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Accumulation and translocation of sparingly soluble manure phosphorus in different types of soils after long-term excessive inputs

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When phosphorus (P) is applied to soils in excess of plant P demand, P accumulation takes place. By means of P fractionation, we studied the fate of P in 35 soils that had received long-term surplus P rates as fox and mink manure P (F&MM-P), considered as a sparingly soluble P source. We compared these data with those from the same soils under a more typical P management, i.e., fields amended with soluble P sources superphosphate and dairy manure (SP+DM). Fractionation of manures according to the Hedley procedure suggested limited solubility of F&MM-P, two-thirds of the F&MM-P being soluble in acid (HCl) only. In mineral soils, surplus F&MM-P accumulated for the most part as HCl-P (poorly available), whereas in organic soils accumulation occurred largely as NaOH-soluble (moderately available) and labile P. Translocation of F&MM-P was evidenced by P fractionation and by agronomic P test: subsurface soil of F&MM-amended fields contained more P than the same soils in fields amended with SP+DM. In the 35 soils that had received surplus F&MM-P, agronomic P status was classified as "excessive" in 90% of the samples taken from the plough layer, in 75% of those from 20–40 cm depth, and in 50% of those from 40–60 cm depth. In the reference soils amended with SP+DM, "excessive" P status was recorded for 23% of the plough layer samples and 4% of the subsurface samples. These results show that manure P which appears as sparingly soluble in P fractionation may in a longer term increase the content of labile soil P and translocate in the soil profile when applied in high rates.

Key-words: phosphorus saturation, translocation in soils, manure, fur animals, long-term effects, Finnish Agri-Environmental Program

Introduction

Phosphorus (P) is one of the main regulators of the trophic status of surface waters, as shown by increased growth of planktonic algae in lakes when P inputs are increased (Schindler 1977). Agriculture is a major source of P to aquatic environments in many areas, Finland among them (Valpasvuo-Jaatinen et al. 1997). The important role played by agriculture in setting

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trends in water quality of our inland waters was suggested by, e.g., Mitikka and Ekholm (2003) in a study of 253 Finnish lakes. According to their analyses, during the period from 1976 to 2001, the water quality (as reflected in total P, chl-*a*, and Secchi depth values) of a majority of the lakes affected by point-source pollution improved, whereas the lakes located in agricultural areas typically showed accelerating eutrophication.

The ultimate causes of agricultural P losses are soil erosion (accelerated as a result of disturbances by tillage operations) and surplus P balances. High positive P balances are characteristic for areas specialized in animal production where high amounts of P is imported in feed and disposed in fields as manure (Sharpley 1999, Tamminga 2003). As to P forms in animal manures, it is usually supposed that a high percentage of water-soluble P indicates high P loss potential, but that P soluble only in aggressive extractants (such as 1 M HCl) poses a lesser risk for P leaching. This supposition was shown to hold for direct leaching of P by Sharpley and Moyer (2000): in their rainfall simulation study, incidental losses (i.e., losses occuring during and right after manure spreading) of dissolved P from a number of different manure and compost types were governed predominantly by the size of the water-extractable P fraction (see also Moore and Miller 1994, Shreve et al. 1995, and Smith et al. 2001). If runoff P losses are directly related to the water-extractable P content of manure, then manures with a low water-soluble fraction are environmentally less risky than manures with a high water-soluble P fraction. If a certain level of P losses was tolerated, manures with a large fraction of sparingly soluble P could be applied in greater total amounts than manures with a high proportion of water-soluble P. Following this logic, e.g., Dao (1999) suggested that manure application rates could be adjusted according to the soluble P fraction rather than to total P if there is a shortage of land available for spreading manure.

The Finnish Agri-Environmental Program (for an overview, see Valpasvuo-Jaatinen et al. 1997, Ekholm et al. 2007) also shows a preference for extractable P over total P. Current regulations state that only 40% of the total P in (fresh and composted) fox and mink manure (F&MM) is considered available to plants. For cow, swine, and poultry manures, 85% of the total P is considered plant available (until the end of the year 2006, 75% of the total P was taken as plant available). For the farmers participating in the program, maximum allowed P rates are given (they vary according to soil P status and crops), and the low availability index for F&MM thus allows total P application rates that are about twice as high as those of other manures. These availability indices are not the sole guidelines, however: the program also has a feedback mechanism to reduce excessive soil test P concentrations and requires farmers to test their fields for agronomic P status every five years if they wish to be eligible for environmental incentive payments. In the event of high soil test P concentrations, P applications should be reduced. However, if F&MM-P is used, high surplus total P rates (many times the P uptake by normal yields) may be maintained up to the next highest soil test P classes, "good" and "high" P status.

In this work, we assessed how decades of surplus P additions, applied in excess as F&MM with a low percentage of water-soluble P, have modified the P content, P forms, and P status in 35 soil profiles (to 60 cm depth). We compare these data with those obtained from the same soils (neighboring fields) fertilized with superphosphate or dairy manure (usually both; SP+DM), two sources of readily soluble P, at lower P rates. The material for our study was collected from commercial farms, representing two types of real-life P management systems. The samples of this study are not only from coarse-textured soils, which are often identified as vulnerable to downward P movement, but also from fine-textured mineral soils and organic soils.

Material and methods

Manure P fractionation

To obtain comparable data on P solubility in dairy manure and F&MM, samples of fresh dairy cow (*Bos taurus*) manure, fox manure, and composted fox and mink manure (cF&MM) were studied. The manures of farmed fox (*Alopex lagopus* and *Vulpes vulpes*) and mink (*Mustela vison*) are very similar in chemical composition, because their diets are largely the same. The dairy manure sample was retrieved from a manure heap at a dairy barn at Jokioinen (Jokioinen estate farms, Southwest Finland) and the fox manure sample from the fur production research station of MTT Agrifood Research Finland (Kannus, Ostrobothnia, western Finland). A F&MM compost sample was obtained from a commercial composting facility at Kaustinen, Ostrobothnia.

Fractionation of P was performed in duplicate on air-dry, finely ground manures according to the sequential extraction scheme of Hedley et al. (1982) with the following modifications: the anion exchange resin-extraction step in the original method was replaced with two extractions with deionized water, and the fumigation step and the second NaOH extraction were omitted. In brief, the extractions proceeded as follows: (i) 4 h in deionized water, (ii) 16 h in another portion of deionized water, (iii) 16 h in 0.5 M $NaHCO_3$ (pH 8.5), (iv) 16 h in 0.1 M NaOH, and (v) 16 h in 1 M HCl. All extractions were performed at room temperature (+20°C) with 1:50 (w/v) solid-to-solution ratios.

Between each extraction step, manure and solution were separated by centrifuging at 3000 × *g* for 15 min and by decanting the supernatant. The inorganic P in the supernatant was determined after passing it through a 0.2 µm Nuclepore (Whatman, Maidstone, UK) filter, whereas the concentration of total P was determined after autoclave-mediated digestion of the supernatant with sulfuric acid and peroxodisulfate. The difference between total P and inorganic P was assumed to represent organic P. After neutralization and dilution, P concentrations were measured at 882 nm wavelength by the molybdate blue-ascorbic acid method (Murphy and Riley 1962) with a Shimadzu (Kyoto, Japan) UV-120-02 spectrophotometer.

Soils

About 90% of Finland's fur farms, producing some 2–4 million pelts per year (of which about 60% are fox), are located in the Ostrobothnian region, on the east coast of Bothnian Bay. Ostrobothnia is a part of the Podzol region of middle Finland with Cambisols and Histosols, formed on predominantly loamy glacial deposits (ground moraine) overlying igneous and metamorphic rocks. The land is flat and altitudes are typically well below 100 m above the sea level. The mean annual temperature of this region is 1.6–2.1°C and temperatures remain below 0°C from November to March. Annual precipitation is 540–600 mm, being highest during July and August.

During the summer of 2003, 35 fields on Ostrobothnian farms raising fur animals were sampled at three predetermined depths: 0–20 cm (plough layer), 20–40 cm, and 40–60 cm. For each field amended with F&MM, a reference field fertilized with readily soluble P sources, such as SP and DM, was sought in the vicinity. Twenty-one of the paired fields were separated by a ditch or road, the edge-to-edge distance between the field pairs being about 10–20 m. Ten paired fields were 150–600 m apart, and the remaining four paired fields were at a distance of 0.6–3 km from each other. The similarity of the inherent soil properties within each field pair was assessed by comparing the results of the chemical analyses listed in Table 1; six field pairs of the initially larger data set were discarded at this step.

According to a tentative FAO/UNESCO classification of the soils, the group of fine-textured mineral soils of this study comprised Eutric and Gleyic Cambisols, and Dystric Regosols, and the coarse-textured mineral soils Haplic Arenosols, Eutric Cambisols, Gleyic or Haplic Podzols, and Dystric Regosols. The organic soils studied were either Terric Histosols or Umbric Gleysols.

The fields sampled were 0.29–18 ha in size, the median size being 2.3 ha. From each field, 20–25 subsamples were taken by hand corer, and these were combined to form a 1-liter representative sample that was allowed to dry at about +35°C. For representative sampling, the number of subsamples was small when the largest fields were concerned, but this frequency was nevertheless expected to reveal possible differences in soil P characteristics between the P management options. After the soils had been air-dried, soil texture was

Table 1. Summary of some chemical properties in the plough layer (0–20 cm) of the 35 field pairs amended with either soluble P sources (SP+DM, i.e., superphosphate and dairy manure or slurry) or a sparingly soluble P source (F&MM, fox and mink manure). Numbers are averages for the soil groups, followed by standard error in parentheses.

	Fine-textured mineral soils (clayey, loamy and fine silty)		Coarse-textured mineral soils (coarse silty and sandy)		Organic soils (more than 20 % organic C)	
	SP+DM	F&MM	SP+DM	F&MM	SP+DM	F&MM
n	13		17		5	
Volume weight, kg l^{-1}	1.04 (0.3)	1.05 (0.3)	1.09 (0.4)	1.07 (0.3)	0.46 (0.3)	0.50 (0.1)
pH	5.9 (0.1)	6.5 (0.1)	5.6 (0.2)	6.1 (0.1)	4.8 (0.3)	5.1 (0.3)
Total C, %	2.8 (0.2)	2.9 (0.2)	3.9 (1.0)	3.8 (0.8)	30.6 (3.1)	28.6 (1.9)
Total P, mg kg^{-1}	1160 (71)	1690 (126)	990 (60)	1830 (167)	1690 (114)	3200 (223)
M3-P, mg l^{-1}*	165 (25)	527 (92)	204 (27)	674 (110)	85 (17)	639 (152)
M3-Al, mmol kg^{-1}	42 (4)	39 (3)	38 (50)	35 (44)	83 (11)	75 (6)
M3-Fe, mmol kg^{-1}	9.9 (0.2)	9.4 (0.2)	9.7 (0.6)	9.2 (0.6)	22.8 (1.9)	19.2 (1.6)
P_{Ac}, mg l^{-1}**	18 (3)	104 (20)	24 (4)	216 (68)	14 (1)	143 (51)
Ca_{Ac}, mg l^{-1}	1260 (114)	2280 (170)	1120 (141)	2070 (178)	2360 (227)	3220 (546)
Mg_{Ac}, mg l^{-1}	215 (24)	256 (19)	138 (25)	186 (26)	335 (76)	475 (77)
K_{Ac}, mg l^{-1}	140 (14)	138 (13)	73 (10)	93 (13)	56 (8)	116 (19)

* M3 = Mehlich 3-extractable elements

** Ac = Acid ammonium acetate-extractable elements (equal estimates of exchangeable Ca, Mg, and K were also obtained by Mehlich 3 extraction; relationships between the results had slope values between 0.9 and 1.1, with r2 ≥ 0.96; n = 220; not shown).

estimated by finger assessment, and the samples were ground to pass through a 2-mm sieve for further analyses.

P management and cropping

For the period 1970–2002, data on cropping were collected from farmers' records (based on written notes when the more recent dates were concerned, but also on the memory of the farmers). The farmers were asked about manure and superphosphate fertilizer (SP) application rates (m^3 ha^{-1} for manure and kg ha^{-1} for SP), manure type for F&MM (fresh/composted, compost age when applicable), other manures applied (in these cases they were always cow manure or cow slurry), P concentration of the cow manure or slurry if determined, timing of manure spreading (before sowing/autumn cultivation, or other), and crop rotations. These data from the most recent years are probably relatively accurate (written notes being available in almost all farms), but only indicative when the data from the 1970's and 1980's are concerned. The P rates applied with F&MM (see Table 2) were approximated from the tabulated values for the P content (10 kg m^{-3}) and volume weight (400 kg m^{-3}) of stored F&MM (Viljavuuspalvelu Oy 2000).

In the Ostrobothnian area, with its abundant dairy farms, crop rotation typically consists of grass that is ploughed every 3–4 years, followed by a season with a cereal such as barley (*Hordeum vulgare*) with simultaneous undersowing of grass. In this type of rotation, manure is usually applied before the third or fourth year grass is ploughed in the autumn. However, in the material of our study both dairy manure/slurry and F&MM application intervals tended to be shorter than 3–4 yr, because many farms (more often those that utilized F&MM) interrupted grass-cereal rotation with a third crop such as potato (*Solanum tuberosum*) or sugarbeet (*Beta vulgaris* var. *conditiva*). Alternatively, and especially on the farms that relied on SP and almost always also applied dairy manure or slurry, longer periods of cereal production were common. As

Table 2. Average annual P application rates during 1970–2002 to the field pairs studied by sequential P fractionation. One of the fields within each numbered field pair had received moderate inputs of easily soluble P sources, superphosphate and dairy manure (SP+DM), whereas the other field was amended with excessive rates of fox and mink manure (F&MM). Calculation of the P-application rates as F&MM is discussed in the Material and methods section.

Soil group/ field pair ID	1970–1979 SP+DM	1970–1979 F&MM	1980–1989 SP+DM	1980–1989 F&MM	1990–2002 SP+DM	1990–2002 F&MM	1970–2002 SP+DM	1970–2002 F&MM
	kg P ha^{-1} yr^{-1}							
Fine-textured mineral soils								
F-1	26	124	34	150	41	158	34	145[3]
F-2	15	150	10	150	16	110	14	135
F-3	0	0	25	120	23	128	16	85[2]
F-4	28	0	30	74	21	80	26	53[2]
Coarse-textured mineral soils								
C-1	27	14	17	150	14	102	19	89[1]
C-2	12	99	12	103	5	271	9	165
C-3	0	35	14	59	24	50	13	48[1]
C-4	23	209	23	378	10	0	18	183[2]
C-5	20	0	14	109	20	91	18	68
Organic soils								
O-1	30	34	19	34	12	43	20	37
O-2	20	36	21	24	16	30	19	30
O-3	25	49	21	45	25	67	24	541
O-4	19	0	19	85	14	89	17	60[1]
Average	19	58	20	114	19	94	19	89

[1] Less than 6% of the P applied as soluble P sources (SP or DM).

[2] Between 6% and 12% of the P applied as soluble P sources.

[3] Between 12% and 16% of the P applied as soluble P sources.

for the used F&MM rates, some farms had long intervals between F&MM applications, but the application rates were then higher.

Chemical analyses of all soil samples

The total carbon content of the soils was determined with a LECO CN-2000 (St. Joseph, MI, USA) analyzer, and pH was measured in 1:2.5 (v/v) soil-water suspension, every tenth sample with a duplicate. Total P was determined by the Aqua Regia-HF digestion method as described by Bowman (1988), with three replicates. Organic P was approximated (with duplicate samples) by the Saunders-Williams ignition method as described by Olsen and Sommers (1982) except that, instead of molybdate colorimetry, the P concentrations in the acid extracts were measured with an inductively coupled plasma–atomic emission spectrometer (ICP–AES; Thermo Jarrel Ash, Franklin MA, USA).

The soils were also extracted (with duplicates) with the Mehlich 3 (M3) solution as outlined by Mehlich (1984) and with ammonium acetate (pH 4.65) as described by Vuorinen and Mäkitie (1955). Extractable P was determined by the ascorbic acid–molybdate blue method with a Bran+Luebbe (Norderstedt, Germany) continuous flow analyzer equipped with a digital photometer and 880 nm filter. Macronutrient cations (Mehlich 3 and ammonium acetate-extractable), and Mehlich 3-extractable Al and Fe, were measured with the ICP-AES.

Further chemical analyses of a subset of 13 field pairs

Modified Hedley's P fractionation, the same procedure as described under the manure fractionation subheading above, was performed for samples (with three replicates) retrieved from nine mineral soils and four organic soils. The soils chosen were those in which, in the corresponding soil layers within the field pairs, the amounts of M3-extractable Al and Fe at all sampled depths, and pH and the concentrations of extractable macronutrient cations (Ca, Mg, K) in the subsurface layers (20–40 and 40–60 cm layers) were similar.

Statistical analyses

The data analyses included comparisons of the P concentrations in the fields amended with the different P sources (F&MM vs. SP+DM) by the paired t-test. The material was analyzed as whole or as grouped according to organic matter content and soil textural class (as in Table 1, later referred to as "soil group data"; in grouping the soils, texture assessment of the subsurface layers weighted more than that of the plough layer if soil texture varied with depth). When necessary, the data were logarithm transformed to normalize the residuals.

The fields represented the different soil types in the region, but they were not a random sample. Our primary goal was to sample fields with a long history of F&MM applications, and the results can be generalized accordingly. It is unknown to us how well these data represents the situation in Ostrobothnian region in general.

Results and discussion

Manure P

Fresh fox manure contained 30–35 mg P g^{-1} dry matter, composted F&MM (cF&MM) about 25 mg P g^{-1} dry matter (due to peat addition before composting), whereas the dairy manure sample contained somewhat less than 4 mg P g^{-1} dry matter (Table 3). The values of total P in manure and compost samples collected for this study were comparable to the tabulated values for their nutrient contents (Viljavuuspalvelu Oy 2000). The extremely high P concentration in fox (and mink) manure is due to the diet of these animals, which is based largely on meat and bone meal and commercially less valuable components of the fish catch (roach, small Baltic herring, etc.).

Inorganic P made up about 85–95% of the extractable P in both dairy and fur animal manures and compost of the latter, but the dairy manure clearly differed from the other two in its apparent P solubility (Table 3). About 70% of the dairy manure P was extractable by water and about 80% in water and bicarbonate (i.e., labile P). In the fox manure and cF&MM, only about 20–25% of the P was soluble in water and about 25–30% of the total amount was labile, leaving 65–70% acid-extractable P. The data on fox manure and cF&MM seemed to differ from most of the published data on animal manures (e.g., Sharpley and Moyer 2000) in that the inorganic acid-extractable pool was such a dominant P fraction.

P application rates during 1970–2002

Averaged over 10–year periods, annual P application rates as F&MM-P were 50–100 kg ha^{-1} (in

Table 3. Inorganic (-i) and organic (-o) P fractions in a fresh fox manure, a composted fox and mink manure (cF&MM; a mixture of manure and peat) and a dairy cow manure sample; values are means of two replicates. Total P is mean of three replicates, based on extraction of separate subsamples by Aqua Regia and HF in a microwave oven.

	Fox manure	cF&MM	Dairy manure
	mg P g^{-1} dry mass		
P_w-i	6.90	5.61	3.18
P_w-o	1.48	1.36	0.24
P_{NaHCO3}-i	1.70	0.85	0.21
P_{NaHCO3}-o	0.12	0.25	0.21
P_{NaOH}-i	0.30	0.21	0.07
P_{NaOH}-o	0.08	0.31	0.06
P_{HCl}-i	19.2	17.5	0.22
P_{HCl}-o	n.d.*	n.d.	0.16
ΣP-i	28.1	24.2	3.7
ΣP-o	1.7	1.9	0.7
Total P	34.3	25.7	3.8

* Not detected

most fields this includes some kilograms of SP), but in the reference fields amended with SP and DM the annual rate was about 20 kg P ha^{-1} (data partly shown in Table 2). According to the farmer interviews, average annual P rates as F&MM-P were higher after 1980 than they had been during the 1970–1980 period. These higher F&MM-P rates after 1980 may be due to the increased specialization of the farms (though the farmers were not asked about this), resulting in a greater number of animals on a farm yet a relatively smaller field area for F&MM disposal.

During 1970–2002, F&MM was applied from 4 to 32 times, on average 16 times, and an average single F&MM application rate was estimated to contain 210 kg P ha^{-1} (range 70–420 kg P ha^{-1}). Most of the higher single F&MM-P rates were associated with fields receiving fewer than 10 manure applications. Clearly, P balances (P inputs less removal by plant yields) were highly positive in the fields that received F&MM, with an estimated mean annual P surplus of around 80 kg ha^{-1}. The large surpluses are due, not merely to the low availability index for F&MM-P, but largely also to past recommendations for P and manure applications (many times the average P harvest). Assuming that the annual P uptake in cereal-grass rotations in this area is 12–17 kg P ha^{-1} (see Turtola and Kemppainen 1998), then the SP+DM-amended fields received a few kilograms more P than was removed in the harvest.

The application rates and calculated P-surpluses should be regarded as indicative only, because there are obvious uncertainties in the P application rates assessed from tabulated values for P and dry matter. It is noted that the calculated 30-year P surpluses and total mass of soil P in the 0–60 cm layer correlated rather poorly (r^2 less than 0.20, not shown), which may be due to several reasons, among them uncertainties in our estimates of P rates, in P removal by crops, and in farmers' notes and memory. In any event, total P applications during 1970–2002 have been far greater to F&MM-amended fields than to fields receiving SP+DM (Table 2), which means that we cannot compare the effects of the two contrasting types of manures on soil P forms, but just describe the effects of the past excessive F&MM-P rates. Then, the comparisons between F&MM-amended fields and the (SP+DM-amended) control fields show the different outcomes from the (past-term) F&MM-P management and a modern, more sustainable, P management system that balances P inputs and P harvests (Table 2). As for the subsurface soil layers, which may have a different parent material and, thus, different native P content than the surface soil, the SP+DM-amended soils is taken to represent the level of native soil P status of the subsurface soil layers. If a subsurface soil layer of a F&MM-amended soils contains more P than the corresponding layer of the reference field, F&MM-P displacement downward in the soil profile has probably occured; however, when the 20–40 cm layer is concerned, P content may also be affected by occasional ploughing deeper than the expected 20 cm depth.

Soil total P concentration

As a direct consequence of the high F&MM-P dressings, accumulation of P has been greater in F&MM-amended fields than in fields fertilized with SP and DM (Fig. 1; two-tailed *p*-values of the paired t-test equaled 0.0003 or less for the different soil groups). High P contents were also found in the subsurface soil layers of the F&MM-amended soils, suggesting translocation of P in the soil profile as a result of excessive P inputs. In this point, our data

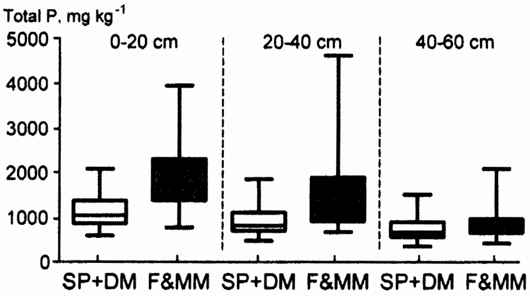

Fig. 1. Total P concentration of soil samples retrieved from three depths of fields fertilized with either superphosphate and dairy manure (SP+DM, open boxes, $n = 35$), or with fox and mink manure (F&MM, gray boxes, $n = 35$) as the main P source. Soil data by group are discussed in the text.

are consistent with those for soils amended with large amounts of cattle manure (e.g. Eghball et al. 1996), poultry litter (e.g. Kingery et al. 1994), swine manure (e.g. Novak et al. 2000), and other biosolids (e.g. Maguire et al. 2000).

As for the three soil groups, the P accumulation rate due to surplus F&MM-P applications (i.e. the difference in the total P concentration between the fields within a pair) was highest in organic soils, followed by coarse-textured mineral soils, and lowest in fine-textured mineral soils. In the plough layer (0–20 cm) samples, F&MM-amended fine-textured, coarse-textured, and organic soils contained 460, 890, and 1520 mg kg^{-1} more total P, respectively, than did the fields fertilized with SP+DM (Table 1). The differences associated with soil group were also apparent in the soil layer below a typical ploughing depth (20–40 cm layer), where F&MM-amended fine-textured, coarse-textured, and organic soils contained 260, 660, and 1580 mg kg^{-1} more P, respectively, than did the SP+DM-cured fields. Some of the P input into the 20–40 cm layer may be due to occasionally deeper ploughing, but the differences between the field pairs were so distinct and applicable for all of the field pairs that this can only be a partial explanation. At the depth of 40–60 cm, there was no longer any clear difference in the total P concentration of the fine-textured mineral soils (only 20 mg kg^{-1} more in the F&MM-treated soils), whereas F&MM-treated coarse-textured mineral soils and organic soils contained 230 and 470 mg kg^{-1} more total P, respectively, than did their SP+DM-amended counterparts. At this depth, variable ploughing depth no longer serves as an explanation for elevated total P content in F&MM-amended fields.

Except for the fine-textured mineral soils at 40–60 cm depth (with p = 0.6187), all of the differences in total P concentrations discussed above were statistically significant (with p-values 0.0076–0.0312), showing that F&MM-P may migrate to great depths. Even though P translocation to 40–60 cm depth did not seem to have occured in any measurable extent in the fine-textured mineral soils, preferential flow along macropores may in fine-textured soils control the transport of particulate matter and pollutants to drainage pipes (e.g. Jensen et al. 1998, Djodjic et al. 1999, Shipitalo and Gibbs 2000). As the volume of macropore walls is only a small percentage of the total subsurface soil volume, the present data could underestimate the potential for P translocation down to the pipe drainage depth in a fine-textured soil profile.

We also estimated the total organic P concentration of the soils by the Saunders-Williams ignition method (data partly shown in Table 4), but found no differences in organic P concentration between the soils amended with F&MM-P and those that received much smaller P dressings as SP+DM. This finding was in agreement with the data on soil organic matter contents (see Table 1) and applied to both topsoil and subsurface samples (most of the subsurface samples contained too little organic P for its concentration to be confidently determined by this method). In contrast, Sharpley et al. (2004) found a significant increase in organic P forms in 20 manured soils of New York, Pennsylvania and Oklahoma, as compared to unmanured control soils. Hooda et al. (2001) also noted that high P-input levels sometimes changed the P distribution between inorganic and organic forms. However, across the whole of their data on 10 sandy and clayey UK loam soils, organic P as a proportion of total P was similar in both low and high P-input practices. In our data, the results of the modified Hedley fractionation (conducted for samples from 13 field pairs, discussed below) also showed that F&MM-P surpluses tended to accumulate in inorganic form though there were some differences between the soils (see Table 4).

Soil P fractions

For the sequential extractions, soil pairs with as similar inherent chemical characteristics as possible were selected to represent the three soil groups listed in Table 1 (see Material and methods section for details). In the topsoils, a F&MM-P surplus had accumulated most notably in the inorganic P fractions extractable by HCl (29–59% of F&MM-P surplus) and NaOH (19–36% of F&MM-P surplus; Table

Table 4. Soil inorganic (-i) and organic (-o) P pools in plough layer (0–20 cm) of fields fertilized with superphosphate and dairy manure (SP+DM) and fields amended with fox and mink manure (F&MM). Accumulation of F&MM-P surplus in a P fraction was calculated for the measured P fractions, assuming that it equals the difference in P concentrations between SP+DM- and F&MM-amended soils. Values are mean values, followed by range in parentheses.

	SP+DM	F&MM	Accumulation of F&MM-P in a P pool
	mg P kg^{-1}		
Fine-textured mineral soils (*n* = 4)			
P_w-i	20 (7–32)	54 (30–70)	34 (23–55)
P_w-o	17 (13–23)	27 (20–38)	10 (–3–26)
P_{NaHCO3}-i	107 (45–203)	159 (111–233)	52 (15–97)
P_{NaHCO3}-o	69 (46–91)	80 (53–133)	11 (–34–75)
P_{NaOH}-i	259 (145–517)	416 (181–831)	157 (–35–314)
P_{NaOH}-o	222 (178–303)	194 (154–215)	–28 (–149–33)
P_{HCl}-i	288 (230–374)	498 (339–667)	210 (108–294)
P_{HCl}-o	35 (14–65)	57 (14–97)	22 (–7–83)
$P_{residual}$-i *	165 (127–204)	185 (124–315)	
Organic $P_{S\text{-}W}$	250 (200–330)	220 (100–290)	
$P_{residual}$-o **	–93 (–155–6)	–141 (–212––66)	
Coarse-textured mineral soils (*n* = 5)			
P_w-i	28 (5–43)	105 (31–171)	77 (50–133)
P_w-o	19 (14–22)	36 (23–61)	17 (4–41)
P_{NaHCO3}-i	88 (60–110)	216 (130–306)	128 (54–202)
P_{NaHCO3}-o	76 (40–128)	73 (28–95)	–4 (–47–19)
P_{NaOH}-i	130 (74–177)	318 (199–524)	188 (47–347)
P_{NaOH}-o	207 (80–331)	189 (81–350)	–18 (–166–114)
P_{HCl}-i	210 (120–295)	764 (235–1790)	554 (–13–1630)
P_{HCl}-o	25 (0–45)	111 (17–349)	87 (–10–326)
$P_{residual}$-i	140 (110–160)	211 (51–514)	
Organic $P_{S\text{-}W}$	250 (80–440)	260 (0–600)	
$P_{residual}$-o	–76 (–115–129)	–152 (–370–20)	
Organic soils (*n* = 4)			
P_w-i	69 (13–156)	354 (32–691)	285 (14–601)
P_w-o	74 (51–109)	163 (50–379)	89 (–1–296)
P_{NaHCO3}-i	86 (16–124)	273 (162–409)	188 (77–293)
P_{NaHCO3}-o	174 (131–214)	229 (135–384)	55 (–35–170)
P_{NaOH}-i	183 (106–328)	656 (345–915)	473 (197–587)
P_{NaOH}-o	325 (215–425)	416 (333–531)	92 (–92–243)
P_{HCl}-i	129 (65–220)	509 (229–999)	380 (52–935)
P_{HCl}-o	22 (13–29)	67 (0–213)	45 (–13–183)
$P_{residual}$-i	300 (260–350)	530 (260–890)	
Organic $P_{S\text{-}W}$	730 (580–830)	720 (610–940)	
$P_{residual}$-o	130 (90–180)	–150 (–420–20)	

*Total soil P less the sum of $OP_{S\text{-}W}$ (organic P by the Saunders-Williams ignition method) and the sum of the inorganic P-fractions, i.e., TP – ($OP_{S\text{-}W}$ + ΣP-i)

**The difference between $OP_{S\text{-}W}$ and the sum of the organic P-fractions, i.e., $OP_{S\text{-}W}$ – ΣP-o

4, Figs. 2 and 3). In the mineral soils (Fig. 2), the sum of water- and bicarbonate-extractable P_i pools corresponded to about 20% of the total extractable P_i, and there was considerable accumulation of surplus F&MM-P to the acid-soluble P_i pool (see also Table 4). In the organic soils (Fig. 3), NaOH-P_i was a more important pool for the F&MM-P surplus, and a significant proportion (average about 35%) of the accumulated inorganic F&MM-P was also present in the easily soluble fractions, water- and bicarbonate-extractable P_i.

The concentrations of all P pools declined gradually with soil depth (Figs. 2 and 3). An exception was one of the organic soils (O–4 in Table 2), in which the concentration of water-extractable P_i was very high in the 20–40 cm layer. In that sample,

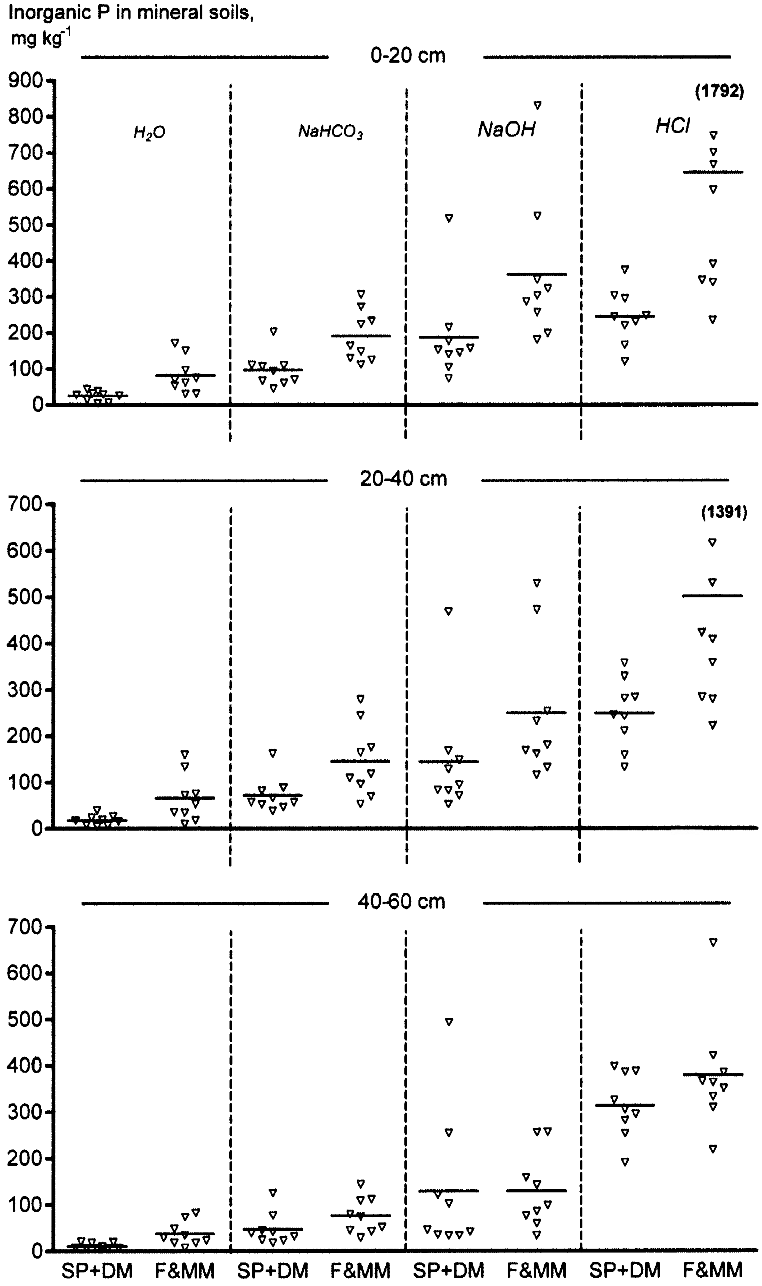

Fig. 2. Concentrations of inorganic P extracted by the modified Hedley scheme (water-extractable P is the sum of the two subsequent water extractions) in mineral soils at three depths, the horizontal bars indicate mean values. During 1970–2002, the main P sources of the fields were either easily soluble P (superphosphate and dairy manure, SP+DM) or sparsely soluble P (fox and mink manures, F&MM). Note the different y-scale of the uppermost figure.

the concentration of P_w–i was greater than that measured in the topsoil (see Fig. 3) and the sum of inorganic P_w and P_{NaHCO3} at 20–40 cm depth was about 1500 mg kg^{-1}, or 50% of the sum of the P_i fractions. This particular soil received 17 tn ha^{-1} of F&MM about one month before the sampling, and after manure application it was probably ploughed deeper than 20 cm, turning a manure-enriched layer below the 20-cm depth.

Another general trend was that, as compared to topsoil P distribution, relatively more (albeit less in actual amounts) surplus F&MM-P was re-

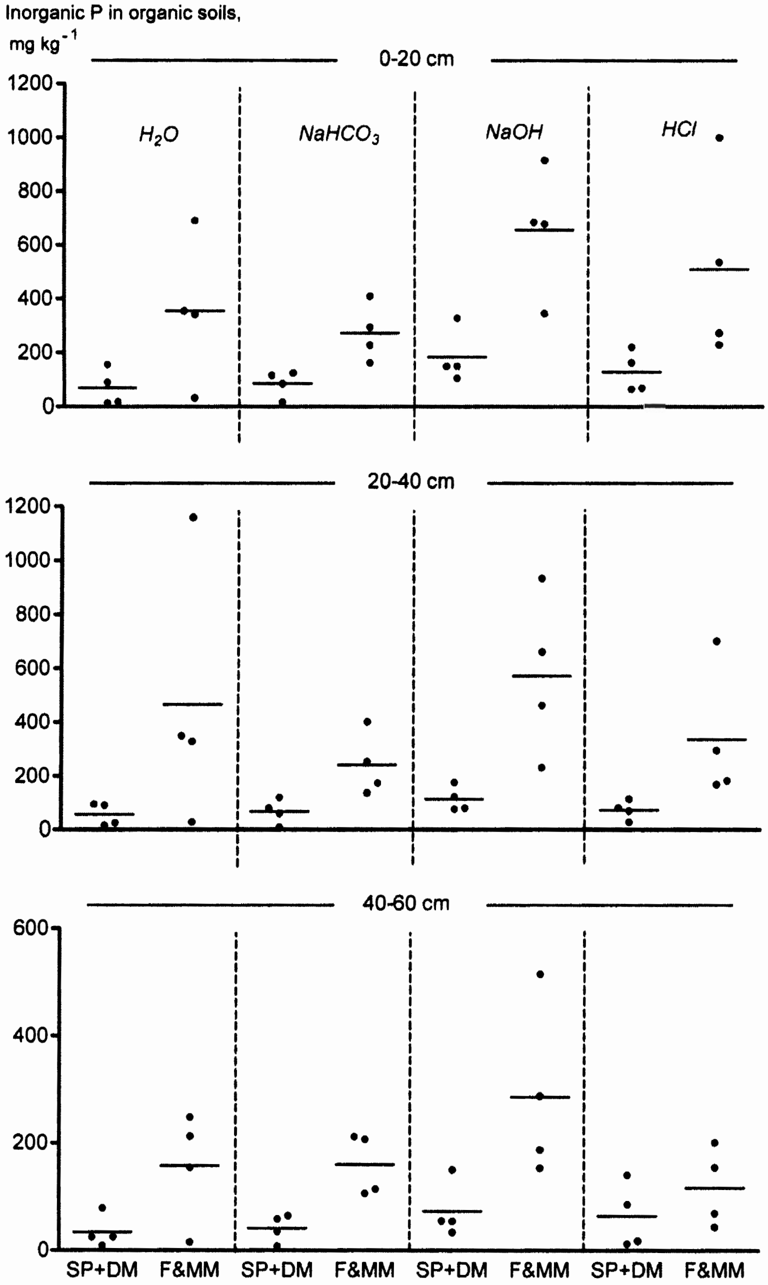

Fig. 3. Concentrations of inorganic P extracted by the modified Hedley scheme (water-extractable P is the sum of the two subsequent water extractions) in organic soils at three depths, the horizontal bars indicate mean values. During 1970–2002, the main P sources of the fields were either easily soluble P (superphosphate and dairy manure, SP+DM) or sparsely soluble P (fox and mink manures, F&MM). Note the different y-scale of the lowermost figure.

covered in the water- and bicarbonate-extractable pools in the deeper soil layers. Still at a depth of 40–60 cm in the organic soils, the water- and bicarbonate-extractable P_i pools, in addition to NaOH-P_i, were clearly greater in the F&MM-amended soils than in the soils fertilized with SP and DM (Fig. 3).

The high proportion of acid-soluble P in F&MM-amended soils might be due to partial solubilization of F&MM-P (with abundant Ca-P originating from bone meal and fish) in the soil, and due to recovery of these Ca-P associations in the acid-soluble fraction. However, the acid-extractable pool may also have acted as a major sink for solubilized F&MM-P in soils. As discussed by Beauchemin et al. (2003), this would happen most readily in soils with high P saturation and a high Ca content, both of which prerequisites were fulfilled in the F&MM-amended soils (Table 1). Further, Sharpley et al. (2004) concluded that additions of P and Ca with manures shift P chemistry from Al- and Fe-associated P to Ca-associated P. Sharpley et al. (2004) reported a close relationship between the ratio of water-extractable P-to-M3-P *vs.* exchangeable Ca. No such relationship was found in our data (R^2 less than 0.03; not shown), but then the variability in Ca concentrations was also narrower in our material (in topsoils, 0.7–3.7 g Ca_{exch} kg^{-1}). In the SP+DM-amended soils, and also in the deepest layers of F&MM-amended soils, acid-extractable P was probably mainly the native apatite type of P, which often accounts for a considerable proportion of the P in Finnish soils (Hartikainen 1979, Peltovuori et al. 2002). Nevertheless, some of the P only soluble in acid must have been translocated in F&MM-amended soils from the (P-saturated) upper horizons (see Figs. 2 and 3), either as soluble P that has precipitated in the deeper soil layers, or in particulate form. As example, Shipitalo and Gibbs (2000) showed that macropores may rapidly transport animal wastes to tile drainage depth.

Soluble organic P compounds have previously been found to be relatively mobile in the soil profile (Frossard et al. 1989, Chardon et al. 1997). In our data, the only general trend with regard to organic P, and applicable to both mineral soils and organic soils, was that the concentrations of water-extractable P_o were higher in the fields amended with F&MM than in those amended with SP+DM (p = 0.0165 or less). Also, when the organic soils were concerned, the concentrations of bicarbonate-extractable P_o were higher (p = 0.0155) in the samples from F&MM-amended fields than in their reference fields. The concentrations of NaOH-P_o were largely the same between the field pairs. The greatest differences in all P concentrations due to manure type were found in the topsoils (data shown in Table 4), and the differences in the deeper layers were small. Thus, there was no evidence that organic P compounds would have played an important role in downward P movement in these soils.

Agronomic P status

The average P_{Ac} (ammonium acetate-extractable P) concentrations for topsoils are given in Table 1 (the P_{Ac} test results also correlated well with the Mehlich 3-extractable P, but because there is no interpretation for M3-P in Finland, our discussion is limited to P_{Ac} concentrations). The agronomic P status of the topsoils of the fields fertilized with SP+DM corresponded to "satisfactory" (most of the fine-textured mineral soils) or "good" [the majority of coarse-textured mineral soils and organic soils; for the P status classification, see Peltovuori (1999)]. In the 35 fields fertilized with SP+DM, "excessive" P status was recorded for eight of the topsoil samples and for three samples from 20–40 cm depth. For the F&MM-amended fields, soil test P concentrations were "excessive" in 32 of the 35 topsoil samples. Of concern is that an "excessive" P status was also found in about 75% of the samples retrieved from the 20–40-cm layer of the F&MM-amended soils, and in about half of the samples retrieved from the 40–60 cm depth of the F&MM-amended soils.

As discussed by Jaakkola et al. (1997), soil P_{Ac} concentration may in heavily limed soils indicate high P status, but at the same time water-soluble P may be less affected by P accumulation. Because the acidic soil test extractant used in Finland also

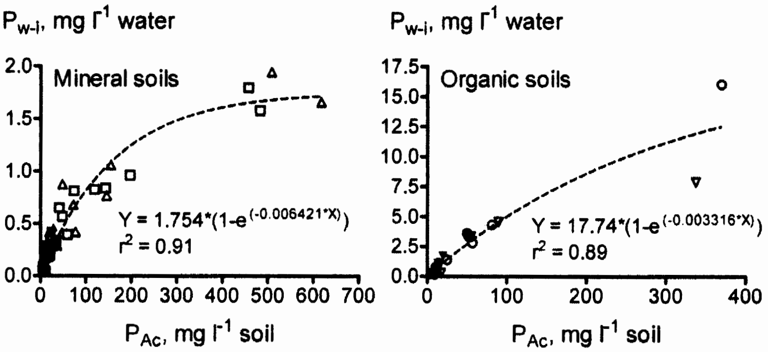

Fig. 4. Relationships between agronomic soil test P concentration (P_{Ac}) and the inorganic P concentration in soil water extracts (1:50 soil-to-water ratio, extraction time 4 h; soil samples from all depths included, triangle markers indicate topsoil samples). Open markers indicate the samples retrieved from the fields amended with fox and mink manure, and black markers those from the fields amended with superphosphate and dairy manure. In the equations, the term "e" refers to the root of the natural logarithm.

dissolves secondary Ca-phosphates that may not be immediately water-soluble, the concentration of readily soluble P does not necessarily always follow the changes in soil test P. However, in our material the concentrations of soil test P and water-soluble P both indicated high levels of easily soluble P in those samples that were retreived from F&MM-amended fields (Fig. 4, showing the P concentration of the first water extracts of the modified Hedley scheme in the y-axis). In high P_{Ac} concentrations, the relationships in Fig. 4 do appear to approach a plateau (notably when mineral soils were concerned), which might be due to dissolution of Ca-phosphates (originating from F&MM) in the pH 4.65 acetate buffer. On the other hand, it may also be due to the high P concentration in water extracts and, consequently, resoption or precipitation of dissolved P during the extraction. In any event, the high amounts of water-soluble P (especially when organic soils were concerned), showed that classifying the agronomic P status of the F&MM-amended soils as "excessive", when applicable, appears reasonable.

Conclusions

Fox and mink manure have a high P content, with a high share of sparingly soluble P associations. Based on the immediate solubility, P application rates that clearly exceed plant P uptake have been considered necessary when F&MM is utilized as a P source in plant production. In a long term, such practice not only builds up soil total P content and accumulates relatively stable P forms in soils, but it also increases those P forms that may easily solubilize in water, leach in surface runoff, and migrate down in soil profile. In our material, elevation of easily soluble P in the soil profile due to abundant F&MM-P use was most distinct in organic soils, followed by coarse-textured mineral soils, and least in fine-textured mineral soils. Taken that the agronomic soil test and water extraction both suggested that there were high concentrations of easily-soluble P in the F&MM-amended fields studied, a definitive conclusion is that no P fertilization is needed when these fields are cropped. The high P concentrations also suggest that the majority of the F&MM-amended soils of our study remain as hot-spots of P leaching for many years into the future even if they were cropped without P.

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SELOSTUS

Niukkaliukoisenkin fosforiyhdisteen pitkäaikainen runsas käyttö johtaa maan fosforikyllästyksen kasvuun

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Turkiseläinten lanta sisältää runsaasti fosforia, joka on pääosin niukkaliukoista. Maassa turkiseläinlannan lannoitusvaikutus on siten aluksi heikompi kuin esimerkiksi naudan lannan lannoitusvaikutus. Turkiseläinten lantaa hyödyntävässä viljelyssä on tämän vuoksi suositeltu muihin lantalajeihin nähden suurempien fosforin kokonaismäärien lisäämistä peltoon. Tässä työssä tutkittiin maan fosforin muotoja 35 peltolohkolla, joille tiedettiin pitkän ajan kuluessa lisätyn suuria määriä turkiseläinten lantaa.

Pitkän ajan kuluessa kasvien fosforin ottoa suuremmat lisäysmäärät turkiseläinten lantaa saaneilla lohkoilla olivat kasvattaneet maan fosforin kokonaispitoisuutta huomattavasti. Vaikka määrällisesti suurin osa ketun tai minkin lannan mukana maahan lisätystä fosforista oli maan fraktiointianalyysin tulkinnan mukaan kertynyt kasveille huonosti käyttökelpoiseen muotoon, alunperin hyvin niukkaliukoinen turkiseläinten lannan fosfori oli kuitenkin kasvattanut myös kasveille käyttökelpoisen ja huuhtoutumiselle alttiina olevan fosforin pitoisuutta maassa. Pitkän ajan kuluessa maahan lisätyt suuret fosforimäärät olivat aiheuttaneet maan fosforinpidätyspaikkojen täyttymisen pintamaan lisäksi myös syvemmissä maakerroksissa. Tällöin on uhkana fosforin kulkeutumien pintavalunnan ja salaojavesien mukana vesistöihin. Maan fosforikyllästysaste ja helppoliukoisen fosforin pitoisuus olivat erittäin suuria turkiseläinten lantaa saaneilla lohkoilla 60 cm:n syvyyteen saakka.

Vaikka maatalouden ympäristöohjelman puitteissa on turkiseläinten lantaa hyödynnettäessä mahdollista käyttää yli kaksinkertaisia fosforilisäyksiä kivennäislannoitteisiin verrattuna, lisäyksiä on syytä rajoittaa lohkoilla, joilla turkiseläinten lannan mukana on pitkään lisätty suuria määriä fosforia. Koska turkiseläinten lanta on hyvin fosforipitoista ja sen kuiva-ainepitoisuus on suhteellisen suuri, ketun ja minkin lannan kuljettaminen on edullisempaa kuin useiden muiden lantalajien. Näin ollen sitä kannattaa levittää myöskin kauempana lannan syntypaikasta sijaitseville pelloille. Tämän tutkimuksen aineistoon oli tietoisesti etsitty pitkään turkiseläinten lantaa saaneita peltoja, minkä vuoksi tutkimusaineiston maiden fosforipitoisuus oli korkea. Vaikka tällaisten peltolohkojen osuus peltoalasta olisi suhteellisen pieni, maan fosforikyllästystä tulisi pyrkiä alentamaan, sillä yksittäiseen vesistöön päätyvästä kuormituksesta saattaa suuri osa olla peräisin muutamalta fosforilla kyllästetyltä peltolohkolta.