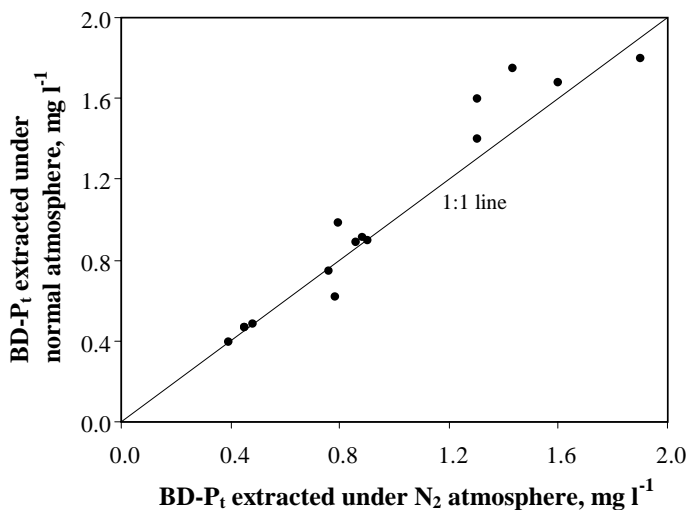


Fig. 7. Extraction of P from 15 runoff samples by bicarbonate-buffered dithionite (BD-P_i) under N₂ atmosphere and under normal laboratory atmosphere; $p = 0.0644$ (paired t -test, one-tailed distribution). The graph shows that the BD-P_i yields were practically unaffected by the variation in oxygen concentrations during the extraction and filtration steps.

Short-term effects (up to 22–24 days of storage at +4°C) on the extractability of P, Fe, Al, and Ca are shown in Fig. 8. This test was conducted on the very same runoff samples and with triplicates, and one portion of runoff was taken for BD extraction at intervals. As compared to the concentrations in the original runoff samples (time zero concentrations) of total dissolved P (TDP) and Fe, solubilization of these two elements due to BD extraction was substantial. Short-term sample storage did not result in constant alterations in their extractability, even though BD-Fe concentrations fluctuated notably between the extractions. Aluminum did not behave regularly at all, the Al concentrations of one of the samples (labeled Oj in Fig. 8) being much higher after BD extractions than initially in runoff. As Al may partly substitute for Fe in Fe oxides (and the degree of substitution affects reductive oxide dissolution; e.g., Torrent et al., 1987), the source of dissolved Al may have been Al-substituted Fe(III) oxides that respond to the redox environment. The addition of BD chemicals to runoff did not affect the concentrations of dissolved Ca, which were also very constant over time. Neither was long-term sample storage found to have a significant effect on BD-P_i yields, similar BD-PP vs. PP slopes, 0.30 and 0.28 (t -test $p = 0.7298$), being recorded for the samples analyzed within 9 weeks and for those analyzed 6–25 months after they had been taken (Paper III).

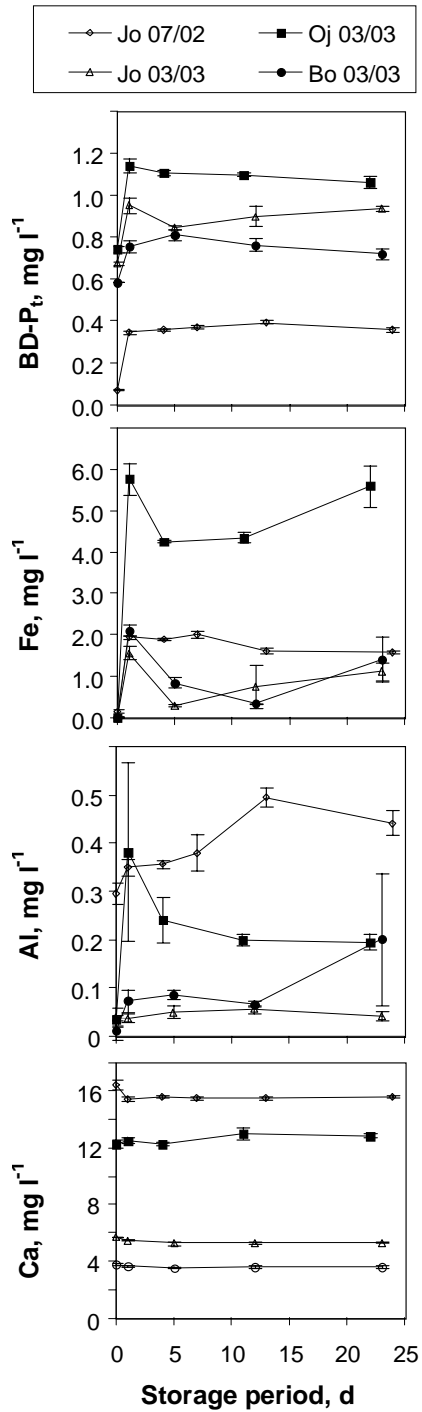


Fig. 8. The effects of sample storage on the solubilization of P, Fe, Al, and Ca by bicarbonate-dithionite (BD) extraction in four runoff samples. Time zero concentrations represent dissolved elements in samples not extracted by BD.

The routine for digesting the BD-extracted and filtered samples in an autoclave in order to eliminate disturbances in photometric P analysis raises the question of the possible contribution of organic P included in the estimates of BD-P_t. Psenner et al. (1984) reported that the BD extracts of a sediment core (25–50% organic C) digested in an autoclave contained about twice as much molybdate-reactive P as extracts that were only bubbled with air (which is another way of eliminating dithionite interferences in photometric P analysis). In their P speciation scheme, the above authors use this difference in BD-P concentrations as an estimate of organic BD-extractable P. For their part, Pacini and Gächter (1999) reported that much less, on average 12% (range 3–27%), of BD-extractable stream sediment PP was supposedly organic P (i.e., no color reaction by molybdate reagent unless digested). In the present study, we assumed that organic P made only a small contribution to runoff BD-P_t because of the relatively small amounts of organic C present in sediment matter: 2–3% organic C in a mass unit of TSS (unpublished data on the chemical composition of Jokioinen and Sjäokulla runoff sediment).

3.6 Soil P and runoff P

Here, we knew the source of the sediment matter studied and so could make tentative comparisons between soil P and runoff P. These comparisons are to be taken as indicative only, because the material of the study is not ideal for a comparison of soil P status and runoff P pools (especially DRP). This is because different soils are compared and soil properties affect P status vs. runoff P relationships (e.g., see Hesketh and Brookes, 2000). In the present study, the soils were characterized by the Olsen agronomic P test and by a sequential fractionation scheme. In recent years, agronomic soil tests, in particular, have been studied as environmental soil tests, and most often soil test P is compared with runoff DRP.

The Aurajoki soil produced runoff with a typical DRP concentration of 0.404 mg l⁻¹ which was about 10 times that at Jokioinen (0.041 mg DRP l⁻¹), and about 4–6 times that at Lintupaju (0.104 mg DRP l⁻¹) and at Sjäokulla (0.066 mg DRP l⁻¹). Judging by the spectacular relative differences in DRP concentrations between Aurajoki and the other sites in the present study, the Aurajoki soil has reached a level of soil P saturation that has increased the DRP loss potential. At the same time, when the DRP concentration of Aurajoki runoff was about 10 times that of Jokioinen runoff, the Olsen P concentration of the Aurajoki soil was about twice that of the Jokioinen soil. Were these soils directly comparable, this would result in curvilinear Olsen P vs. DRP relationships, probably similar to that reported by Heckrath et al. (1995) for a Broadbalk (UK) soil fertilized with different levels of P. In turn, the results of Chang-Jackson P fractionation of the soils provided no apparent information on DRP regulation. The NaOH- and H₂SO₄-extractable P

fractions in the Aurajoki soil were obviously enriched in fertilizer P, and exceeded the P concentrations in the other soils; otherwise there were no marked differences between the P fractions of the four soils (Paper III).

When a typical DRP concentration in an edge-of-field runoff sample is largely controlled by the P saturation status of the immobile surfaces that take part in exchange reactions (Yli-Halla et al., 1995), comparisons between runoff PP concentrations and soil P status are only warranted when normalized to the concentrations of eroded sediment (Uusitalo et al., 2000). The concentrations of AER- and BD-extractable sediment P were much greater than the Olsen P concentration of soil (Table 3). However, the relative differences in Olsen P status between the four soils, and the differences in the AER-PP and BD-PP concentrations of the sediment transported from these soils (AER-PP/TSS and BD-PP/TSS; Table 3), were roughly similar to each other. The AER-PP/TSS and BD-PP/TSS ratios at Aurajoki were 2.5–3 times those at Jokioinen, and about twice those at Lintupaju and Sjäokulla. At the same time, the Olsen P value of the Aurajoki soil was about twice that at Jokioinen and 1.8–2.0 times the values at Lintupaju and Sjäokulla. Thus, the relative differences in the sediment PP pools followed the Olsen P status more closely than did the average DRP concentrations. Olsen P could therefore prove to be a cost-effective and accessible tool for predicting the eutrophication potential associated with soil loss. Because PP losses often dominate over DRP losses, it may in many cases be even more important to estimate potentially algal-available PP than the average DRP concentrations (Jokela et al., 1998).

Table 3. Topsoil (Ap/Ap1 horizon) concentrations of bicarbonate-extractable P (P_{Olsen}), the sum of (NH_4Cl -P), NH_4F -P, and NaOH-P of the Chang-Jackson scheme (i.e., non-apatite inorganic P, NAIP), and total soil P (by HF-Aqua Regia extraction). Further, extractability of runoff sediment-associated P by AER (AER-PP/TSS) and BD (BD-PP/TSS) procedures, and total sediment P concentration (PP/TSS) as calculated from runoff analyses of total P (peroxodisulfate digestion TP less DRP) and evaporation residue (TSS).

	P_{Olsen}	NAIP	Total P	AER-PP/TSS	BD-PP/TSS	PP/TSS
	— mg kg ⁻¹ soil —			— mg kg ⁻¹ sediment —		
Aurajoki	74	677	1762	161	829	1685
Jokioinen	36	436	1320	55	328	824
Lintupaju	41	447	1320	78	485	1002
Sjäokulla	38	388	1150	80	425	1143

For the redox-labile runoff P, the amounts of BD-PP in 1 kg of runoff sediment matter exported from the four sites were similar to the sum of Chang-Jackson P fractions extracted by NH_4F and NaOH, assumed to

approximate non-apatite P (NAIP), in the soil samples retrieved from the Ap horizons of the fields. The average runoff BD-PP/TSS values corresponded to 75–122% of the NAIP (Table 3), suggesting that BD-PP refers to the entire labile P pool of the eroded soil. However, the similarity in the concentrations of NAIP in the source soil and the concentrations of BD-P in runoff sediment does not mean that the P extracted by these methods necessarily originates from the same associations. The runoff sediment and its source may differ in chemical constitution as a result of selective erosion according to particle size and density (the selectivity also being influenced by slope characteristics, soil structure, and other factors affecting flow velocity). Neither can the target-specificity of the extractants be taken for granted.

3.7 Transport of P forms via surface pathway from arable clayey soils

The bulk of the surface runoff from the fields occurred during and after snow- and frostmelt in spring, and again in autumn. This is exemplified by the Jokioinen flow graph shown in Fig. 9. In autumn, turbidity of runoff increased as soon as the soils were cultivated, and the concentrations of PP peaked during autumn flow (Fig. 9). Wintertime precipitation fell (in most years) largely as snow that partly evaporated and partly ran off during spring flow peaks, whereas summertime precipitation generally produced little runoff owing to the demand for evapotranspiration. Even though there was some variation between the four sites, the trend illustrated in Fig. 9 was in general repeated at the other sites. Runoff at the four study sites was also similar in that PP was the dominant P fraction: the average proportion of PP as a percentage of the P transported by runoff ranged from 73% to 94%.

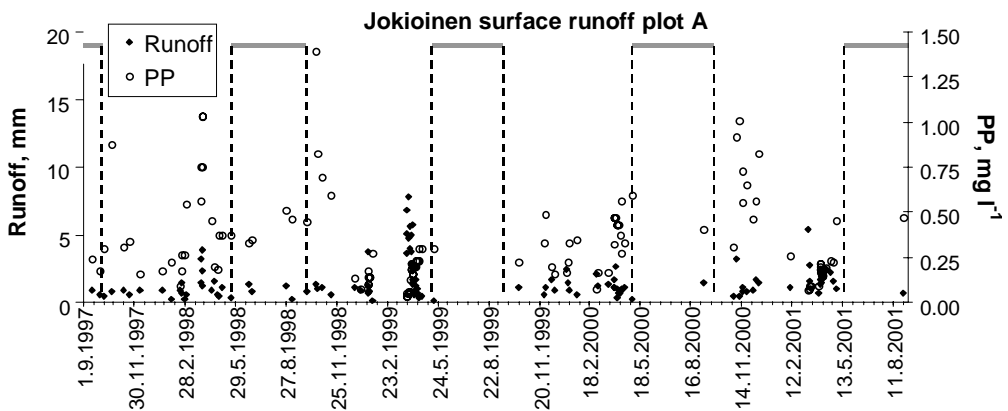


Fig. 9. Sampling-wise runoff volume readings (black diamonds) and particulate P (PP) concentrations (white circles) at one of the Jokioinen 0.5-ha surface runoff plots. The time between spring sowing and autumn plowing is indicated by horizontal bars and vertical dotted lines.

As is typical of P losses in general (Schoumans and Chardon, 2003), actual PP losses varied considerably between the sites and also from one year to another (Table 4). Sediment-associated P transport by surface runoff was highest from the Aurajoki soil with the high soil P status and relatively great annual soil losses. Particle P transport via surface pathway was lowest from the Jokioinen field with the moderate P status and little erosion. Averaged over the 4 study years, the estimates of algal-available PP (i.e., $1.9 \times$ AER-PP; see Fig. 3 and section 3.2.) surface runoff losses from Aurajoki, Lintupaju, and Jokioinen (a continuum representing soils with “good” – “satisfactory” – “fair” agronomic P status) were 394, 182, and 36 g ha⁻¹, respectively. The BD-PP losses were about three times that: 1100, 485, and 102 g ha⁻¹, respectively. Considering the average surface pathway DRP losses of 461, 161, and 43 g ha⁻¹ (for Aurajoki, Lintupaju, and Jokioinen, respectively), it is concluded that the PP losses contribute to the transport of bioavailable P at least at the same rate as DRP.

Table 4. Precipitation (Prec.), measured surface runoff volumes (Runoff), surface pathway losses of dissolved molybdate-reactive P (DRP) and particulate P (PP), and erosion. The estimated losses of anion exchange resin-extractable PP (AER-PP) and bicarbonate-dithionite-extractable PP (BD-PP) were calculated as described in Paper III; shown here are the average predicted values.

	Prec.	Runoff	DRP	PP	AER-PP	BD-PP	Erosion
	— mm —		g ha ⁻¹				kg ha ⁻¹
Aurajoki							
Sept 97 – Aug 98	830	136	425	2650	270	1340	1500
Sept 98 – Aug 99	590	235	497	2410	250	1300	1170
Sept 99 – Aug 00	769	238	411	1680	170	950	1030
Sept 00 – Aug 01	727	221	511	1390	140	810	920
Jokioinen							
Sept 97 – Aug 98	654	64	35	353	25	118	400
Sept 98 – Aug 99	496	125	73	232	13	97	248
Sept 99 – Aug 00	694	60	29	281	20	99	296
Sept 00 – Aug 01	598	68	34	261	18	94	291
Lintupaju							
Sept 97 – Aug 98	654	121	183	1022	87	430	1325
Sept 98 – Aug 99	496	209	197	802	57	360	923
Sept 99 – Aug 00	694	174	139	847	65	370	1037
Sept 00 – Aug 01	598	163	125	1974	175	780	2271

At Aurajoki, the maximum annual variations in surface runoff losses of potentially bioavailable PP forms were 130 g ha^{-1} for AER-PP, which translates to about 250 g ha^{-1} algal-available PP (*viz.* $1.9 \times$ AER-PP loss), and 530 g ha^{-1} for BD-PP. The maximum variation in annual DRP loss, which was affected not by erosion but by runoff timing and volumes, equaled 100 g ha^{-1} at Aurajoki. At Lintupaju, the maximum difference in DRP transport between the study years was about 70 g ha^{-1} , while the transport of algal-available PP varied by more than 220 g ha^{-1} , and BD-PP losses by 420 g ha^{-1} . At Jokioinen, erosion via the surface pathway was equally modest in all years, and variation in the transports of BD-PP and algal-available PP amounted to less than 25 g ha^{-1} . Unlike at the other sites, variations in DRP losses by surface runoff at Jokioinen were greater than those of other P forms owing to the voluminous runoff via this pathway in the second study year. Then, the transport of DRP rose from 30–35 to a maximum of 73 g ha^{-1} .

As shown by the natural variation in the estimates of bioavailable PP losses via the surface pathway at Aurajoki and Lintupaju, reductions in bioavailable P losses by erosion control may be considerable. However, erosion control is only one piece in the puzzle. Mueller et al. (1984), for example, measured smaller algal-available (estimated by AER extraction) P losses from no-till plots, where erosion losses were effectively reduced, but only on unmanured soil. Spreading manure on the soil surface reversed the situation, and the no-till plots lost much more algal-available P than did conventionally managed ones. The reason for this was that manure was not mixed with soil (manure could only react with a small soil volume) in the no-till plots and also because (surface) runoff was greater in the no-till soil. Hence, even if an immediate effect on P losses could be achieved by controlling erosion, fertilization practices (including rates, techniques, and timing), as well as soil P status, should also be taken into account.

3.8 Relative sizes of the potentially bioavailable fractions of particulate P in runoff

Calculating algal-available PP by multiplying the AER-PP by a constant value of 1.9 (from the equation presented in Fig. 3) suggested that a 10–20% fraction of total runoff PP became algal-available as a result of desorption to aerobic water with near-zero P concentration. Similar or greater percentages of runoff PP availability for algae, 4–41%, 21–24% and 9–45% of PP, were reported in the review of Ekholm (1998), and the studies of Dorich et al. (1985) and Cowen et al. (1978), respectively.

In the present study, the highest proportions of AER-PP were extracted from the Aurajoki samples and the lowest from the Jokioinen samples. The differences in AER-extractability of PP at the four sites were assumed to reflect the different P saturation degrees of the soils and, consequently, runoff sediment. A mechanistic explanation would be that at high P saturation, a

large part of the P sorbed is associated with sorption sites having a low affinity for P, and that these low energy sites release P readily with a decrease in ambient P concentration. However, direct confirmation of this supposition could not be found in any published runoff studies, which (like the present study) tend to have a case-study character. Therefore, soil studies were consulted.

Raven and Hossner (1993) reported that desorption of P by AER from five different types of Texas soil low in P were relatively unaffected by initial enrichment in P: plotting AER-P vs. P enrichment produced a linear relationship, thus contradicting the suggestion that an increase in P saturation increases the AER-P catch. This finding was probably due to the low initial P saturation status of the soils in their study. In relation to the low P saturation status, Raven and Hossner (1993) also applied relatively moderate amounts of P to the soils, 100 mg P kg⁻¹ at most. In contrast, Barrow and Shaw (1977) had earlier reported that upon excessive P additions, up to 1500 mg P kg⁻¹ soil, relatively more AER-P was extracted from soils to which greater amounts of P were added. Even though historical fertilizer and manure P applications to the Aurajoki soil have probably been closer to the P rates of Raven and Hossner (1993) than to those of Barrow and Shaw (1977), the long-term surplus P balance of the Aurajoki soil seems to be associated with the increased extractability of runoff PP.

The BD-extractable proportions of PP in runoff from these soils, 35–60%, were somewhat lower than the estimates for maximum bioavailabilities of PP in stream sediment reported by Pacini and Gächter (1999). Using a P fractionation scheme that included NH₄Cl, BD, and NaOH extraction steps, they estimated that not less than 51–73% of sediment PP would become bioavailable. When the estimate was based on NH₄Cl and BD-extractable pools only, the figure for (“minimum”) bioavailability P equaled 25–60% of PP, which is a similar percentage to that in the present study. James et al. (2002) assessed the composition of sediment P, weighted according to flow volumes, for the agriculturally affected basin of the Redwood River (Minnesota, USA). They found that NH₄Cl and BD-extractable molybdate-reactive P amounted to 43% of PP, whereas inclusion of NaOH-extractable P (77% of which was non-reactive before digestion, i.e., organic P) raised this proportion to 69% of PP. Using sequential NaOH and citrate-dithionite-bicarbonate extractions, Logan et al. (1979) measured amounts corresponding to 43–89% of sediment-associated P in samples obtained from streams draining into Lake Erie. Because of the diversity of methods used in earlier studies of the maximum likelihood of PP bioavailability (a practice unfortunately continued in the present work), the published figures are not directly comparable. Even so, they all tend to be relatively high for dithionite-extractable PP.

3.9 Subsurface losses of P

Surface runoff and subsurface drainage flow were monitored at two of the field sites, Jokioinen and Sjäokulla. From September 1997 to August 2001, more than 70% of runoff from the relatively flat Jokioinen field drained via the subsurface pathway. At Sjäokulla, flow monitoring proceeded smoothly in 1998 only, and in that year drainflow was estimated to account for about half of the runoff. Sjäokulla differs from the relatively flat Aurajoki field in having undulating topography and an old drainage system dating back to 1950.

It is generally accepted that subsurface drainage is beneficial where P losses are concerned. As example, Grazhdani et al. (1996) measured 24–31% lower soil losses and 29–35% lower DRP losses from drained southeast Albanian clayey field plots than from undrained plots. Likewise, Haygarth et al. (1998) reported that subdrained plots of a clayey grassland (in Devon, UK) lost about 30% less TP than undrained counterparts. At Jokioinen and Sjäokulla, we had no undrained control soils with which to make comparisons. However, Turtola and Paajanen (1995) estimated that soil and P losses from the Jokioinen field decreased by 15–20% after the poorly functioning old drains were replaced by new ones. Before the drainage improvement, about 80% of the flow ran off via the surface pathway; afterwards, the bulk of runoff (currently about 70%) was subsurface drainflow. Further, it can be noted that the concentration of total P in drainflow sediment was about 90% of that in eroded soil carried by surface runoff in both Jokioinen and Sjäokulla soils (Paper III). The lower P concentrations in drainflow were perhaps a result of sorption of ortho-P by, and entrapment of PP at, subsoil horizons, especially during the base flow periods.

Due to the relatively high proportion of flow via subsurface drainage at Jokioinen, losses of DRP and PP via this pathway were greater than those via surface runoff (Fig. 10). Averaged over the 4 years monitored, Jokioinen surface runoff losses of DRP and PP accounted for only 36% and 25%, respectively, of the mean total annual losses of DRP (118 g) and PP (1127 g) from a field hectare by both runoff pathways. The relative enrichment in PP of subsurface flow as compared to surface runoff had already been pointed out by Turtola and Paajanen (1995) in an earlier Jokioinen study. More recently, the same phenomenon has been reported by Simard et al. (2000) in their summary of three studies conducted on Canadian and English soils. As to the concentrations measured during the present study, DRP and PP at Jokioinen differed from each other in that the DRP concentrations in drainflow were lower than, and those of PP equal to, the concentrations measured in surface runoff (Fig. 10).

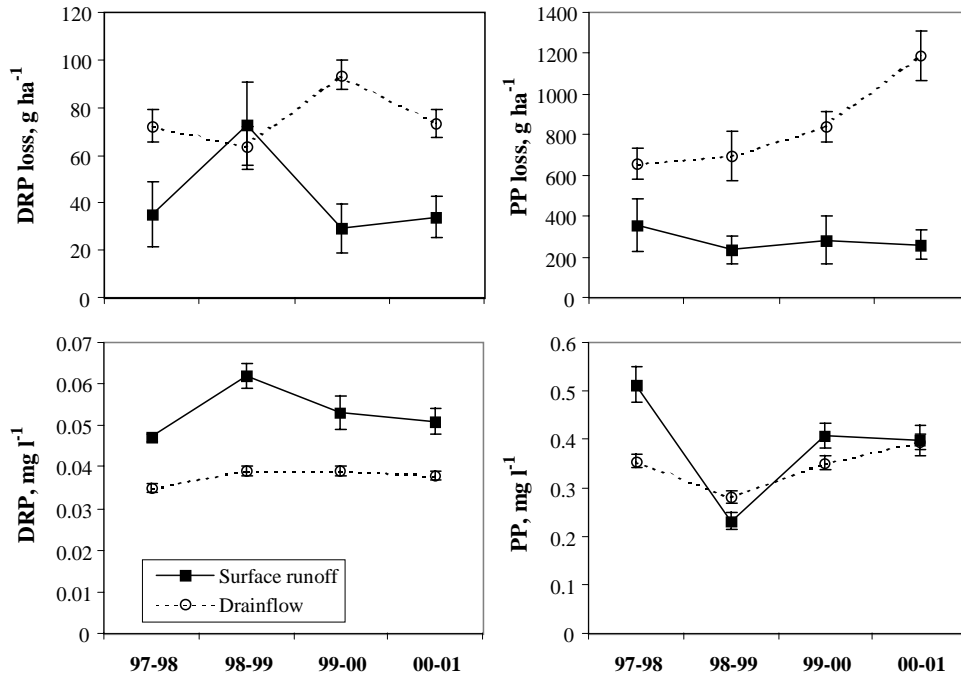


Fig. 10. Average losses (upper graphs) and concentrations (lower graphs) of dissolved molybdate-reactive P (DRP) and particulate P (PP) via surface (black squares) and subsurface (white circles) pathways during 4 years in the Jokioinen field. The markers indicate the average of the four surface runoff plots and 16 drainflow sampling plots, and the error bars show the standard error of the mean. Each annual average is based on a number of samples ranging from 96 to 171 for surface runoff and from 384 to 592 for drainflow.

At Sjöckulla, the approximately equal distribution of flow by surface and subsurface pathways and the slightly lower PP concentrations of subsurface runoff sediment suggest that subsurface P losses at this site may be lower than surface runoff losses. On the basis of the runoff fractions sampled, surface runoff losses of DRP and PP were 60 and 2030 g ha⁻¹, respectively. Via the drainage pathway, DRP and PP losses amounted to about 30 and 900 g ha⁻¹, respectively (calculated as the average of the two drainflow weirs D3 and D4). Because flow sampling was not continuous at Sjöckulla but concentrated on peak flow events, these figures probably overestimate the relative share of PP losses, and especially the importance of surface pathway PP losses as compared to those via the drainage pipes. These values are, however, underestimates of the total losses, as no interpolation between the samplings was made.

To compare the Jokioinen and Sjöckulla data with the results presented by Laubel et al. (1999) for two winter storm drainflow events in a Danish sandy loam, P losses in surface and subsurface runoff were related to the amount of

water draining via these pathways. In accordance with Laubel et al. (1999), these estimates are called “P loss coefficients”. At the two sites studied here, DRP loss coefficients were greater for surface runoff than for subsurface drainflow: at Jokioinen, 0.53 and 0.37 g DRP ha⁻¹ mm⁻¹, respectively, and at Sjäokulla, 0.73 and 0.52 g DRP ha⁻¹ mm⁻¹, respectively. Due to the difference in sampling strategies (flow-weighted sampling at Jokioinen and grab sampling at Sjäokulla), the results calculated for the two sites substantially differed in respect of PP loss coefficients. At Jokioinen, surface and subsurface runoff contained 3.6 and 4.2 g PP ha⁻¹ mm⁻¹, respectively, whereas the Sjäokulla PP loss coefficients for surface and subsurface runoff were 25 and 13 g ha⁻¹ mm⁻¹, respectively. As compared to the PP loss coefficients for the Danish sandy loam, with 0.57–1.75 g PP ha⁻¹ mm⁻¹, the average PP loss coefficients were manyfold at Jokioinen and at an entirely different level at Sjäokulla. The cause of the greater PP loss coefficients in the present study was probably the higher erodibility of Finnish clay soils studied. Even so, the difference between Sjäokulla soil and the soil reported by Laubel et al. (1999) was surprisingly great, especially as runoff peaks were sampled at both sites.

3.10 Origin of soil particles transported by subsurface drainflow

At Jokioinen and Sjäokulla, similar ¹³⁷Cs activities were measured by gamma spectrometer for the sediment matter delivered by surface runoff and the sediment transported by subsurface flow (Fig. 11; Paper IV). The amount of ¹³⁷Cs in runoff sediment was about twice as high as that in topsoil, in accordance with the findings of Laubel et al. (1999) and Chapman et al. (2001). Because ¹³⁷Cs attaches strongly to soil particles and, unless carried by eroded soil matter, is immobile in soil (e.g., Mahara, 1993; Facchinelli et al., 2001), the relative enrichment of drainflow in ¹³⁷Cs indicates topsoil translocation to the drains. For the other half of the Jokioinen field, however, the only justified conclusion is that the sediment matter transported by drainflow was not subsoil, because the backfill of the drains at the upper end of the Jokioinen field also contained topsoil exposed to ¹³⁷Cs. The topsoil was (in 1991) used as backfill for the drainage excavation at the upper end of the field, whereas the backfill material at the lower end of the field was wood chips. At Sjäokulla, where the drains date back to 1950, the equal activity of ¹³⁷Cs in surface and subsurface runoff revealed that topsoil was the sediment source in both pathways. The conclusion that the bulk of the drainflow sediment in the fields studied originated from the topsoil is supported by the finding that drainflow sediment matter contained almost as much AER-extractable P as did the sediment delivered by surface runoff (Paper IV).

Especially in wet soil during peak flow periods, flow through a soil profile may occur largely via macropores, e.g., cracks and biochannels, that facilitate the transport of reactive elements and compounds in soils (e.g., Jensen et al., 1998; Albrecht et al., 2003). In many cases, cracking of soil below the Ap

horizon is more frequent at the drain excavation than between the drains (Turtola and Paajanen, 1995; Øygarden et al., 1997); moreover, earthworms may be present in greater numbers in soil above the drains than in the undisturbed soil between them (Nuutinen et al., 2001). The burrows of *Lumbricus terrestris* sometimes terminate on the drainage tile surface (Nuutinen and Butt, 2003) or at a few centimeters from the drainage pipes (Shipitalo and Gibbs, 2000). Then, biochannels at the drain excavation can operate as major bypass flow routes and, together with cracks and voids, promote rapid transport of solutes and particulates through a soil profile into drainage pipes and off the field (see Shipitalo and Gibbs, 2000).

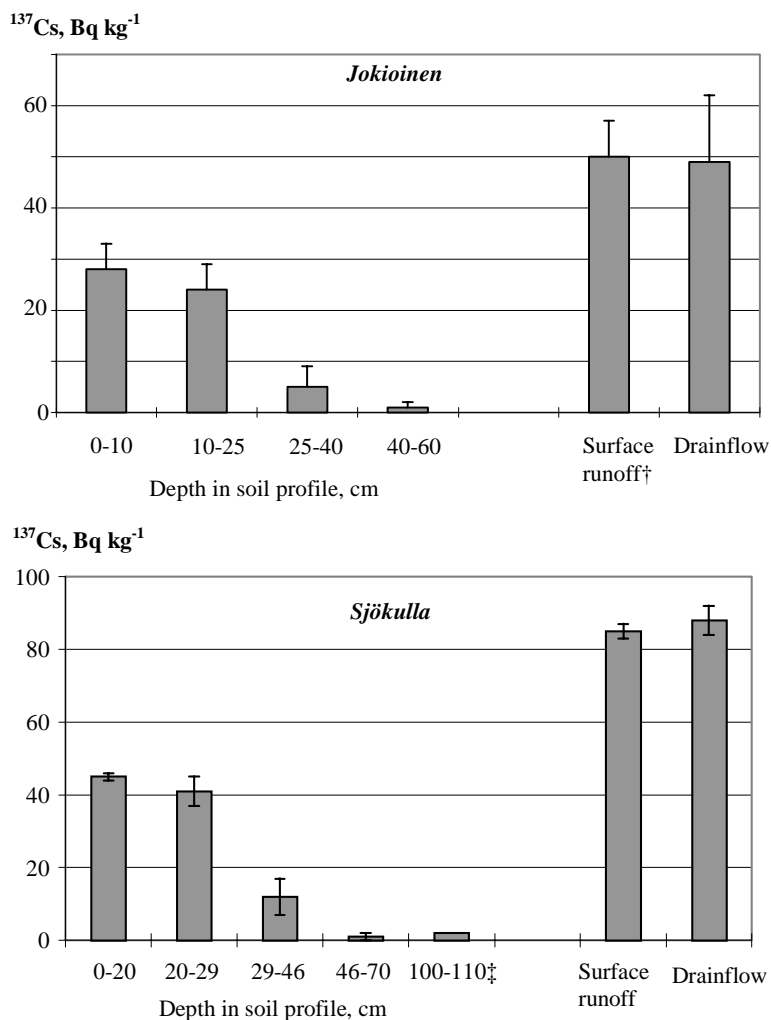


Fig 11. Activity of ^{137}Cs in the soil profiles and suspended soil material carried by surface runoff and subsurface drainage waters. At Jokioinen $n = 8$ ($\dagger n = 4$), error bars indicate SD. At Sjökölla $n = 2$ ($\ddagger n = 1$, sampled just above the tile-drain), error bars indicate range.

Matter containing organic P has also been found to be mobile in soils, and organic P may migrate through the profile to the depth of drainage pipes (see Frossard et al., 1989; Chardon et al., 1997). Still, the contribution of organic P compounds delivered to the eutrophying P load by field runoff is largely unknown. Organic P concentrations are frequently small, making analyses of organic P in runoff, soil solution, and weak soil extractants a challenging task (e.g., Espinosa et al., 1999; see also Koopmans et al., 2003; Turner et al., 2003). Here, organic P was not separated as a distinct P fraction, but all of the P forms analyzed may include a contribution by organic P (see e.g., Chardon et al., 1997; Hens and Merckx, 2001). Nevertheless, in the material of this study, the major contribution was by the inorganic pool.

3.11 Concentration of clay-sized matter and P in soil and runoff

According to the few particle count analyses made on Jokioinen and Sjököulla composite runoff samples, both runoff pathways were enriched in fine-sized separates as compared to topsoils (Paper IV). The enrichment ratio for clay-sized matter relative to the topsoil was around 2, suggesting that clay particles were selectively washed away from the fields. Further, high surface-reactivity of the eroded matter was suggested by the observations that the ^{137}Cs concentration of runoff sediment was about twice that of the bulk topsoil matter (Fig. 11). Due to the high surface-reactivity of the fine-earth fraction of soil and the important role played by clay separate in determining the P desorption-sorption properties of soils (Sinaj et al., 1997), the selective erosion of clay-sized particles may also be associated with enrichment of runoff in plant nutrients. As an example, Sharpley (1985) measured enrichment ratios of 1.4–1.9 for clay particles, 1.3–1.7 for total P, and 1.4–1.6 for bioavailable (NaOH-extractable) P in runoff sediment mobilized during rainfall simulations of six soils in Oklahoma and Texas. Earlier, Stoltenberg and White (1953) had reported that the total P concentration of eroded sediment derived from 12 Indiana silt loam watersheds (slope 2–5%, under natural rainfall) during 4 years was about twice that measured for the topsoils.

In contrast to these reports (as well as the enrichment of runoff in ^{137}Cs), the average P concentration of Jokioinen and Sjököulla runoff sediment was 20% less than that measured on topsoil samples by total P analysis (values shown in Table 3). This result was partly due to the methods used. Peroxodisulfate digestion, which is employed in runoff sediment P analysis, is known to underestimate the actual P concentration of a turbid runoff sample, and does not give as good TP yields as does the Aqua Regia-HF extraction employed in soil analysis (Turtola, 1996). However, as the underestimate of the actual P concentration by peroxodisulphate digestion should not be more than 10–20% (Turtola, 1999), the P concentration of the runoff sediment may in reality have been similar to the concentration in the source soils.

The non-existing P enrichment, and the dissimilarity of P and ^{137}Cs transport, is hypothetically attributed to the fact that P sorption density in these soils is located, not in the finer and lighter particles, but in Fe concentrations. The oxides of Fe, known to have a high P sorption capacity, are also known to aggregate soil particles (Barberis et al., 1991). As suggested by the cover photo, Fe was not equally distributed in the soil matrix. Because Fe is a heavy element as compared to the other main soil constituents, aggregates with high concentrations of Fe probably have a high P sorption density but are less susceptible to transport by water than aggregates of similar size but with less Fe. In contrast, ^{137}Cs is immobilized onto accessible cation exchange sites (see Anderson and Sposito, 1991), and the runoff concentration of clay particles and ^{137}Cs are intimately related. In these predominantly fine-textured soils, further enrichment in the runoff of the finer dispersible clay and, consequently, ^{137}Cs occurred, whereas aggregation of clay particles and other soil constituents by Fe affected both the P sorption distribution and susceptibility of these aggregates to erosion.

4 Conclusions

Characterization of PP to estimate ease of transformation into a bioavailable form (potential bioavailability) facilitates design of effective eutrophication control protocols. The layout of such protocols should be adjusted according to catchment and runoff characteristics, and the properties of receiving waters (Reynolds and Davies, 2001; Withers and Lord, 2002). Although a relatively small proportion of PP is transformed into an algal-available (ortho-P) form (e.g., Ekholm, 1994), the effects of PP transport on P-induced eutrophication may be highly significant due to large transports of particulate matter.

When selecting the methods of this study, we originally wanted to find a mechanistically relevant method that could be used for large surveys and that would perform well enough to allow their use in the P extraction of field runoff from the soils of this study. Eventually, the potential bioavailability of PP was estimated in two different ways. Anion exchange resin extraction probably gives conservative estimates of the potential desorption of PP in natural waters, but there was a functional relationship and the results correlated well with algal-available PP. Hence, a conversion coefficient between AER-PP and algal-available PP was determined.

Runoff PP exceeding the estimates of algal-available PP was solubilized when runoff samples were chemically reduced by bicarbonate-buffered dithionite. It was suggested that the mechanism behind P solubilization by BD is Fe(III) oxide dissolution, which affects P-Fe(III) associations or radically reduces the sediment P sorption capacity, or both, thereby increasing P concentrations in solution. The interpretations of BD extractions rely on the assumption that chemically reducible, presumably Fe-associated, P may become bioavailable in a severely reduced environment. Because the

redox cycling of P mostly occurs in deeper water layers, and the redox-sensitive PP may be of limited access for primary producers (Reynolds and Davies, 2001), the relevance of the BD-extractable PP for eutrophication is perhaps more diffuse than that of the AER-extractable fraction. However, owing to the likelihood of anoxic conditions in some sediments, assessment of the amount of P associated with reducible Fe is also desirable (Paludan and Jensen, 1995).

The dominant P form in runoff from the four soils studied was PP, accounting for 73–94% of total P. The runoff of sediment-associated P from the fields studied here would likely accelerate eutrophication of the receiving waters: as a contributor to the algal-available P transported, PP was as important as DRP, and the estimated redox-sensitive PP losses were about 2–3 times the DRP losses. Since the transport of potentially bioavailable PP may greatly exceed the DRP losses, erosion control, when applicable, appears to be an effective and rapid way of curbing losses of bioavailable P from these soils.

As an example in modeling work, there is an obvious need to assess losses of bioavailable PP. For this purpose, simple and accessible methods that can be used in combination with erosion data are required. As a preliminary supposition, drawn from the results for the four field sites studied here, topsoil Olsen-P concentrations could perhaps be used as indicators of the concentrations of AER-PP and BD-PP in eroded soil matter. This suggestion is based on the observed similarity in the relative differences between topsoil concentrations of Olsen P and AER- and BD-extractable runoff sediment P. The Olsen test clearly fails to discriminate between easily leached soil P and the more tightly sorbed fractions, and the DRP thresholds based on Olsen P should therefore be adjusted according to the P sorption properties of the soils. Nevertheless, the Olsen test may have good potential in estimation of the differences in bioavailability of PP, as it is related to the reserves of surface-sorbed P.

At Jokioinen and Sjökölla, flow through the soil profile is probably characterized by macropore flow, especially during peak flow periods. The sediment carried by surface and subsurface runoff contained roughly the same amounts of P as did the topsoil of the fields, whereas the runoff of both pathways carried about twice as high an amount of clay-sized particles and (clay-associated) ¹³⁷Cs as was present in the topsoil samples. At Jokioinen, drainflow was the main pathway for water, P, and soil losses. At Sjökölla, flow and P losses were probably somewhat greater in surface runoff. Notably at Jokioinen, where drainflow was such an important carrier of potentially bioavailable PP, dispersion of topsoil in the whole field area should be decreased to reduce the losses of bioavailable P from the field.

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