

A rainfall simulation study on the relationships between soil test P *versus* dissolved and potentially bioavailable particulate phosphorus forms in runoff

Risto Uusitalo and Erkki Aura

MTT Agrifood Research Finland, Soils and Environment, FI-31600 Jokioinen, Finland,

e-mail: risto.uusitalo@mtt.fi

Runoff from clayey soils often contains abundant particulate phosphorus (PP), part of which may solubilize in surface waters. Monitoring losses of potentially bioavailable forms of PP is expensive, calling for other ways to predict them. Such predictions could be based on soil loss and available soil P indices, e.g., agronomic P status. To study correlations between P pools in runoff *versus* soil P saturation (by Mehlich 3 extraction; DPS_{M3}) and acetate soil test P (P_{Ac}), 15 clayey soils of south Finland were subjected to laboratory rainfall simulation. Runoff from these simulations was analyzed for concentrations of suspended soil (TSS), dissolved molybdate-reactive P (DRP), total P (TP), and, as normalized to soil loss, potentially bioavailable forms of PP: desorbable (anion exchange resin-extractable, AER-PP/TSS) and redox-labile PP (bicarbonate-dithionite-extractable, BD-PP/TSS). Correlation coefficients (r^2) between DPS_{M3} and DRP, AER-PP/TSS, and BD-PP/TSS equaled 0.92, 0.77, and 0.45, respectively. Runoff P forms were also correlated to soil P_{Ac} with r^2 values of 0.84, 0.56, and 0.58 for DRP, AER-PP/TSS, and BD-PP/TSS, respectively. Prediction of soil loss-normalized concentrations of potentially bioavailable PP by the agronomic P_{Ac} test was considered possible. However, such predictions have a high degree of uncertainty, evidenced by comparison to published field data. Acceptably accurate predictive equations would require a large material as a basis for their construction, and soils should probably also be grouped according to other soil properties that would account for variation in P sorption capacity.

Key words: phosphorus, bioavailability, erosion, rainfall simulation

Introduction

In areas where clayey soils are abundant, particulate phosphorus (PP) is the major form of P in field

runoff (see Pietiläinen and Rekolainen 1991, Turtola and Paajanen 1995, Puustinen et al. 2005). Depending on soil characteristics and environmental conditions, a variable part of the runoff PP may become algal-available over time (Logan et al.

1979, Ekholm 1994) and accelerate eutrophication of surface waters in the same manner as dissolved molybdate-reactive phosphorus (DRP) does.

Data abound on the effects of different land management options on concentrations and losses of DRP and PP (the Finnish studies include Puustinen 1994, Turtola 1999, Uusi-Kämppeä et al. 2000). From these work we learn that the total off-site P losses are often reduced by erosion control measures, such as vegetated buffers, but that this decrease may be counterbalanced by increased losses of DRP (see also Culley et al. 1983, Bundy et al. 2001). Because of the nonequivalent effects of DRP and PP on eutrophication – DRP is fully and immediately algal-available, whereas a variable part of the PP may solubilize –, the findings of studies on land management practices cannot be fully utilized in efficient eutrophication control. To be able to predict the net effects of field management on eutrophying P losses, we should be able to assess the pollution potential of PP in different situations.

Quantitative estimates of the losses of potentially bioavailable P forms have been made at four field sites in southern Finland (Uusitalo et al. 2003, Uusitalo 2004). At these sites desorbable PP (anion exchange resin-extractable PP, AER-PP) was found to make up as great a part of the P losses as did DRP; on average 10–20% of runoff PP was estimated to become algal-available at low ambient P concentration in an oxic water column. In case the eroded soil would end up in an anoxic sediment, solubilization of redox-labile PP (assessed by bicarbonate-dithionite extraction; BD-PP) could increase the bioavailability to 35–60% of runoff PP. At these four sites, potential bioavailability of runoff PP was the higher, the higher was the agronomic P status of the source soil.

The use of agronomic soil P tests in assessing the potential for phosphorus release from soil to runoff have been evaluated in a number of research papers (e.g. Sharpley et al. 1978, Heckrath et al. 1995, Pote et al. 1996). Soil test P has usually been found to correlate well with the concentration of DRP in runoff, whereas PP – in many cases the major form of runoff P – has received little attention (Jokela et al. 1998). Calculating direct corre-

lations between PP concentration in runoff and soil test P is also meaningless because the concentrations of PP are mainly governed by the erosion rates. However, when normalized to soil loss, P contents and P solubility indices of the source soil do affect losses and concentration of bioavailable PP. This is because PP/TSS ratio increases with soil P content, and the erosion rate-normalized losses of algal-available PP increases with soil P phytoavailability (agronomic P status). Combined with soil loss data, soil P tests could, as example, help in assessing whether a management practice implemented at a particular site is to reduce the losses of those PP pools that are relevant for eutrophication more than they are known to increase the losses of DRP.

In this paper, we report results of a rainfall simulation study in which we tested the potential of acid ammonium acetate buffer, the agronomic soil test of Finland, and an estimate of soil P saturation, based on extraction using Mehlich-3 solution, for their abilities to predict the concentrations of (i) DRP in runoff and (ii) the content of potentially bioavailable P forms (i.e., desorbable and redox-sensitive PP/TSS) in sediment. The reason for selecting P_{Ac} as a soil P-test is obvious: the large database of P_{Ac} concentrations of Finnish agricultural soils. As a soil P saturation index we used a procedure based on Mehlich 3 extractant, a rapid method that is used as an agri-environmental P saturation index in Delaware, USA (see Sims et al. 2002). According to our unpublished data, DPS_{M3} also correlates well with the DPS index used in recent Finnish studies (Turtola and Yli-Halla 1999, Peltovuori et al. 2002) where non-apatite soil P was related to oxalate-extractable Al and Fe.

Material and methods

Soils and soil analyses

During the summer of 2002, about 50-l soil samples were retrieved from the Ap horizons (0–20 cm

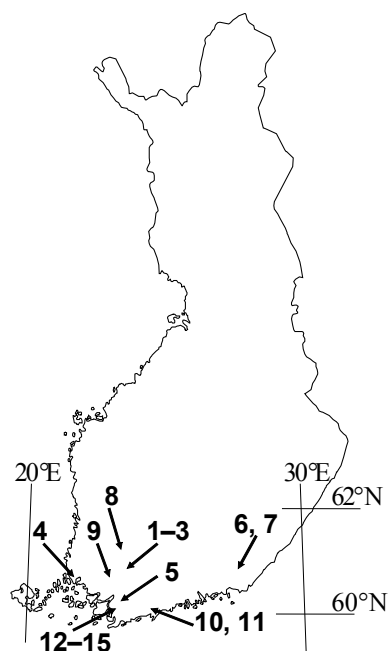


Fig. 1. Map of Finland showing sampling locations of the 15 soils used in rainfall simulations. Soil characteristics are given in Table 1.

depth) of 15 fields located in southern Finland (Fig. 1). Soil samples were taken with a spade, thoroughly mixed, and a 1-l subsample of each soil was taken for laboratory analyses. This subsample was air-dried at +35°C and ground to pass through a 2-mm sieve, whereas the rest of the sample was stored field-moist in a plastic bag in a storage (at outdoor temperatures) for one to four months prior to rainfall simulations.

An overview of the physical and chemical properties of the soils is given in Table 1. Particle-size distribution was determined by the pipette method of Elonen (1971), soil pH was measured in 1:2.5 (v/v) water suspension with a glass electrode, and total C was analyzed with a LECO (St. Joseph, MI, USA) CN-2000 analyzer. For oxalate-extractable Al and Fe, the method of Schwertmann (1964) was used; the concentrations of Al and Fe were determined with an inductively coupled plasma-atomic emission spectrometer (ICP-AES; Thermo Jarrell Ash, Franklin, MA, USA). The agronomic P status was assessed using an extraction with acid (pH 4.65) ammonium acetate buffer (P_{Ac} ; Vuorinen and Mäkitie 1955), whereas extraction with Meh-

Table 1. Physical and chemical properties of the soils studied. Sampling locations of the soils are shown in Fig. 1. The numbers below the texture class indicate particle size in micrometers.

Soil number	Clay	Fine silt	Coarse silt	Sand	pH_w	Tot. C	P_{Ac}	Al_{ox}	Fe_{ox}
	<2	2–20	20–200	>200					
					%		mg l ⁻¹	– mmol kg ⁻¹ –	
1	57	22	12	9	6.4	3.3	3.0	101	207
2	47	31	12	10	5.7	2.4	4.9	89	214
3	41	26	24	9	6.7	3.1	39.5	64	172
4	63	23	11	3	5.7	2.3	7.5	74	175
5	39	34	18	9	6.4	2.1	16.9	54	145
6	57	16	20	7	5.6	2.7	4.6	91	183
7	51	25	16	8	6.7	2.3	22.8	65	137
8	31	33	29	7	5.0	2.1	7.6	78	175
9	62	32	4	2	5.4	4.2	8.3	105	118
10	45	30	19	6	5.9	2.9	8.6	83	163
11	44	23	16	17	5.6	4.2	7.5	117	127
12	45	21	23	11	7.0	3.0	3.4	71	179
13	40	26	30	4	7.4	1.5	46.4	46	118
14	36	29	25	10	6.9	2.1	15.2	51	124
15	40	26	28	6	6.7	2.3	10.9	57	127

P_{Ac} = soil P extractable by ammonium acetate buffer (pH 4.6)

Al_{ox} , Fe_{ox} = oxalate-extractable Al and Fe

lich 3 (M3) solution (Mehlich 1984) was conducted for an assessment of soil P saturation (DPS_{M3} ; see, e.g. Sims et al. 2002). In calculating DPS_{M3} , the molar concentration of M3-extractable P was related to the molar concentrations of M3-Al and M3-Fe:

$$DPS_{M3} (\%) = 100 \times \text{M3-P (mol)} / [\text{M3-Al (mol)} + \text{M3-Fe (mol)}]$$

Phosphorus, for P_{Ac} and M3-P, was determined by molybdate colorimetry using a Bran + Luebbe (Norderstedt, Germany) autoanalyzer with 880 nm filter, and Al and Fe in the M3-extracts were determined with the ICP-AES.

Rainfall simulation

The rainfall simulator used was a drop former-type stationary laboratory simulator, a modification of the drip-type simulator described by Bowyer-Bower and Burt (1989). In the used equipment, deionized water is pumped to a column where water level above the drop former is kept at a constant level by regulating bypass flow; in this work, the water head height was maintained at 40 mm. From the column, water is conducted to 0.020-mm (inner diameter) capillary tubes which form the drops, and with the above noted water head setting, a single drop has an average weight of 37.5 mg. There are 96 drop-forming capillars attached to a one-square meter steel frame. The drop fall height is adjustable, in this work set to 2.3 m. Kinetic energy of the simulated rain at impact on the sample surface is undefined and variable, as a screen, of 0.5-mm stainless steel wire and with 3-mm openings, breaks the drops 0.53 m below the drop former, or 1.8 m above the sample surface.

For the rainfall simulation experiments, conducted unreplicated, the soils were brought in a saturated state to simulate the conditions during the main runoff periods in winter and spring when most of the soils of south Finland are plowed, bare and wet. Field-moist soil was spread into a 40 × 60 cm plywood box in several about 1-cm layers. The addition of a layer of soil was followed by dripping it with deionized water until moist.

After a 5–7-cm soil layer was reached, the box was set on a 2.5–2.8° angle under the rainfall simulator, and rainfall with 5 mm h⁻¹ intensity was applied until runoff was just about to start. The soil was then covered by a plastic sheet and left to stand for two or three days at +4–5°C in order to obtain uniform moisture. After this, the box with soil was again placed under the rainfall simulator, set on a 2.5–2.8° angle, and rainfall with an intended intensity of 5 mm h⁻¹ (actual intensity varying from 4.4 to 6.0 mm h⁻¹) was applied at the room temperature (about +20°C). Runoff was collected in 2-l polyethene containers which were after a 2-h runoff period thoroughly shaken, and two subsamples were taken in 0.5-l plastic bottles. These were stored at +4–5°C in the darkness until analyzed.

Runoff analyses

The P chemistry of the water samples obtained from runoff simulations is summarized in Table 2. Concentration of DRP in runoff was determined after filtration of a subsample through a 0.2 µm Nuclepore filter (Whatman, Maidstone, UK) and that of TP after an autoclave-mediated digestion (added K₂S₂O₈ and H₂SO₄, 120°C, 100 kPa, 30 min) of an unfiltered subsample. The concentration of PP was taken as the difference between TP and DRP. Modification of the molybdenum blue method (Murphy and Riley 1962) was employed in P analyses with a LaChat (Milwaukee, WI, USA) QC analyzer equipped with 880 nm wavelength filter. The concentration of total suspended solids (TSS) was estimated by weighing the evaporation residue of 50 ml of runoff.

To estimate the amount of readily algal-available PP in runoff (see Uusitalo and Ekholm 2003), 40-ml portions of each runoff sample were measured into three 50-ml capacity centrifuge tubes. Into each of the tubes, a nylon netting bag containing 1 g of Dowex (Fluka, Neu-Ulm, Germany) 1 × 8 strongly basic AER, saturated with HCO₃⁻ ions (see Sibbesen 1977, 1978), was added. The tubes were capped and placed on an end-over-end shaker and shaken at 37 rpm. After 20 h of shaking, the

Table 2. Concentrations of dissolved molybdate-reactive P, anion exchange resin-extractable P, redox-labile P, total P, and total suspended solids in the runoff samples obtained from rainfall simulations. Source soil numbering as in Table 1.

Source soil number	Dissolved molybdate-reactive P, mg l ⁻¹	Anion exchange resin-extractable P, mg l ⁻¹	Redox-labile P, mg l ⁻¹	Total P, mg l ⁻¹	Total suspended solids, g l ⁻¹
1	0.009	0.085	0.427	0.99	2.44
2	0.015	0.110	0.375	0.84	1.64
3	0.865	1.423	2.153	3.94	2.76
4	0.036	0.132	0.477	0.80	1.26
5	0.108	0.420	1.360	2.55	2.15
6	0.038	0.097	0.330	0.43	0.88
7	0.220	0.328	0.682	1.00	1.44
8	0.046	0.317	0.396	1.57	1.72
9	0.042	0.249	0.436	1.11	1.65
10	0.097	0.453	0.716	2.31	3.19
11	0.061	0.232	0.394	0.98	1.38
12	0.001	0.064	0.494	1.00	1.46
13	0.547	0.760	1.329	1.96	1.23
14	0.093	0.258	0.916	2.43	1.98
15	0.068	0.369	0.996	4.07	3.66

AER bag was removed from the sample and washed with deionized water. The AER with sorbed P was thereafter shaken for 4 h in 40 ml of 0.5 M NaCl to displace P from the AER into the solution. The NaCl solution with P was acidified with 1 ml of 6 M HCl and allowed to stand overnight before P determination; acidification was done to reduce CO₂ evolution during the P determination. To obtain an estimate for desorbable PP (AER-PP), DRP was subtracted from AER-extractable P.

To approximate redox-labile PP, runoff was amended with bicarbonate and dithionite solutions (detailed description of the method is given in Uusitalo and Turtola 2003). In short: triplicate 40-ml subsamples of runoff were measured into 50-ml capacity centrifuge tubes, and 1 ml of 0.298 M NaHCO₃ and 1 ml of 0.574 M Na₂S₂O₄ solutions (dithionite prepared just before the extraction) were added in each tube. The tubes were capped and shaken for 15 min on an orbital shaker at 120 rpm. After shaking, the sample was immediately decanted into a suction filter device equipped with a 0.2 µm Nuclepore membrane. For colorimetric P determination, 10 ml of the filtrate was digested in

an autoclave with peroxodisulfate and sulfuric acid, as in TP analysis. The digestion was conducted to eliminate disturbances (by dithionite and soluble Fe) during the P determination. The amount of BD-PP was calculated as BD-extractable P (BD-P_i) less DRP. Calculated this way, BD-PP also includes some unreactive dissolved P [strictly, total dissolved P (i.e., TP_{<0.2 µm}) should be used instead of DRP], but earlier findings suggest that in turbid runoff the error due to this incoherence is small [in a material of 49 field runoff samples, 6% overestimation in BD-PP was recorded by Uusitalo et al. (2003)].

Results and discussion

Agronomic P status and P saturation of the soils

Ammonium acetate is a weak extract for soil P, the amounts of soil P extractable in the acetate buffer

(in 1:10 soil-to-solution ratio) being approximately the same as those solubilized in 1:60 soil-to-water suspension (Yli-Halla 1989, Saarela et al. 2003). The relationship between DPS_{M3} and P_{Ac} (Fig. 2) curves at the higher DPS levels in a manner typical for quantity-intensity relationships. With increasing P saturation, P sorption occurs with decreasing bonding energy, and the concentration of easily soluble P (here, P_{Ac}) starts to increase more rapidly for each one percent increase in P saturation (see Olsen and Watanabe 1957, Ballaux and Peaslee 1975).

When the agronomic P status for clayey soils with 3–6% organic matter (1.8–3.5% C) is inferred from the amount of soil P_{Ac} , the limits between “satisfactory” and “good” P status is at 14 mg P_{Ac} l⁻¹, that between “good” and “high” at 23 mg P_{Ac} l⁻¹, whereas the limit between “high” and “excessive” P status is at 40 mg P_{Ac} l⁻¹ (Viljavuuspalvelu Oy 2000). According to the equation in Fig. 2, these limits would correspond to DPS_{M3} values of about 5, 8, and 11%, respectively. For comparison, Sims et al. (2002) described the agri-environmental interpretation of DPS_{M3} used in Delaware, USA, in which soils having DPS_{M3} between 6 and 11% are classified as having “optimum P level”, with “economic response to P unlikely”. The soils having higher DPS_{M3} than 11% are “above optimum, no P recommended”. Further, for soils having DPS_{M3} higher than 15% “improved P management to reduce potential for nonpoint P pollution” should be implemented (Sims et al. 2002).

Soil P saturation and runoff P forms

In our material, there were only two soils with DPS_{M3} about 11%, and these produced runoff with DRP concentrations above 0.5 mg l⁻¹ (Fig. 3 and Table 2). According to our data, a DPS_{M3} value as low as 5% would be close to a critical point above which runoff DRP starts to rapidly increase with increasing DPS_{M3} . If economic response to P would be unlikely at DPS_{M3} above 6%, as is the case in Delaware soils (Sims et al. 2002), Fig. 3 further suggests that the environmental risks of surplus P additions start to accumulate after this

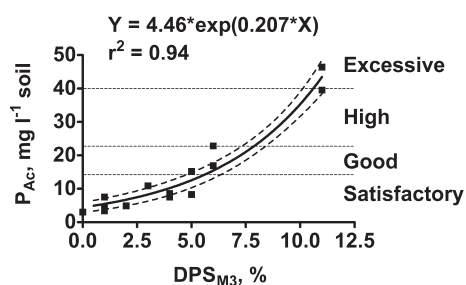


Fig. 2. Relationship between the degree of P saturation in soils (DPS_{M3}) and ammonium acetate-extractable P (P_{Ac}); the parallel dotted lines indicate the 95% confidence band of the fitted curve. The agronomic interpretation of P_{Ac} concentrations for clayey soils (with 1.75–3.5% total C) at the upper end of the scale is inserted, the limits being indicated by the horizontal lines.

DPS_{M3} level is exceeded. Assuming that the relationship between DPS_{M3} and P_{Ac} would be applicable for several types of Finnish soils, the 5% DPS_{M3} would correspond to a typical P_{Ac} concentration of the Finnish agricultural soils, 12–13 mg P_{Ac} l⁻¹ (Saarela et al. 2003).

Whilst the relationship between soil P saturation and the DRP concentration in runoff (Fig. 3) has a shape similar to many of the published curves between soil P and runoff DRP concentration (e.g. Heckrath et al. 1995, McDowell and Sharpley 2001), the contents of AER-PP and BD-PP in eroded sediment were in our material linearly related with DPS_{M3} (Fig. 3). However, there are a limited number of sorption sites in a kilogram of sediment matter, and the concentrations of these P forms must level out at some higher P saturation level (that was not covered by our material; i.e., the relationship actually has a shape of a Langmuir-type curve). By comparing the paper of Raven and Hossner (1993) to that of Barrow and Shaw (1977), it seems that at least some soils require excessive P additions to show a saturation of surface sorption sites. The former authors reported linear increase in AER-extractable P upon relatively modest P additions of up to 100 mg P kg⁻¹. In turn, Barrow and Shaw (1977) could show saturation phenomenon by AER extractions, but the amounts of P they added were up to 1500 mg kg⁻¹ soil.

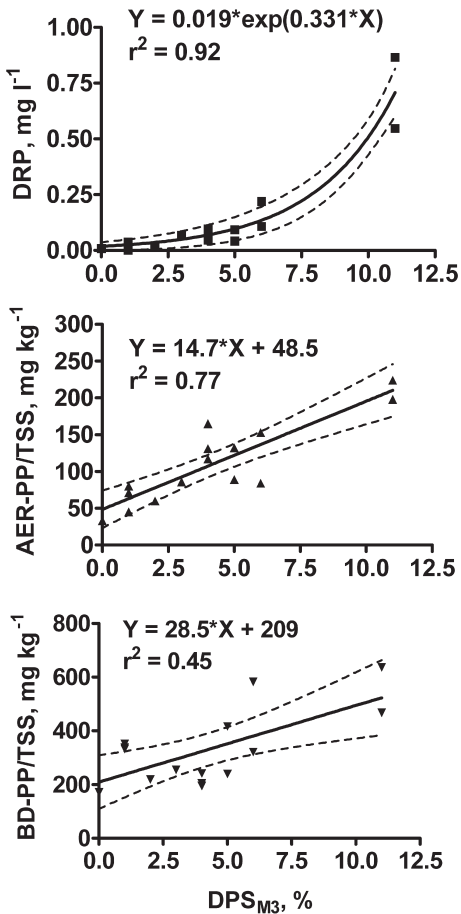


Fig. 3. The concentrations of dissolved molybdate-reactive P (DRP) in runoff water (uppermost figure), and desorbable PP (AER-extractable PP; figure in the middle) and redox-labile PP (solubilized at the negative redox potential of BD extraction; lowermost figure) in a kilogram of runoff sediment, as a function of the degree of soil P saturation (DPS_{M3}). The dotted lines indicate 95% confidence bands of the (solid) fitted lines. For details on runoff chemistry, see Table 2.

Agronomic P_{Ac} test versus runoff P forms

Runoff P forms – DRP in runoff and AER- or BD-extractable sediment P – are not outcomes of soil P_{Ac} , but all of these variables reflect the P saturation density of P sorbing compounds in soils and

eroded matter. Therefore, we acknowledge that the theoretical basis for predicting runoff P forms from soil P_{Ac} is somewhat slender (see Fried and Shapiro 1956). The equations for P_{Ac} and runoff P forms presented in Table 3 are merely descriptions of the correlation between P_{Ac} and the P forms in runoff, not causal relationships. However, the use of P_{Ac} to assess the TSS-normalized content of potentially bioavailable runoff P is emphasized for practical reasons; the data of soil P_{Ac} cover well the area of agricultural soils of Finland, there are long time-series of soil P_{Ac} concentrations, and these data are readily available.

The different P forms in runoff increased with the concentration of P_{Ac} of the source soils (Fig. 4), and the linear equations for runoff P forms and soil P_{Ac} are given in Table 3. Our material was not evenly distributed along the P_{Ac} axis – two soils had higher P_{Ac} content than the other soils, and applied leverage to the fitted lines. We therefore ran the fitting procedure twice, with and without these two soils, and there are two estimates for the slope and intercept values listed (in Table 3 indicated with suffixes 50_ and 25_).

Runoff DRP concentration correlated better with soil P_{Ac} than did the two forms of runoff sediment-normalized PP. The slope value estimate for the P_{Ac} versus 50_DRP relationship was essentially equal to that earlier reported by Uusitalo and Jansson (2002) for P_{Ac} versus edge-of-field runoff DRP: 0.015–0.018 $mg\ l^{-1}$ increase in DRP concentration for each unit increase in soil P_{Ac} . For the narrower range of P_{Ac} (25_DRP), increase in runoff DRP concentration was more modest, 0.009 $mg\ l^{-1}$ for a unit increase in P_{Ac} ; also this slope was significantly different from zero, and the correlation coefficient had an equally high value as the one for the whole material (Table 3). Uusitalo and Jansson (2002) made an assessment that DRP concentration of edge-of-field runoff sampled from a small, about 200-ha, catchment could in 95% of the cases be inferred from soil P_{Ac} data with an accuracy of about 0.1 $mg\ l^{-1}$. The wide deviation in slope values for the 50_DRP and 25_DRP data sets (and the C.I.s of the slope estimates) suggest that the accuracy in predicted DRP concentrations for the material of the present study is not better than that.

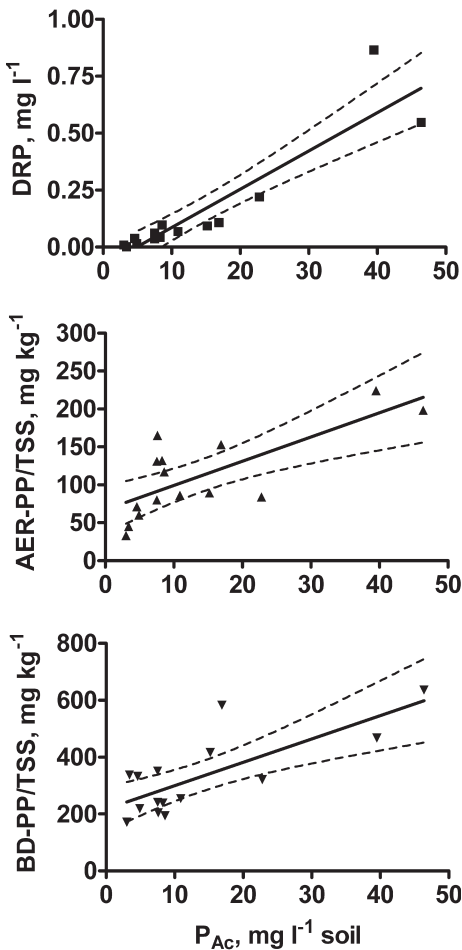
Table 3. Table of results, with standard errors and confidence intervals (CI), for the linear relationships between the concentration of soil P_{Ac} and P forms in runoff (see Fig. 3). The units are: $mg\ l^{-1}$ soil for P_{Ac} , $mg\ l^{-1}$ runoff water for DRP, and $mg\ kg^{-1}$ eroded sediment for AER-PP/TSS and BD-PP/TSS. The estimates associated with the headings with a suffix 50_ are for the whole studied material ($n = 15$; P_{Ac} scale up to about 50), whereas those with the suffix 25_ are estimates after omitting the two soils with P_{Ac} concentrations of about 40 and 46 $mg\ l^{-1}$ ($n = 13$; P_{Ac} scale up to about 25).

	50_DRP	25_DRP	50_AER-PP/TSS	25_AER-PP/TSS	50_BD-PP/TSS	25_BD-PP/TSS
Slope \pm SE	0.017 \pm 0.002	0.009 \pm 0.001	3.19 \pm 0.78	2.4 \pm 2.0	8.2 \pm 2.0	10.3 \pm 4.9
Y-intercept \pm SE	-0.085 \pm 0.039	-0.023 \pm 0.011	67 \pm 15	73 \pm 22	218 \pm 36	201 \pm 54
95% CI slope	0.012–0.021	0.007–0.012	1.49–4.88	-1.9–6.8	4.0–12.4	-0.6–21.2
95% CI Y-intercept	-0.165–0.001	-0.048–0.003	36–99	26–121	139–296	83–319
Goodness of fit, r^2	0.84	0.88	0.56	0.12	0.58	0.28
Slope \neq 0?, P -value	<0.0001	<0.0001	0.0013	0.2461	0.0010	0.0619

DRP = dissolved (<0.2 μm) molybdate-reactive P

AER-PP/TSS = concentrations of anion exchange resin-extractable PP as normalized to a kilogram of eroded sediment

BD-PP/TSS = concentrations of PP solubilized after additions of bicarbonate and ditionite solutions as normalized to a kilogram of eroded sediment



It seems that prediction of the sediment content of AER-extractable P and BD-P from soil P_{Ac} could also be possible. However, due to the limited number of observations and the diversity of the properties of the soils studied here (e.g. clay content, pH, Al/Fe ratio; Table 1), the estimates presented in Table 3 have a high degree of uncertainty. As example, the slope values of the P_{Ac} versus AER-PP/TSS and BD-PP/TSS relationships significantly differed from value zero when the whole material of 15 soils was utilized, but not when the two soils with the highest P_{Ac} were omitted (Table 3).

To compare our rainfall simulation data on PP losses to those of field studies, the estimates of mean slope and intercept for the whole P_{Ac} range (50_P forms) were utilized to predict concentra-

Fig. 4. The concentrations of dissolved molybdate-reactive P (DRP) in runoff water (uppermost figure), and desorbable PP (AER-extractable PP; figure in the middle) and redox-labile PP (solubilized at the negative redox potential of BD extraction; lowermost figure) in a kilogram of runoff sediment, plotted against ammonium acetate-extractable soil P (P_{Ac}). The dotted lines indicate their 95% confidence bands of the (solid) fitted lines. The estimates of the slopes and intercepts of these lines are given in Table 3.

Table 4. Observed mean concentrations of potentially bioavailable PP in runoff from four clayey fields of southwest Finland where runoff analyses have included determinations of AER-P and BD-P (data retrieved from Uusitalo 2004), and predicted mean concentrations for these soils, calculated using the average values for slopes and intercepts listed in Table 3 (50₋values) and the soil test P (P_{Ac}) values given here in parentheses.

	P _{Ac} mg l ⁻¹ soil	AER-PP/TSS mg kg ⁻¹		BD-PP/TSS mg kg ⁻¹	
	Range in field	Observed	Predicted	Observed	Predicted
Aurajoki	11–23 (18.5)	161	126	829	370
Lintupaju	6–9 (7.5)	78	91	485	280
Sjökulla	6–9 (7.5)	80	91	425	280
Jokioinen	4–6 (5)	55	83	328	259

AER-PP/TSS = concentrations of anion exchange resin-extractable PP as normalized to a kilogram of eroded sediment
 BD-PP/TSS = concentrations of PP solubilized after additions of bicarbonate and ditionite solutions as normalized to a kilogram of eroded sediment

tions of potentially bioavailable P forms in runoff sediment at four field sites that have been intensively monitored (Table 4; observed values retrieved from Uusitalo 2004). Predictions using the mean values of Table 3 overestimated the AER-PP/TSS in runoff by 14–50% at three field sites with P_{Ac} values 4–9 mg l⁻¹ and underestimated this ratio by 22% at one site (Aurajoki) where P_{Ac} was highest (11–23 mg l⁻¹). When using the mean estimates for slope and intercept, BD-PP/TSS was underestimated at all of the four fields, by 21–55%, and the more the higher was soil P_{Ac}. Even if the upper limit-values of the 95% confidence interval for the slope and intercept estimates were used in these calculations, the predicted BD-PP/TSS would have been smaller than the observed mean concentrations. It is noted that the simulated runoff contained more suspended matter than field runoff samples contain, and high concentration of soil matter probably contributed to a relatively low P recoveries in BD extractions of simulated runoff (see Uusitalo and Turtola 2003).

In this material some of the scatter around the trendlines is also because of the diversity in the physical and chemical properties of the soils studied. Parameters such as extractable Al and Fe, pH, CaCO₃, clay content, mineralogy, accessible surface area, content of organic matter, influence P sorption-desorption processes in soils (for a brief review and refs, see Burt et al. 2002). However, as many of the soil properties are partly interrelated,

utilizing the data on soil organic matter content, textural class, pH, and geographic region might be enough to improve the correlation between P_{Ac} and runoff P forms. With predictive equations accurate enough, inexpensive soil characterisazion could help in evaluating how erosion control measures affect the losses of those P forms that are relevant for eutrophication. Our work, with its few data, can be taken as a pre-test on the possibilities to utilize P_{Ac} data to predict sediment P pools.

Acknowledgements. We warmly thank Katariina Saarela, Helena Merkkiniemi, Anja Lehtonen and Päivi Allén for the laboratory work, Leo Tirkkonen and Tuomas Pelto-Huikko for sampling the soils and running the rainfall simulations, and Eila Turtola and the anonymous reviewers of the manuscript for their valuable comments. Ministry of Agriculture and Forestry is acknowledged for funding.

References

- Ballaux, J.C. & Peaslee, D.E. 1975. Relationships between sorption and desorption of phosphorus by soils. *Soil Science Society of America Proceedings* 39: 275–278.
- Barrow, N.J. & Shaw, T.C. 1977. Factors affecting the amount of phosphate extracted from soil by anion exchange resin. *Geoderma* 18: 309–323.
- Bowyer-Bower, T.A.S. & Burt, T.P. 1989. Rainfall simulators for investigating soil response to rainfall. *Soil Technology* 2: 1–16.

- Bundy, L.G., Andraski, T.W. & Powell, J.M. 2001. Management practice effects on phosphorus losses in runoff in corn production systems. *Journal of Environmental Quality* 30: 1822–1828.
- Burt, R., Mays, M.D., Benham, E.C. & Wilson, M.A. 2002. Phosphorus characterization and correlation with properties of selected benchmark soils of the United States. *Communications in Soil Science and Plant Analysis* 33: 117–141.
- Culley, J.L.B., Bolton, E.F. & Bernyk, V. 1983. Suspended solids and phosphorus loads from a clay soil: I. Plot studies. *Journal of Environmental Quality* 12: 493–498.
- Eklholm, P. 1994. Bioavailability of phosphorus in agriculturally loaded rivers in southern Finland. *Hydrobiologia* 287: 179–194.
- Elonen, P. 1971. Particle-size analysis of soil. *Acta Agraria Fennica* 122: 1–122.
- Fried, M. & Shapiro, R.E. 1956. Phosphate supply pattern of various soils. *Soil Science Society Proceedings* 20: 471–475.
- Heckrath, G., Brookes, P.C., Poulton, P.R. & Goulding, K.W.T. 1995. Phosphorus leaching from soils containing different phosphorus concentrations in the Broadbalk experiment. *Journal of Environmental Quality* 24: 904–910.
- Jokela, W.E., Magdoff, F.R. & Durieux, R.P. 1998. Improved phosphorus recommendations using modified Morgan phosphorus and aluminum soil tests. *Communications in Soil Science and Plant Analysis* 29: 1739–1749.
- Logan, T.J., Oloya, T.O. & Yaksich, S.M. 1979. Phosphate characteristics and bioavailability of suspended sediments from streams draining into lake Erie. *Journal of Great Lakes Research* 5: 112–123.
- McDowell, R.W. & Sharpley, A.N. 2001. Approximating phosphorus release from soils to surface runoff and subsurface drainage. *Journal of Environmental Quality* 30: 508–520.
- Mehlich, A. 1984. Mehlich-3 soil extractant: A modification of Mehlich-2 extractant. *Communications in Soil Science and Plant Analysis* 15: 1409–1416.
- Murphy, J. & Riley, J.P. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* 27: 31–36.
- Olsen, S.R. & Watanabe, F.S. 1957. A method to determine adsorption maximum of soils as measured by the Langmuir isotherm. *Soil Science Society Proceedings* 21: 144–149.
- Peltovuori, T., Uusitalo, R. & Kauppila, T. 2002. Phosphorus reserves and apparent phosphorus saturation in four weakly developed cultivated pedons. *Geoderma* 110: 35–47.
- Pietiläinen, O.-P. & Rekolainen, S. 1991. Dissolved reactive and total phosphorus load from agricultural and forested basins to surface waters in Finland. *Aqua Fennica* 21: 127–136.
- Pote, D.H., Daniel, T.C., Sharpley, A.N., Moore, P.A., Jr., Edwards, D.R. & Nichols, D.J. 1996. Relating extractable soil phosphorus to phosphorus losses in runoff. *Soil Science Society of America Journal* 60: 588–859.
- Puustinen, M. 1994. Effects of soil tillage on erosion and nutrient transport in plough layer runoff. *Publications of Water Research Institute (Helsinki)* 17: 71–90.
- Puustinen, M., Koskiahio, J. & Peltonen, K. 2005. Influence of cultivation methods on suspended solids and phosphorus concentrations in surface runoff on sloped fields. *Agriculture, Ecosystems & Environment* 105: 565–579.
- Raven, K.P. & Hossner, L.R. 1993. Phosphorus quantity–intensity relationships in soils. *Soil Science Society of American Journal* 57: 1501–1508.
- Saarela, I., Järvi, A., Hakkola, H. & Rinne, K. 2003. Phosphorus status of diverse soils in Finland as influenced by long-term P fertilisation I. Native and previously applied P at 24 experimental sites. *Agriculture and Food Science in Finland* 12: 117–132.
- Schwertmann, U. 1964. Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat Lösung. *Zeitschrift für Pflanzenernährung und Bodenkunde* 105: 194–202.
- Sharpley, A.N., Syers, J.K. & Tillman, R.W. 1978. An improved soil-sampling procedure for the prediction of dissolved inorganic phosphate concentrations in surface runoff from pasture. *Journal of Environmental Quality* 7: 455–456.
- Sibbesen, E. 1977. A simple ion exchange resin procedure for extracting plant-available elements from soil. *Plant and Soil* 46: 665–669.
- Sibbesen, E. 1978. An investigation of the anion-exchange resin method for soil phosphate extraction. *Plant and Soil* 50: 305–321.
- Sims, J.T., Maguire, R.O., Leytem, A.B., Gartley, K.L. & Pautler, M.C. 2002. Evaluation of Mehlich 3 as an agricultural soil phosphorus test for the Mid-Atlantic United States of America. *Soil Science Society of American Journal* 66: 2016–2032.
- Turtola, E. 1999. *Phosphorus in surface runoff and drainage water affected by cultivation practices*. Academic dissertation. Agricultural Research Centre of Finland, Jokioinen. 108 p.
- Turtola, E. & Paajanen, A. 1995. Influence of improved subsurface drainage on phosphorus losses and nitrogen leaching from a heavy clay soil. *Agricultural Water Management* 28: 295–310.
- Turtola, E. & Yli-Halla, M. 1999. Fate of phosphorus applied in slurry and mineral fertilizer: Accumulation in soil and release into surface runoff. *Nutrient Cycling in Agroecosystems* 55: 165–174.
- Uusi-Kämpä, J., Braskerud, B., Jansson, H., Syversen, N. & Uusitalo, R. 2000. Buffer zones and constructed wetlands as filters for agricultural phosphorus. *Journal of Environmental Quality* 29: 151–158.
- Uusitalo, R. 2004. Potential bioavailability of particulate phosphorus in runoff from arable clayey soils. *Agrifood Research Reports* 53. MTT Agrifood Research Finland, Jokioinen, Finland. 99 p.
- Uusitalo, R. & Eklholm, P. 2003. Phosphorus in runoff assessed by anion exchange resin extraction and an algal assay. *Journal of Environmental Quality* 32: 633–641.
- Uusitalo, R. & Jansson, H. 2002. Dissolved reactive phosphorus in runoff assessed by soil extraction with an acetate buffer. *Agriculture and Food Science in Finland* 11: 343–353.
- Uusitalo, R. & Turtola, E. 2003. Determination of redox-sensitive phosphorus in field runoff without sediment pre-

- concentration. *Journal of Environmental Quality* 32: 70–77.
- Uusitalo, R., Turtola, E., Puustinen, M., Paasonen-Kivekäs, M. & Uusi-Kämpä, J. 2003. Contribution of particulate phosphorus to runoff phosphorus bioavailability. *Journal of Environmental Quality* 32: 2007–2016.
- Viljavuuspalvelu Oy 2000. Viljavuustutkimuksen tulkinta peltoviljelyssä. Viljavuuspalvelu Oy, Mikkeli, Finland. 31 p. (in Finnish).
- Vuorinen, J. & Mäkitie, O. 1955. The method of soil testing in use in Finland. *Agrogeological Publications* 63: 1–44.
- Yli-Halla, M. 1989. Reversibly adsorbed P in mineral soils of Finland. *Communications in Soil Science and Plant Analysis* 20: 695–709.

SELOSTUS

Viljavuustutkimuksen fosforiluvun käyttökelpoisuus vesistöjä rehevöittävien fosforijakeiden kuormituksen arvioinnissa

Risto Uusitalo ja Erkki Aura

MTT (Maa- ja elintarviketalouden tutkimuskeskus)

Valumavesiin liuenneen fosforin lisäksi osa maa-aineksen mukana pelloilta kulkeutuvasta fosforista kiihdyttää vesistöjen rehevöitymistä. Koska maa-ainesfosforin rehevöittävien muotojen määrittäminen valumavesistä on kallista, näiden rehevöittävien fosforijakeiden suuruus tunnetaan huonosti. Tämän työn tarkoituksena oli arvioida mahdollisuuksia käyttää viljavuustutkimuksen fosforilukua rehevöittävien fosforijakeiden pitoisuuden arviointiin siten, että tulokseksi saadaan rehevöittävän fosforin määrä erodoitunutta maa-aineskiloa kohden. Yhdistämällä tämä tieto mitattuihin eroosiomääriin, voitaisiin kenttäkoetuloksista laskea arvioita rehevöittävästä fosforikuormista nykyistä luotettavammin.

Tutkimuksen aineisto koostui 15 maanäytteestä, jotka oli haettu savimailta eri puolilta Etelä-Suomea. Maiden savespitoisuudet vaihtelivat välillä 31–63 %, pH-luvut 5,0–7,4, hiilipitoisuudet 1,5–4,2 % ja viljavuusuton fosforiluvut 3–46 mg P/l. Maanäytteet pakattiin laboratoriossa vanerilaatikoihin ja kostutettiin vedellä kyllästyneeseen tilaan, jollaisessa ne ovat usein talven ja kevään valuntahuippujen aikana. Laatikot asetettiin 2,5–2,8 asteen kallistukseen ja niitä sadetettiin sadesimulaattorissa 2 tuntia intensiteetillä 5 mm/h. Sadetuksen aikana

laatikoista poistuneesta valumavedestä määritettiin veden liuenneen fosforin pitoisuus, sekä veden mukana kulkeutuneen maa-aineksen fosforijakeista leville helposti käyttökelpoinen jae ja pelkistyneissä oloissa veden liukeneva jae.

Valumaveden liuenneen fosforin pitoisuus suureni selkeästi maan fosforiluvun kasvaessa (r^2 0,84), kun taas maan fosforiluvun ja erodoituneen maa-aineksen sisältämän rehevöittävän fosforin välinen yhteys oli heikompi (r^2 0,56–0,58; rehevöittävä maa-ainesfosfori suhteutettuna maa-aineskiloa kohden). Eroosioaineksen sisältämän rehevöittävän fosforin pitoisuuden ennustaminen maan fosforiluvun perusteella näyttäisi olevan mahdollista. Ennusteiden luotettavuuden kannalta maan fosforiluvun ja eroosioaineksen sisältämien fosforijakeiden väliset yhteydet olisi kuitenkin määritettävä erikseen useista, ominaisuuksiltaan melko yhtenäisistä maa-ainestoista, koska muutkin maan ominaisuudet kuin pelkkä fosforiluku vaikuttavat ennusteyhtälöihin. Esimerkiksi tämän työn tuloksiin pohjautuvaa ennusteyhtälöä käyttämällä valuman mukana poistuvan eroosioaineksen rehevöittävän fosforin pitoisuuksista olisi saatu liian pieniä arvioita neljältä koekentältä.