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Phosphorus status of diverse soils in Finland as influenced by long-term P fertilisation

I. Native and previously applied P at 24 experimental sites

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The native reserves of phosphorus (P) in Finnish soils are sizeable but poorly available to plants. The P status has been generally poor, but large rates of P applied since the 1940s have substantially enhanced the supply of P from the soil. As a means of optimising P fertilisation of crops grown in the improved soils and promoting agro-environmental sustainability of agriculture, long-term field experiments were established in 1977–1981 on various soil types around Finland, between the latitudes of 60 and 65 N. The experimental sites (8 Cambisols, 9 Regosols, 6 Histosols, 1 Podsol) were moderately acidic (pH_w 5.6, range 4.6–6.6) and contained 1.6–31.2% organic C, and (mineral soils) 3–74% clay. The concentration of total P was 1.22 (0.66–1.87) g kg^{-1}, and the inorganic fraction separated with fluoride and hydroxide extractions (Al,Fe-P) was 8.2% (4.5–12.4%) of oxalate extractable Al+Fe (P saturation index). In mineral topsoil the pool of Al,Fe-P was 850 kg ha^{-1}, which is 300 kg ha^{-1} larger than was obtained in the early 1960s and 600 kg ha^{-1} larger than found in virgin soils. The soil test P value was 13.1 (3.7–60) mg dm^{-3} by the acid ammonium acetate method, 11.5 (1.6–42) mg dm^{-3} by a water extraction method (1:60 v/v) and 61 (23–131) mg kg^{-1} with a modified Olsen method. The intensity factor of soil P status has remained at a relatively low level in a major part of the cultivated area.

Key words: Acetate method, phosphorus, Olsen P, P saturation index, secondary inorganic P, total P, water extractable P

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Introduction

The role of phosphorus in Finnish agriculture has been established in comprehensive chemical and agronomic studies, as reviewed by Saarela (2002). The strong sorption of phosphate anions in Finland's acid soils is detrimental not only for the availability of native P reserves but also for the utilisation of applied P. Quite large amounts of P fertiliser has thus been required to obtain maximum yields even when the yield responses were small. Earlier recommendations to apply several times larger amounts of P than were removed by crops were well grounded, in particular for sugar beet and potato but also for cereals and even leys.

Over the years, the availability of soil P has gradually improved as a result of balance surpluses, and note needs to be taken of this so that heavy P applications are not continued for an unnecessarily long time. During the 1960s and 1970s increasing rates of fertilisation were applied to almost all cultivated Finnish soils and the soil test P values (STP) determined by the Finnish acid ammonium acetate method (P_{Ac}, Vuorinen and Mäkitie 1955) increased sharply. According to summaries from routine soil testing (Kähäri et al. 1987), the mean P_{Ac} value of all cultivated Finnish soils more than doubled in the period 1960–1965 to 1976–1980, from 5.0 mg dm^{-3} to 11.1 mg dm^{-3}. The improvement of the P status of agricultural soils has been a general trend in developed countries since the 1950s, and even greater changes have been recorded in other parts of Europe than in Finland (Tunney 1992).

The improved availability of soil P and the possibility to obtain normal yields with smaller amounts of applied P than generally used were demonstrated in field experiments during the seventies (Jaakkola et al. 1977, Sippola 1980). Moreover, employment of the placement method in fertiliser application to annual crops presumably enhanced the supply of P to plants (Elonen 1983). Added to this, domestic and international surplus production of all main crops had reduced the demand for and price of the additional yield produced by applied P, and the debate over the environmental damage caused by long-term excessive P application was established on a more scientific basis.

Comprehensive experimental research was necessary, however, to optimise the P fertilisation of crops grown on soils containing large amounts of accumulated P. This project was primarily intended for agricultural purposes. The target of environmental protection was indirect and aimed at by avoiding any unnecessary application of P, which was to made possible by means of the fertiliser recommendations revised in the project. Environmental aspects are only briefly discussed in this paper.

Large project for optimising P fertilisation

In view of this need for optimisation, a series of long-term field experiments with five rates of annual P fertilisation supplying 0–60 kg P ha^{-1} was established in 1977–1981 at 24 sites on diverse soil types at MTT Agrifood Research Finland's research stations. The experiments were run for 9–18 years. In line with the strategy employed by the late Professor Paavo Elonen who initiated the project, a major objective was to obtain results that could be directly applied by farmers without any complicated modelling. Several rates of P were therefore applied to enable the production of response curves simply on the basis of the original yields. Single and triple superphosphate (8.7 or 20% P) were used as the P fertilisers and applied annually at rates 0, 15, 30, 45 and 60 kg P ha^{-1}. The requirement of P fertilisation for sustainable agriculture was investigated through monitoring the changes of soil P status in relation to the differences in P balance.

Soil samples and yield data from the field experiments have already been used in several subprojects. Different chemical soil testing methods have been compared (Sippola and Saarela

1986, Saarela et al. 1996), a plant test has been evaluated (Saarela 1990), chemical fractions of soil P have been assessed (Hartikainen 1989), and the soils have been investigated with a pot experiment (Saarela and Sippola 1990, Saarela 1992). In addition, the mycorrhiza populations and their role in P nutrition of crops have been examined at two sites (Kahiluoto et al. 2001). Summaries of the results have been reported in Finnish (Saarela and Elonen 1982, Saarela et al. 1995).

The changes in soil P status in 22 of the 24 long-term experiments and the crop yields will be reported in forthcoming papers. In this paper, the initial soil data are presented and compared with the corresponding values of Finnish soils at various earlier dates to demonstrate the highly significant increase in the P supplying power of the cultivated soils. Most of the data have been obtained by routine agricultural methods and published in Finnish (Saarela and Elonen 1982, Saarela et al. 1995). Now, it was considered of interest to present the results in detail to international readers, together with some additional chemical analyses (total P and Olsen P) and calculations (P saturation index).

Material and methods

Experimental sites

The 24 long-term field experiments were distributed over the main agricultural area of Finland (Table 1). The soils of Northern Europe, formed around ten thousand years ago at the end of the last glacial period, are weakly weathered and covered with large swamps under the cold and humid climate. The sites, located at MTT's research stations, represent most of the common soil types of Finland, but they include only one well-sorted sandy soil (14). This kind of soils where the main fraction is coarser than 0.06 mm and the percentage of clay less than 5% are common in the central and northern areas of Finland. Most of the sites are parts of broad cultivated fields in flat terrain; fields 10 and 16 are exceptional in being moderately sloping. According to the FAO/Unesco system, most of the mineral soils are Cambisols or Regosols.

Textural soil classes vary from clay to loamy sand (Table 1). Two of the soils (9 and 16), which were analytically classified as silty clay loam (more than 30% clay), had a clearly silty appearance and the physical properties of silt loam. These soils obviously had large coarse clay fractions and only small portion of fine colloidal material (Sippola 1974). Sites 12 and 13 are silt loams in river valleys evidently deposited in a slow stream. The soils were divided into five groups: mineral soils into two textural/regional groups, coastal clay and loam soils, CL- (Cambisols) and inland silty and sandy soils, SS- (Regosols or Podsols), both subdivided into two different STP levels, -P1 and -P2, denoted together as CLPM and SSPM (mean), and all organic soils in one group, OSPM (Histosols).

Most of the experimental fields have been cultivated for centuries by employing the traditional farming systems based on fallow and organic fertilisers. For several decades prior to the establishment of the experiments the soils had been cultivated conventionally using mineral fertilisers, including abundant P, up till the 1950s mainly as superphosphate and since then NPK compounds, but (except sites 8 and 18) seldom or no manure. Up till the 1960s cereals and clover-grass ley were normally grown in rotation. Later on cereals have dominated, but sugar beet (sites 8 and 18), potato (18), grass ley (2 and 5) and occasionally pea and oilseed rape were also grown. The Histosols appeared to have been amended with fine mineral soil or sand (site 21).

Soil analyses

Soil samples were obtained from two layers of each plot before the first fertiliser application in the spring of the establishing year and subsequently every third season autumn. The two layers were the ploughed topsoil to a depth of 20 or

Table 1. Location, texture and tentative classification of experimental fields with physical soil characteristics in the 20 cm deep (in soil 15 about 25 cm deep) ploughed topsoil layer and in the subsurface soil (subss) from 20 to 40 cm (25 to 45 cm in soil 15).

No	Municipal location	Geographic location	Altitude*	Texture or peat type ¤	Soil class #	Organic C, % topsoil	Organic C, % subss	Clay, % (< 2 µm) topsoil	Clay, % (< 2 µm) subss	BD** kg dm^{-3}
1	Mietoinen	60.38 N 21.52 E	2	c	CMv/RGe	1.9	0.8	74	80	1.00
2	Pälkäne	61.20 N 24.13 E	106	l	CMe	2.3	0.8	12	13	1.06
3	Mietoinen	60.38 N 21.52 E	2	c	CMe/RGe	2.1	1.1	59	70	0.98
4	Ylistaro	62.56 N 22.30 E	26	l	CMd	6.9	2.7	27	23	0.79
1–4, clay and loam soils with lower STP, CLP1						**3.3**	**1.3**	**43**	**47**	**0.96**
5	Mietoinen	60.38 N 21.51 E	2	scl	CMe	1.7	0.4	24	20	1.13
6	Kokemäki	61.16 N 22.14 E	38	l	CMe	8.1	1.2	25	34	0.83
7	Mietoinen	60.38 N 21.51 E	3	cl	CMe/RGe	2.1	0.8	35	52	1.05
8	Jokioinen	60.48 N 23.28 E	88	c	CMv	2.7	0.9	43	54	1.04
5–8, clay and loam soils with higher STP, CLP2						**3.7**	**0.8**	**32**	**40**	**1.01**
9	Mouhijärvi	61.31 N 22.57 E	75	sicl	RGe	2.4	1.1	35	36	0.95
10	Tohmajärvi	62.13 N 30.22 E	160	sl	RGd	3.5	1.0	5	4	1.03
11	Toholampi	63.48 N 24.10 E	80	sil	PZh/PZg	2.9	0.9	6	6	1.08
12	Anjalankoski	60.41 N 26.47 E	23	sil	RGu/RGe	9.8	0.7	25	28	0.83
13	Toholampi	63.49 N 24.11 E	70	sil	RGu/RGe	9.7	1.2	18	15	0.75
14	Mikkeli	61.40 N 27.13 E	100	ls	RGd	4.6	2.6	3	2	1.01
9–14, silt and sand soils with lower STP, SSP1						**5.5**	**1.2**	**15**	**15**	**0.94**
15	Maaninka	63.09 N 27.19 E	90	sl	RGe	1.6	0.7	8	6	1.03
16	Mouhijärvi	61.31 N 22.58 E	82	sicl	RGe	2.9	1.0	33	32	0.93
17	Laukaa	62.20 N 25.59 E	82	sil	RGe	2.7	0.6	26	21	0.98
18	Jokioinen	60.52 N 23.27 E	102	ls	RGe	2.9	0.6	10	12	1.04
15–18, silt and sand soils with higher STP, SSP2						**2.5**	**0.7**	**19**	**18**	**1.00**
1–18, mineral soils						**3.9**	**1.1**	**26**	**28**	**0.97**
19	Tohmajärvi	62.13 N 30.21 E	88	Carex peat	HSs	31.2	35.8	n.d.	n.d.	0.43
20	Toholampi	63.49 N 24.11 E	70	Carex peat	HSs	24.9	29.5	n.d.	n.d.	0.43
21	Vaala	64.31 N 26.27 E	115	sCarex peat	HSs	15.0	41.6	n.d.	n.d.	0.61
22	Jokioinen	60.54 N 23.31 E	107	Clayey mull	HSs	22.5	35.8	n.d.	n.d.	0.56
23	Tohmajärvi	62.13 N 30.21 E	88	Carex peat	HSs	28.3	31.8	n.d.	n.d.	0.45
24	Ruukki	64.41 N 25.05 E	45	Sandy mull	HSs/RGu	17.9	8.1	10	12	0.60
19–24, organic soils with low to medium STP, OSPM						**23.3**	**30.4**	**–**	**–**	**0.51**
1–24, all soils		**Mean**				**8.8**	**8.4**	**25**	**27**	**0.86**
		SD				**9.3**	**14.1**	**19**	**23**	**0.23**

* Altitude is the height above sea level in metres

¤ Abbreviations of soils texture (FAO/Unesco system) are as follows: c = clay, l = loam, scl = sandy clay loam, cl = clay loam, sicl = silty clay loam, sl = sandy loam, sil = silt loam, ls = loamy sand, sCarex = sandy Carex

\# Abbreviations of tentative soil classes according to the FAO/Unesco system (FAO 1988) are as follows: CMv = Vertic Cambisol, RGe = Eutric Regosol, CMe = Eutric Cambisol, CMd = Dystric Cambisol, RGd = Dystric Regosol, PZh = Haplic Podzol, PZg = Gleyic Podzol, RGu = Umbric Regosol, HSs = Terric Histosol

** Bulk density (BD) is for ground dried topsoil samples

n.d. = not determined

25 cm and the subsurface soil within the next 20 cm. Each sample comprised about 0.5 l soil, which was a composite of five or more subsamples obtained with an auger. The samples were air-dried in cardboard boxes at 40°C or less, crushed gently to save the gravel and passed through a 2 mm sieve.

The percentage of organic carbon was determined by a dichromate combustion method (Tares and Sippola 1978). Particle size distribution was determined by Elonen's (1971) pipette method. Soil pH was measured in water suspension (v/v 1/2.5, pH_w). Exchangeable macrocations (Ca, Mg, K) were determined by single extraction using the acid ammonium acetate method (Vuorinen and Mäkitie 1955, 0.5 M ammonium acetate – 0.5 M acetic acid, pH 4.65, 25 mg soil in 250 ml, extraction time 1 h). The cations were measured by atomic absorption spectrophotometry.

Extractable soil phosphorus was determined for all samples (20 or 40/site/layer/sampling) by the acid ammonium acetate method (P_{Ac}, STP) employing molybdenum blue colouring with Sn(II)chloride reduction (Vuorinen and Mäkitie 1955). One topsoil sample from each block including the five treatments (4 or 8/site) was extracted with water (P_w, v/v 1/60, Sissingh 1971) and hot 2 M HCl (Egnér et al. 1960). Total, water extractable and bicarbonate soluble phosphorus (modified Olsen P, P_{Olm}) were measured in two composite samples from each site, one from the topsoil and the other from the subsurface soil. The samples were formed by combining equal amounts of soil from four replicate plots.

For measurement of total P, small amount of soil was digested by sodium carbonate fusion and analysed by ICP-AES. For measurement of water extractable P, a double-filtering modification according to Saarela (1992) was employed. P_{Olm} was extracted in 0.5 M sodium bicarbonate solution in (w/v 1/20) and determined by colorimetry (Olsen et al. 1954), but the normal extraction time of 30 min was lengthened to one hour (Sillanpää 1982). This increased the P values by about 20% relative to the normal method. For determination of the sorption index, soil samples treated with 200 mg P dm^{-3} were incubated for 7 days at field capacity, then 5 ml of soil was extracted with 50 ml of 0.005 M $CaCl_2$ for one hour. The P sorption index was calculated as the amount of sorbed P (mg dm^{-3} soil) divided by the P concentration (µg dm^{-3}) remaining in the solution (Saarela 1992). Yield data from a pot experiment conducted on these soils (Saarela 1992) are presented to compare them with soil characteristics.

The P saturation index (PSI) of the experimental soils (Schoumans 2000) was calculated according to Turtola and Yli-Halla (1999) from published data (Hartikainen 1989) of oxalate extractable soil Al and Fe and the corresponding P pools extracted with ammonium fluoride (Al-P) and sodium hydroxide (Fe-P). The PSI was expressed as the ratio sorbed P/sorbing Al+Fe (Al,Fe-P)/(Al_{Ox} + Fe_{Ox}) in the same way as the P saturation index (PSI) of Schoumans (2000) and the identical degree of soil saturation with phosphorus (DSSP) of Hooda et al. (2000), but here the sorbed P was determined differently. The indices of Schoumans and Hooda et al. were based on the amounts of P, Al and Fe extracted with the same oxalate solution, $P_{Ox}/(Al_{Ox} + Fe_{Ox})$, but here the P assumed to be bound to Al and Fe (Al-P + Fe-P, denoted Al,Fe-P) were extracted separately with ammonium fluoride and sodium hydroxide.

Because acid ammonium oxalate dissolves large amounts of apatitic calcium phosphate from Finland's young soils, this extractant is not suitable for quantifying the P pool fixed to Al and Fe (Uusitalo and Tuhkanen 2000, Peltovuori et al. 2002), though it is successfully used for more weathered soils (Hooda et al. 2000, Maguire at al. 2001). The Fe_{Ox} and Al_{Ox} values used in this study (Hartikainen 1989) were obtained with a less concentrated ammonium oxalate solution than is generally used, 0.05 M vs 0.2 M, and according to some later studies the Al and Fe concentrations were as much as 30 % lower and the PSI values correspondingly higher.

Physical and chemical soil characteristics

Soil texture and organic matter content are used in calibrating the STP values determined by the acid ammonium acetate method, and pH as such is a highly critical factor for the availability of P to plants (Sippola 1980, Saarela 1992 and 2002). The concentrations of organic carbon (C_{org}) and clay (< 2 µm) in the soils indicated a wide di-

Table 2. Chemical soil characteristics at the experimental sites in topsoil and subsurface soil (subss).

Site no	pH (H_20)		CATSUM$_{Ac}$#		Ca$_{Ac}$, mg dm^{-3}		Mg$_{Ac}$, mg dm^{-3}		K$_{Ac}$, mg dm^{-1}	
group*	topsoil	subss	topsoil	subss	topsoil	subss	topsoil	subss	topsoil	subss
1	6.5	7.0	21.0	22.1	2550	1900	890	1417	360	362
2	5.6	6.0	6.3	3.5	1110	570	44	47	147	91
3	6.2	6.5	15.3	16.7	2040	1670	514	920	322	296
4	5.4	4.6	5.4	2.0	820	260	103	61	177	87
CLP1	**5.9**	**6.0**	**12.0**	**11.0**	**1630**	**1100**	**388**	**611**	**252**	**209**
5	5.7	5.4	7.2	6.4	1110	810	123	246	238	122
6	5.7	4.6	10.5	5.2	1850	760	93	138	176	91
7	5.8	6.8	10.0	16.1	1450	1790	262	806	218	212
8	6.6	6.7	18.3	23.1	2870	3010	368	901	370	234
CLP2	**6.0**	**5.9**	**11.5**	**12.7**	**1820**	**1593**	**212**	**523**	**251**	**165**
9	5.7	6.0	8.5	10.3	1350	1400	186	377	96	90
10	5.6	5.9	4.9	1.7	790	220	50	19	231	155
11	5.4	5.3	2.3	1.0	280	110	68	39	131	51
12	6.0	6.0	12.3	10.2	2200	1340	109	403	136	58
13	4.9	5.1	3.3	3.8	490	530	75	126	88	45
14	5.8	5.2	4.8	0.8	730	50	67	21	260	167
SSP1	**5.6**	**5.6**	**6.0**	**4.6**	**973**	**608**	**93**	**164**	**157**	**94**
15	6.1	6.3	8.4	6.7	1400	1080	150	137	73	60
16	6.5	6.5	11.5	10.2	1940	1470	158	302	200	129
17	6.2	6.7	10.6	7.9	1680	1140	230	245	114	64
18	6.4	6.0	11.2	2.0	1830	240	97	29	511	223
SSP2	**6.3**	**6.4**	**10.4**	**6.7**	**1713**	**983**	**159**	**178**	**225**	**119**
Mineral	**5.9**	**5.9**	**9.5**	**8.3**	**1472**	**1019**	**199**	**346**	**214**	**141**
19	4.8	4.7	10.3	9.9	1870	1800	91	89	86	68
20	4.8	4.7	6.8	5.9	1060	920	149	141	97	58
21	4.6	4.3	4.8	4.5	770	710	109	112	30	25
22	5.3	4.7	18.8	13.2	2800	1780	534	503	175	70
23	4.6	4.4	8.0	8.2	1350	1360	121	131	103	111
24	4.7	4.6	6.3	4.8	960	700	154	136	80	50
OSPM	**4.8**	**4.6**	**9.2**	**7.8**	**1468**	**1212**	**193**	**185**	**95**	**64**
All soils										
Mean	**5.6**	**5.6**	**9.5**	**8.2**	**1471**	**1068**	**198**	**306**	**184**	**122**
SD	**0.6**	**0.9**	**4.9**	**6.3**	**706**	**717**	**198**	**360**	**119**	**87**

* Abbreviations for soils groups: CL- = clay and loam soils, SS- = silt and sand soils, OS- = organic soils, -P1 = low STP, -P2 = high STP, -PM = medium STP

\# CATSUM$_{Ac}$ = sum of Ca, Mg and K extracted with acid ammonium acetate (Ac) as cmol(+) dm^{-3} soil

versity among the sites (Table 1). The loam soils 4 and 6, as well as the subsoil at site 24, were young sulphic sediments with higher C_{org} contents. The mean percentage of mineral components in the topsoils of the six Histosols (60%) is almost tenfold that of virgin peat (Kaila 1956). The data presented in Table 2, when compared with advisory soil tests from the same period (Kurki 1982) show that the experimental sites represent cultivated Finnish soils fairly well, in spite of the fewer sandy soils. Finnish clays are minerologically dominated by weakly weathered trioctahedral mica and are very rich in Mg and Fe (Sippola 1974), and the high content of extractable Mg in the deeper layer is typical for non-sulphic clays (Marttila 1965).

The "problem" soils, where the availability of P was exceptionally poor in relation to the content on extractable P, had low contents of extractable macrocations in the deeper layer as well as in the topsoil (Saarela et al. 1995). Exchangeable cations are seldom used as indicators of the P status of soil, and the possible causal mechanisms are poorly known, but the statistical dependencies may be useful as such. Since the macrocations are determined in every soil sample in routine soil testing, their use as a correction factor in interpreting the STP values would be easy and inexpensive.

Results and discussion

Total and acid-extractable P

Total concentrations of soil P at the start of the experiment (Table 3) agreed well with the earlier results for Finnish soils (Kaila 1963), as the somewhat higher minimum and mean values reflect the continuous accumulation of fertiliser P over the intervening years. The accumulation has also continued after the initial sampling in 1977–1981. Of the three richest soils, one (15) was located close to the phosphate mining area in Siilinjärvi, and two (8, 18) were enriched with large amounts of applied P (Fig. 1). The amounts of total P per hectare, which were calculated on the basis of bulk density of ground soil and inexact soil depth (Table 3), are not very accurate, but support earlier estimates that the total amount of P in cultivated topsoils is now about three tonnes per hectare (Saarela 2002).

As much as 75% of the total amount of P in mineral soils was extracted with hot 2 M HCl (Table 3), which, like acid ammonium oxalate (Uusitalo and Tuhkanen 2000), dissolved most of the inorganic P fractions. A major portion of the P dissolved by strong acid originates from native apatite, which is most abundant in mineral subsoils (Kaila 1964a, Hartikainen 1989, Turtola and Yli-Halla 1999, Peltovuori et al. 2002). The remaining 25% of P in mineral topsoil must have been mainly organic, but it included also resistant and occluded inorganic compounds. According to data on P fractions compiled from several of Kaila's papers from the 1960s and based on the same soil samples, 20–25% of total P in mineral topsoils was not dissolved during the fractionation procedure (Saarela 2002). In mineral subsoils, where the concentration of organic matter is much lower, most of the insoluble P is probably inorganic.

Much smaller portions of P were extracted with strong acid from organic soils (Table 3), but even these values, 180 to 580 mg dm^{-3}, mean 330 mg dm^{-3}, were many times higher than the inorganic fraction of P found by Kaila (1956) in different virgin peat soils, 35–63 mg dm^{-3}, which is equal to no more than 70–128 kg ha^{-1} 0.2 m^{-1}. The amounts of acid-soluble P have remained very small also in some poor cultivated peats, but native or applied mixtures of mineral soil, like the Histosols of the present study, have resulted in much richer acid-extractable P reserves (Barkoff 1959).

Fluoride and hydroxide extractable P

The sum of the more labile fractions extracted with ammonium fluoride and sodium hydroxide (Al,Fe-P) was less than 50% of the acid extractable pool in the mineral soils, and in the naturally rich soil 15 it was less than a fourth. Soils 8 and 18, which were enriched with large amounts of manure and fertiliser (Fig. 1), apparently (approximated from P_{HCl} and the differences in total P of the two layers) contained more than two tonnes of secondary inorganic P per hectare. These two rich soils raised the mean pool of Al,Fe-P (730 kg ha^{-1} for 16 soils, Table 3) to approximately 850 kg ha^{-1} for the 18 mineral soils, which is about 300 kg ha^{-1} or 50% larger than the amounts obtained in the 1960s (Kaila 1964a). This increase is in agreement with the continuous accumulation of fertiliser P in Finnish soils during the 1960s and 1970s.

According to the STP values obtained in routine soil testing (Kurki 1982), the present soils were richer in extractable P than the average

Table 3. Total concentration and amount of soil P and its chemical fractions at experimental sites in topsoil and subsurface soil (subss).

Site no	Total P, g kg^{-1}		Total P, t ha^{-1}			$P_{HCl,}$ g dm^{-3}	Al,Fe-P topsoil**	
group*	topsoil	subss	topsoil#	subss	to 40 cm	topsoil	g kg^{-1}	tn ha^{-1}
1	1.04	0.76	2.29	1.40	3.69	0.88	0.24	0.53
2	0.89	0.48	2.07	0.97	3.04	0.52	0.18	0.43
3	1.19	0.78	2.58	1.47	4.05	0.99	0.29	0.63
4	1.31	0.71	2.28	1.14	3.42	0.75	0.42	0.72
CLP1	**1.11**	**0.68**	**2.30**	**1.24**	**3.54**	**0.78**	**0.28**	**0.58**
5	0.91	0.64	2.27	1.45	3.72	0.87	0.25	0.61
6	1.49	0.63	2.71	1.17	3.88	0.71	0.52	0.95
7	1.29	0.60	2.99	1.16	4.15	1.01	0.44	1.03
8	1.61	0.75	3.68	1.49	5.17	1.47	n.d.	n.d.
CLP2	**1.33**	**0.65**	**2.91**	**1.32**	**4.23**	**1.02**	**0.40**	**0.86**
9	0.86	0.52	1.80	0.94	2.74	0.62	0.23	0.47
10	1.00	0.55	2.26	1.17	3.43	0.77	0.36	0.87
11	0.85	0.61	2.01	1.39	3.40	0.60	0.23	0.55
12	n.d.	n.d.	n.d.	n.d.	n.d.	0.47	0.29	0.54
13	n.d.	n.d.	n.d.	n.d.	n.d.	0.66	0.57	0.92
14	0.78	0.42	1.73	0.89	2.62	0.55	0.39	0.87
SSP1	**0.87**	**0.53**	**1.95**	**1.10**	**3.05**	**0.61**	**0.35**	**0.70**
15	1.87	1.56	4.31	3.31	7.62	1.88	0.41	0.93
16	1.41	0.86	3.01	1.66	4.67	0.81	0.45	0.96
17	1.22	0.71	2.70	1.47	4.17	1.14	0.34	0.75
18	1.62	0.63	3.95	1.45	5.40	1.44	n.d.	n.d.
SSP2	**1.53**	**0.94**	**3.50**	**1.97**	**5.47**	**1.32**	**0.40**	**0.88**
Mineral	**1.21**	**0.70**	**2.67**	**1.41**	**4.07**	**0.90**	**0.35**	**0.73**
19	1.33	1.20	1.26	0.95	2.21	0.27	n.d.	n.d.
20	1.85	1.48	1.75	1.33	3.12	0.34	n.d.	n.d.
21	0.66	0.69	0.88	0.44	1.32	0.18	n.d.	n.d.
22	1.64	0.99	2.05	0.75	2.80	0.58	n.d.	n.d.
$24^{23''}$	0.87	0.60	1.15	1.00	2.15	$0.32^{0.40''}$	n.d.	n.d.
OSPM	**1.27**	**0.99**	**1.42**	**0.90**	**2.32**	**0.33**	**–**	**–**
All soils ¤								
Mean	**1.22**	**0.77**	**2.37**	**1.29**	**3.66**	**0.79**	**–**	**–**
SD ¤	**0.36**	**0.30**	**0.88**	**0.55**	**1.34**	**0.41**	**0.11 ¤**	**0.20 ¤**

* Abbreviations for soils groups: CL- = clay and loam soils, SS- = silt and sand soils, OS- = organic soils, -P1 = low STP, -P2 = high STP, -PM = medium STP

\# Total P is calculated to a depth of 22 cm using the bulk densities presented in Table 1

** Al,Fe-P was calculated form the values published by Hartikainen (1989)

¤ SD for Al,Fe-P refer to mineral soils

n.d. = not determined

$0.40'' = P_{HCl}$ for soil 23

cultivated soils in Finland in the late 1970s. Even the less labile P fractions of the experimental soils may have been somewhat larger than in Finnish soils on average, but still higher concentrations occur. Peltovuori et al. (2002) recently measured a Al,Fe-P pool of almost 4.0 t ha^{-1} in a 0.30 m deep sandy loam topsoil in southern Finland that had a P_w value of 50.5 mg dm^{-3}. The

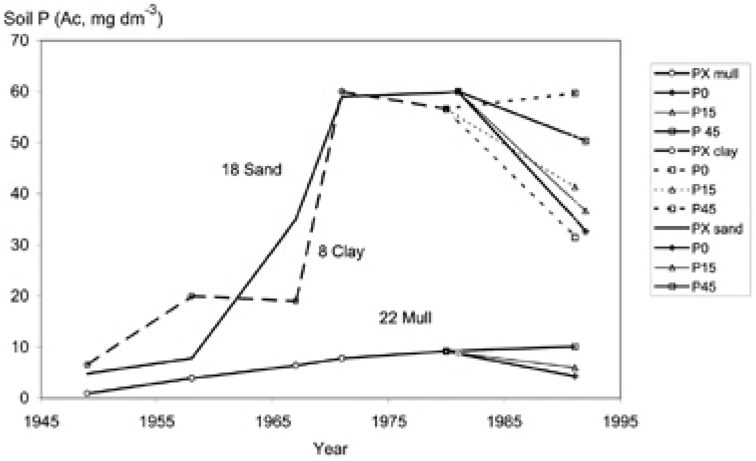

Fig. 1. Changes in the concentration of extractable soil P at three sites in Jokioinen. PX, PO, P15 and P45 indicate the rates of applied P which was not known exactly before the establishment of the experimental fields (PX).

large amounts of secondary P found in the exceptionally fertile soils confirm that the loss of STP is mainly a result of the efficient sorption of soluble P and may occur without any significant transport of P from the sites.

The six organic soils were not analysed for the secondary inorganic P fractions (Tables 3 and 4). However, the comprehensive investigations by Barkoff (1959) have shown that in peat soils containing little inorganic material the KOH soluble pool (similar to AL,Fe-P) represents more than 90% of inorganic P, and only traces remain to be extracted with strong acid. The relative increase in the inorganic secondary P reserves since the 1940s has probably been greatest in organic soils. The chemical investigations are in agreement with the yield responses to P fertilisation, which have decreased with time most sharply in organic soils (Salonen and Tainio 1957, Saarela et al. 1995).

P saturation index

The mean PSI of 8.2% in mineral soils presented in Table 4 is twice the value calculated from Kaila's (1964a) data for cultivated mineral soils (Saarela 2002). The present mean for mineral soils does not, however, include the two richest soils (8 and 18). These soils would probably increase the mean by some 20–25% and compensate for most of the analytical differences caused by the diluted oxalate solution used in these soils, about 30%. The PSI values for virgin soils have usually been about 2%, which is only one fourth of that obtained in this study.

The P fraction extracted with ammonium fluoride (Al-P) in relation to oxalate extractable Al has been shown to be a major determinant of the STP values obtained by water extraction (Hartikainen 1982) and by the acetate method (Hartikainen 1989). In the present material, additional P was sorbed most efficiently by soils 4 and 10 (Table 4), which had the highest concentrations of oxalate extractable Al (Hartikainen 1989). The good short-term sorbing efficiency of oxalate extractable Al is in agreement with Kaila's (1964b) finding that recently retained P is released by fluoride extraction more easily than are older reserves. Sorption was weaker in soils with PSI values higher than 10%.

Acetate and water extractable P

The concentration of P extracted with acid ammonium acetate (P_{Ac}) at the start of the 24 long-term experiments, mean 13.1 and range 3.7–60 mg dm^{-3} for the topsoils (Table 4), was slightly higher than the average value for the whole coun-

Table 4. Phosphorus status in topsoil and subsurface layers by various methods in topsoil and subsurface soils (subss), mg dm^{-3} soil.

Site no	Acetate test		Water extraction		Olsen method		P satu-	Sorption	Rel. yield ¤	
group*	topsoil	subss	topsoil	subss**	topsoil	subss	ration #	index ☐	Unlimed	Limed
1	3.9	0.5	4.6	1.2	33	6	6.2	0.63	54	71
2	4.4	0.4	5.7	0.7	23	7	6.4	0.67	26	33
3	5.5	0.6	5.4	3.3	38	8	7.4	n.d.	n.d.	n.d.
4	5.8	3.7	1.6	1.5	62	31	6.2	2.35	3	21
CLP1	**4.9**	**1.3**	**4.3**	**1.7**	**39**	**13**	**6.5**	**1.21**	**28**	**42**
5	8.9	1.8	5.0	1.1	41	9	9.5	0.29	55	84
6	9.1	6.3	9.8	2.7	82	39	8.8	0.95	58	66
7	14.1	0.7	29.9	1.4	71	10	12.0	0.26	74	94
8	56.6	3.8	33.0	5.6	101	18	n.d.	0.16	100	103
CLP2	**22.2**	**3.2**	**19.4**	**2.7**	**74**	**19**	**10.1**	**0.42**	**72**	**87**
9	3.7	0.9	6.7	3.1	26	10	6.8	0.50	52	75
10	4.6	1.6	4.6	0.9	36	9	6.6	2.10	11	30
11	4.7	2.3	1.6	0.9	40	10	4.5	1.66	4	14
12	6.9	0.5	5.4	n.d.	n.d.	n.d.	6.8	0.49	49	42
13	7.0	6.0	3.5	n.d.	n.d.	n.d.	7.5	1.74	0	38
14	8.2	0.8	5.3	0.8	94	6	7.0	1.57	0	25
SSP1	**5.8**	**2.0**	**4.5**	**1.4**	**49**	**9**	**6.5**	**1.34**	**19**	**37**
15	14.2	3.6	11.4	3.2	44	14	11.7	0.28	74	75
16	15.2	3.0	15.0	3.4	51	21	11.5	0.43	88	88
17	27.8	2.6	18.6	2.4	66	9	12.4	0.11	97	94
18	60.0	6.8	42.0	1.6	117	21	n.d.	0.13	106	95
SSP2	**29.3**	**4.0**	**21.8**	**2.7**	**69**	**16**	**11.9**	**0.24**	**91**	**88**
Mineral	**14.5**	**2.6**	**11.6**	**2.1**	**58**	**14**	**8.2**	**0.84**	**50**	**62**
19	5.2	3.2	5.3	12.4*	50	41	n.d.	0.28	44	16
20	6.5	3.1	4.8	4.4*	60	38	n.d.	n.d.	n.d.	n.d.
21	8.0	3.2	7.0	13.0*	57	29	n.d.	n.d.	4	18
22	9.2	1.2	8.7	6.3*	57	20	n.d.	0.32	69	41
23	11.2	9.1	16.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
24	14.2	11.7	24.2	25.3*	131	80	n.d.	0.08	24	83
OSPM	**9.1**	**5.2**	**11.0**	**12.3***	**71**	**42**	**–**	**0.23**	**35**	**40**
All soils ♦										
Mean	**13.1**	**3.2**	**11.5**	**4.5***	**61**	**21**	**–**	**0.75**	**47**	**35**
SD ♦	**14.9**	**2.9**	**10.8**	**5.9***	**29**	**18**	**2.5 ♦**	**0.72**	**35**	**31**

* Abbreviations for soils groups: CL- = clay and loam soils, SS- = silt and sand soils, OS- = organic soils, -P1 = low STP, -P2 = high STP, -PM = medium STP

** The values of water extractable P in organic subsurface soils may be slightly too high because they were determined for samples stored for 15–18 years (Saarela 2002)

\# P saturation index ($P_{Al,Fe}$ as % of oxalate extractable Al and Fe, PSI)

☐ For sorption index see chapter Methods

¤ Relative barley grain yield of pot-grown barley grown in the topsoils without applied P, as % of those obtained with sufficient P (from Saarela 1992)

♦ SD for P saturation refers to mineral soils

n.d. = not determined

try in advisory soil testing, 11.1 mg dm^{-3} (Kurki 1982). The mean P_{Ac} value was exactly the same as that obtained for 705 soils in a recent monitoring (Mäkelä-Kurtto and Sippola 2002). The 24 long-term experiments seem thus to represent Finland's current cultivated soils fairly well. The

P_{Ac} values of the whole material (36 soils) of this project, including the 12 short-term experiments with grass ley, were closely similar to those of the soil testing data in the late 1970s (Saarela and Elonen 1982).

Water extraction frequently produced P values similar to those of the acetate test; however, in some moderately acidic clay soils and in the organic soils, particularly in the subsurface layer, the P_w values were higher than the P_{Ac} values, and in most sandy soils they were lower. Soils 8 and 18, which were rich in P, did not obey the trend found earlier (Hartikainen 1989), that the relative extraction efficiency of water is stronger when the STP values are high. From the results for other mineral soils with very high STP values (Yli-Halla 1990, Jaakkola et al. 1997, Peltovuori et al. 2002) we can conclude that the P_w values of such soils are typically about 30% lower than their P_{Ac} values.

The STP values determined by the acetate and water extraction methods correlate fairly well in Finnish mineral soils (Uusitalo and Jansson 2002) but not in organic soils (Saarela 1992 and unpublished data). One reason for the different extractability of P with acetate and water in moderately acidic soils may be the concentrations of the main sorbing agents, Al and Fe. According to Kaila (1949), acid acetates more efficiently release phosphate ligands bound to Al than to Fe, and the ratio of oxalate extractable Al to oxalate extractable Fe is generally higher in coarse-textured soils (Kaila 1964a). This relationship seems to have held true for two clay soils in the same location in southern Finland studied by Yli-Halla (1989). The STP values obtained by both these methods were usually very low in the deeper layer of mineral soils, but somewhat higher in acidic sulphic subsurface soils (4, 6, 13), under a heavily fertilised topsoil in clay (8) and in a Terric Histosol (sandy mull) with low sorption index (24). With increasing pH, particularly above 6.5, the P_w value increases less than the P_{Ac} value (Saarela and Sippola 1990), but in the present material that relationship was apparent in only one clay soil (8).

Olsen P

On average, modified Olsen P (P_{Olm}, about 1.2 times standard P_{Ol}) was fivefold the values obtained by the other two methods, P_{Ac} and P_w. The relative difference was smaller in rich and larger in poor soils, and consequently the coefficient of variation (SD/mean) was much smaller with the Olsen test. These relationships were similar to those found in 30 mineral soils by Aura (1978). The same mean P_{Olm} value of 61 mg dm^{-3} for the topsoils of this study has been obtained for 94 Finnish wheat fields by Sillanpää (1982) by using a similar prolonged extraction (but the volumetric extraction ratio which caused little difference in mineral soils). The P_{Ol} values determined in 204 cultivated topsoils by Kaila (1965) with the normal Olsen procedure, 40 mg kg^{-1}, were two thirds of the P_{Olm} values for the soils of this study and fourfold the P_{Ac} values for the same soils (10 mg kg^{-1}). In the 30 mostly very fertile mineral soils (P_{Ac} 40 mg dm^{-3}) studied by Aura (1978) the mean P_{Olm} obtained by a shortened (20 min) extraction with sodium bicarbonate was not higher than 71 mg dm^{-3}.

In a global comparison based on 3538 soil samples from 30 countries, the P_{Olm} values of Finnish soils were fairly high, but the P concentrations of the wheat plants grown on these soils were lower than the soil test would suggest (Sillanpää 1982). The lowest P_{Olm} values found in newly reclaimed Finnish soils assessed in an international micronutrient project (Sillanpää 1990) were only about 4 mg dm^{-3}, which is one sixth of the lowest values for the topsoils of the present study and even lower than any of the 21 subsurface soils studied (Table 4). Although these were not extremely low P_{Olm} values globally, they demonstrate the small quantities of native labile P in Finnish soils and the sharpness of the change in the P status of cultivated soils.

The Olsen method seems to distinguish very poor soils, though the P_{Olm} values for the subsurface soils are rather high compared to the low intensity of P indicated with the low P_w values. The mean P_{Olm} of the subsurface soils, 21 mg kg^{-1}

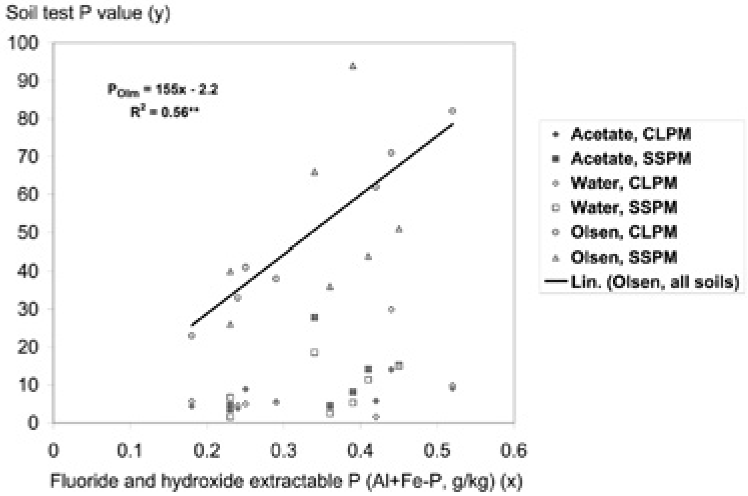

Fig. 2. Plot of STP values measured by three soil testing methods vs. the sum of the P fractions extractable in ammonium fluoride and sodium hydroxide (A1,Fe-P) for two groups of mineral soils: CLPM = clay and loam soils and (Cambisols and Eutric Regosols), SSPM = silty and sandy soils (Umpric/Dystric Regosols and Podzols).

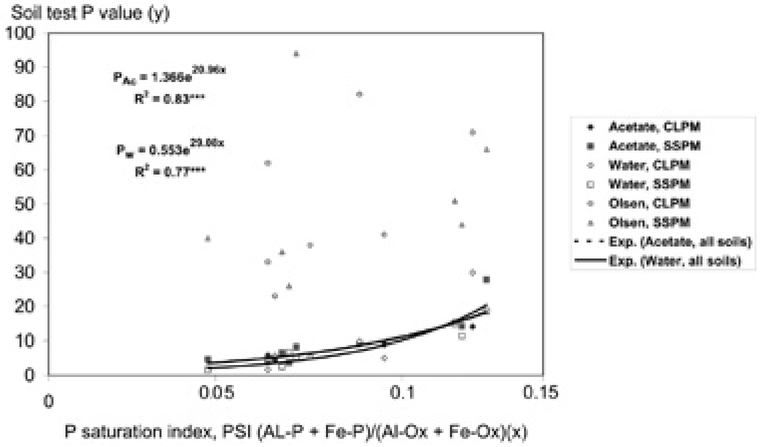

Fig. 3. Plot of STP values against P saturation indices (PSI) for two groups of mineral soils: CLPM = clay and loam soils and (Cambisols and Eutric Regosols), SSPM = silty and sandy soils (Umpric/Dystric Regosols). The data are the same as in Fig. 2 except that the pools of A1,Fe-P are here divided by oxalate extractable A1+Fe.

(Table 4) is also the mean P_{Olm} value (21.1 mg dm^{-3}) for the 3538 topsoils of a global study (Sillanpää 1982). The relatively slow changes of the P_{Ol} values with time and the small coefficient of variation also means that this test is not a sensitive indicator of the intensity factor of the P status of Finnish soils.

Relationship between P indices

The STP values of the modified Olsen method (P_{Olm}) were positively correlated with the P reserves extracted with ammonium fluoride and sodium hydroxide, Al,Fe-P (Table 3, Fig. 2), but not with the P saturation indices, PSI (Table 4, Fig. 3), which is the same pool of P divided by the concentration of the sorbing agents. The STP values obtained by the acetate and water extractions (P_{Ac} and P_w), on the other hand, correlated with the P saturation indices but not with the sizes of the P pools as such. These observations support Kaila's (1965) conclusions that the Olsen method is suitable for measurement of the capacity factor of the soil P status.

Soil suspensions of the strongly buffered sodium bicarbonate have a pH of 8.5 which is several units higher than that found in strongly acid soils. The abnormally high pH values and the low Ca^{2+} concentration due to precipitation of Ca as $CaCO_3$ and the exchange of phosphate ligands with carbonate anions together cause much stronger desorption of phosphate than is possible in acid soils. Although probably most of the Olsen P is labile even in acid soils, moderate P_{Olm} values do not ensure a sufficient phosphate concentration in acid soil solutions.

In agreement with the theoretical discussion presented by Teräsvuori (1954), the acetate test and the water extraction method and even the PSI values appear to be much more sensitive indicators of the intensity factor in Finnish soils than is the Olsen method. The curvilinear relationships of the P_{Ac} and P_w values with PSI indices (Fig. 3) are in agreement with the greater increase of P desorption with DSSP (= PSI) values above 0.10 found in UK (Hooda et al. 2000).

In Finnish mineral soils, the intensity of soil P seemed to be a more critical factor for the supply of P to roots than was the capacity factor, as indicated by the STP values and grain yields of barley (Table 4), in particular for soils 4 and 14, and as found earlier (Saarela 1992). In addition, the high sorption indices of some soils with high P_{Olm} (soils 4 and 14) show that high STP values obtained by this test did not predict the sorption of applied phosphate as accurately as the other two routine methods and the PSI values.

In acidic soils of Northern Ireland (Maguire et al. 2001), in contrast to the results for Finnish soils, water extractable P was more closely correlated with Olsen P ($R^2 = 0.76$) than with the degree of P saturation, DPS ($R^2 = 0.66$). The best agreement with the P_w values in Irish soils was obtained with Morgan P extracted with acid sodium acetate ($R^2 = 0.91$). Similar results from northeastern parts of the United States (Jokela et al. 1998) suggest that various modifications of the acetate buffer method may be useful indicators of the risk of P leaching from acid mineral soils. The same is suggested by actual measurements of P leaching in Finland (Uusitalo and Jansson 2002).

Conclusions

The native phosphorus reserves of Finnish soils are poorly available to plants, but the high rates of P fertilisation applied since the 1940s have significantly improved the P status of cultivated soils. Comprehensive chemical studies done in P fertilisation experiments established at 24 sites in Finland in the late 1970s showed that the long-term P balance surplus have increased mainly the inorganic P fractions extracted with ammonium fluoride (Al-P) and sodium hydroxide (Fe-P). The mean sum of these fractions in mineral soils was many times larger than have been obtained from virgin soils and 50% larger than determined in the early 1960s. Still sharper increases were found in the acid-extractable P pools of cultivated Histosols, which was 730 kg ha^{-1} 0.2 m^{-1} or sevenfold the amount on mineral P found it virgin peat soils.

The mean P_{Ac} value for the initial topsoil samples, 13.1 (3.7–60) mg dm^{-3}, was slightly higher than the corresponding value in the advisory soil testing data at the same time, 11.1 mg dm^{-3}, but similar with some recent values. The mean initial STP value obtained by the water extraction method (P_w) was 11.5 (1.6–42) mg dm^{-3} and that determined by sodium bicarbonate extraction according to the modified Olsen procedure (P_{Olm}) was 61 (23–131) mg dm^{-3}.

The results of the chemical soils studies, particularly the low P_{Ac} and P_w values measured for several sites, showed that, in spite of the substantial amounts of fertiliser P accumulated in cultivated soils in Finland, the intensity factor of soil P status has remained at a relatively low level over a major part of the field area.

Acknowledgements. This research project was initiated by the late Professor Paavo Elonen. The field experiments were conducted by the Soils and Environment unit in Jokioinen and at MTT's research stations by local staff under local direction. The soil and plant samples were analysed in the laboratories of the Institute of Environmental Research. Most of the soil analyses were carried out under the direction of Professor Jouko Sippola. Docent Markku Yli-Halla classified the soils and commented on the arrangement of the contents and on several other details of the manuscript**.** The contributions of all scientists and technical experts who collaborated within this large project are greatly appreciated.

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SELOSTUS

Pitkäaikaisen fosforilannoituksen vaikutus Suomen peltojen fosforitilaan
I. Maan luontainen ja aikaisemmin kertynyt fosfori 24 koepaikalla

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Suomen maaperä sisältää melko runsaasti peruskalliosta jauhautunutta fosforia. Peltojen luontaiset fosforivarat eivät kuitenkaan riitä tehokkaaseen kasvintuotantoon, koska ne ovat vaikealiukoisia ja huonosti kasvien saatavilla. Fosforitila oli ennen yleisesti huono, mutta 1940-luvulla alkanut runsas fosforilannoitus on parantanut viljelymaiden fosforinluovutuskykyä merkittävästi. Parannettujen peltojen fosforilannoituksen optimointia varten perustettiin vuosina 1977–1981 monivuotisia lannoituskokeita 24 koepaikalle maan eri puolille. Kohtalaisen happamista koepaikoista (pH_w 4,6–6,6) kuusi oli eloperäisillä mailla (15–31 % org. C) ja kahdeksantoista kivennäismailla (1,6–9,8 % org. C ja 3–74 % savesta). Fosforin kokonaispitoisuus (21 maata) oli 0,66–1,87 g kg^{-1}, emäsliukoinen fraktio (Al,Fe-P, 16 maata) 0,18–0,57 g kg^{-1} ja oksalaattiuuttoisen alumiinin ja raudan fosforikyllästysindeksi 4,5–12,4 %. Asetaattimenetelmällä määritetyn fosforiluvun keskiarvo oli jonkin verran suurempi kuin samanaikaisten viljavuustutkimusten eli 13,1 mg dm^{-3} (vaihtelu 3,7–60) ja vesiliukoisen fosforin (uuttosuhteella 1:60 v/v) 11,5 mg dm^{-3} (vaihtelu 1,6–42); jälkimmäinen oli pienempi happamilla hiedoilla mutta suurempi eräillä eloperäisillä mailla. Kvantitatiivisempi Olsenin menetelmä tuotti suhteellisesti suurempia fosforipitoisuuksia (keskiarvo 61 mg dm^{-3}, vaihtelu 23–131) kuin muut kaksi menetelmää, jotka happamilla mailla osoittavat pääasiassa fosforin intensiteettiä. Koepaikkojen maaperästä tehdyt kemialliset analyysit osoittivat, että viljelymaihin kertyneistä huomattavista lannoitefosforimääristä huolimatta fosforitilan intensiteettitekijä on pysynyt melko alhaisella tasolla suurella osalla Suomen pelloista.