



Phosphorus in agricultural soils around the Baltic Sea

- Comparisons of different laboratory methods as indices for phosphorus leaching to waters

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Abstract

Eutrophication of the Baltic Sea is a serious problem. A major contributing factor is diffuse losses of phosphorus (P) from agricultural land in surrounding countries. In order to estimate P losses, environmental monitoring of small agriculture-dominated catchments is being carried out in most of these countries. Evaluation of the risk of P leaching to waters is usually based on chemical tests originally developed to quantify the amount of soil P available for plant production. The tests are performed in different ways in the different countries and a number of different extraction agents are in use. The ammonium lactate method (P-AL) is used in Sweden and Lithuania, the double lactate method (P-DL) in Latvia and Poland, the Mehlich 3 method (P-M3) in Estonia and the Olsen method (P-Olsen) in Denmark.

A total of 99 soil samples from five agricultural catchments and two field trials in the Baltic States and Sweden were extracted according to the four methods listed above. The amount of P was then quantified either colorimetrically or by inductively coupled plasma (ICP) spectrometry in accordance with the practices of the respective country. The amount of P determined by ICP spectrometry was nearly always (in 98% of cases) higher than that determined colorimetrically, with an average difference of 19% in plant-available P. The amount of P extracted by the four methods increased in the order Olsen-P < P-DL ≤ P-M3 < P-AL, with Olsen-P values being on average only 24% of P-AL values. The different active agents used in the four methods differ in their efficiency in desorbing and releasing P from minerals and organic compounds.

In the Baltic Sea area, neither a P adsorption index (PSI) or the amounts of P in relation to aluminium (Al-AL) and iron (Fe-AL) in the acidic AL extract is suggested to be a general good predictor of soil capacity to adsorb P or release dissolved reactive P (DRP) to water, based on the results from the limited number of sites in the present study.

Sammanfattning

Det finns idag stora problem med övergödning av Östersjön. En av de bidragande faktorerna till denna är de diffusa utsläppen av fosfor (P) från jordbruksmarken i angränsande länder. För att bedöma storleken av dessa utsläpp sker i de flesta av länderna en miljöövervakning av små jordbruksdominerande avrinningsområden. För att bedöma risken för stora läckage av P använder man sig här, liksom i de flesta andra länder, av jordtester som innebär en kvantifiering av mängden växttillgängligt P. Utförandet av dessa sker på olika sätt och med ett flertal olika extraktionsmedel i de olika länderna. Amoniumlaktat- metoden (P-AL) används i Sverige och Litauen, dubbellaktat- metoden (P-DL) i Lettland och i Polen, Mehlich 3- metoden (P-M3) i Estland och Olsen metoden (Olsen-P) i Danmark.

Sammanlagt 99 jordprov från fem jordbruksdominerande avrinningsområden och två försöksfält som ligger i de baltiska länderna eller Sverige analyserades. Alla jordar extraherades med de fyra ovan nämnda extraktionsmetoderna. Mängden P kvantifierades sedan antingen genom kolorimetrisk bestämning eller genom analys med ICP (Inductively Coupled Plasma) i enlighet med respektive lands rutiner. Mängden P analyserad med ICP resulterade nästan undantagsvis (98% av fallen) i högre mängden P än med kolorimetrisk bestämning, en skillnad som i genomsnitt motsvarade 19% av den tillgängliga fosfor. Mängden P för de fyra olika extraktionsmetoderna som ökade i följande ordning Olsen-P < P-DL ≤ P-M3 < P-AL med ett värde från Olsen-P som i genomsnitt bara var 24% av P-AL värdet. Skillnader i aktiva substanser och i effektiviteten att desorbera eller frigöra P från mineraler och från organiska föreningar diskuterades.

Varken ett sorptionsindex (PSI) eller mängderna aluminium (Al-AL) och järn (Fe-AL) i det sura AL-extraktet verkade vara en allmänt bra indikator i Östersjöområdet för jordens förmåga att sorbera P eller att frigöra reaktiv P (DRP) till vatten baserat på resultatet från det begränsade antalet områden i denna studie.

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Introduction

The agricultural sector plays a major role in the high inputs of nutrients to the Baltic Sea. High nutrient loads from agricultural soils have enriched the nutrient content of the waters and enhanced production of toxic blue-green algae. The Baltic Sea is an enclosed brackish water body that is especially sensitive to eutrophication. The limited possibilities that exist for inflow and exchange of water mean that deeper basins within the Sea have low oxygen levels, which makes it difficult for organisms to survive. When phytoplankton sink to the bottom more oxygen is needed for their degradation, which causes further oxygen consumption and even lack of oxygen at the sea bottom (Helsinki Commission, 2009).

Nitrogen (N), carbon (C) and phosphorus (P) are all essential elements for growth of biota. P is the limiting factor for growth in most waters and P is consequently a key element, with the highest influence on accelerating eutrophication (Lee, 1973; Brady & Weil, 2002; Sharpley *et al.*, 2003). Loads of C and N to waters are harder to control than P loads because of their atmospheric inputs and outputs (Sharpley *et al.*, 2003).

Diffuse P flow from arable land is an important factor in P losses to waters (Sharpley *et al.*, 2003). Soil texture seems to affect the subsurface transport of P by water, *e.g.* Djodjic (2001) reported very rapid subsurface (preferential) flow of dissolved reactive P (DRP) in lysimeters with clay soils. This transport may occur via macropores, thereby bypassing the soil matrix. In contrast, in sandy soils the P in percolating water is in much better contact with the soil matrix, which can adsorb P. In general, preferential flow and surface runoff are the main transport pathways for P from clay soils, while subsurface flow is the main transport pathway of P from sandy soils and peat soils (Chardon & Schoumans, 2007).

It has been shown that higher amounts of easily available P in soils give higher amounts of DRP in drainage water and leachate (Hesketh & Brookes, 2000; Sims *et al.*, 2002). In the lower range of plant-available P amounts in the soil, low levels of P are usually found in drainage water but at higher levels the P concentration in water increases rapidly, a change that occurs at what is sometimes referred to a 'change point'. Sims *et al.* (2002) estimated that this change point occurred at approx. 240 mg P kg⁻¹ soil using the M3-P method. Hesketh & Brookes (2000) estimated that the change point occurred at approx. 60 mg kg⁻¹ using Olsen-P and reported that the pattern of increased P concentration in water varied with the seasons.

Different methods are used for extracting plant-available P in soil in different countries around the Baltic Sea. In Sweden and Lithuania the ammonium lactate (AL) method is used, in Estonia the Mehlich 3 (M3) method, in Latvia and Poland the double lactate (DL) method and in Denmark the Olsen method. The sum of Al and Fe (Al-AL and Fe-AL) in the AL extract (mmol kg⁻¹) has been used as an indicator of the P sorption capacity in Sweden (Ulén, 2006). Similarly, aluminium and iron (Al-M3 and Fe-M3) have been used with the Mehlich 3 method in the USA in order to predict this capacity (Sims *et al.*, 2002)

The aim of the present work was to i) examine the different soil tests used in the Baltic States, Sweden and Denmark; and ii) compare these methods as a tool for evaluating the risk of high P losses based on the soil characteristics.

Materials and Methods

Soil samples

There are a variety of soils around the Baltic Sea. Figure 2 shows the soil regions and the parent material in the different countries neighbouring the Baltic Sea. The soils in northern Sweden are mainly Podsols and Cambisols, while in the central Sweden postglacial deposits of heavy clay dominate. In the Baltic States glacial tills and glaci-fluvial sediments are found, with a more or less clear gradient from the south to the north-west. Gleysols rich in humus are also quite common in central parts of Lithuania and Latvia (Reimann *et al.*, 2003). Table 1 shows the percentage of soils in the main soil texture distribution classes in the Baltic states and Sweden.

Table 1. Distribution of different soil texture classes in Lithuanian, Latvia, Estonia and Sweden.

	Lithuania ¹⁾ (% of arable land)	Latvia ¹⁾ (% of arable land)	Estonia ¹⁾ (% of arable land)	Sweden ²⁾ (% of arable land)
Sand	12	14	15	4
Loamy sand	37	22	31	8
Silt, silt loam	-	-	-	15
Sandy loam, loam	37	56	39	42
Clay	3	6	6	34
Peat	11	2	9	-

¹⁾ Kõlli *et al.*, 2008b

²⁾ Eriksson *et al.*, 1999

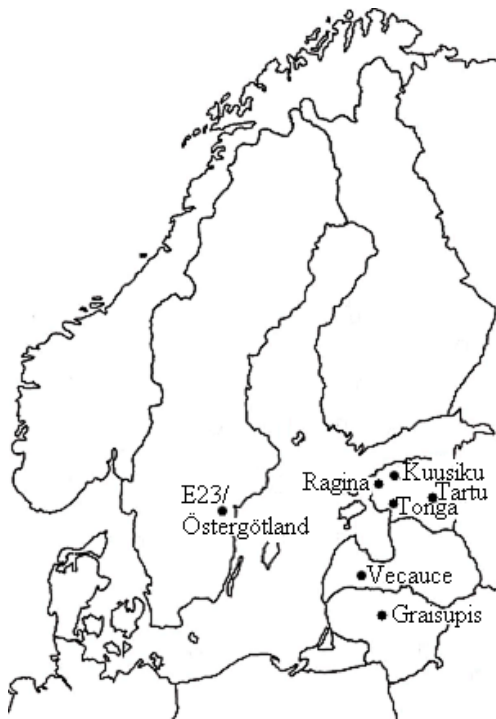


Figure 1. Sites where soil samples used in this investigation was taken.

A total of 99 soil samples were taken from agricultural soils with varying general soil characteristics and P fertilisation history used for monitoring five agricultural catchments (Tonga and Ragina, Estonia; Vecauce, Latvia; Graisupis, Lithuania; and E23/Östergötland, Sweden) and from two field trials in Estonia (Kuusiku and Tartu) (Figure 1). Most samples were from the topsoil, but a few were also taken from the subsoil. All the samples were sent to Sweden for analysis. Information about the different sites is given in Table 2. Available P was extracted using the method in general use in the four countries and, in addition, according to Olsen-P. After extraction, P was either analysed colorimetrically (col) at the research laboratories of the Swedish University of Agricultural Sciences or with Inductively Coupled Plasma (ICP) spectrometry at a commercial Swedish laboratory based on the practice in use in the relevant country (Table 3). P-AL is generally analysed colorimetrically in Lithuania (P-AL col) but by ICP spectrometry in Sweden (P-AL ICP). Soils from Latvia were also analysed for P-DL and soils from Lithuania for P-AL at laboratories in the respective country, in order to establish an intercalibration between these laboratories.

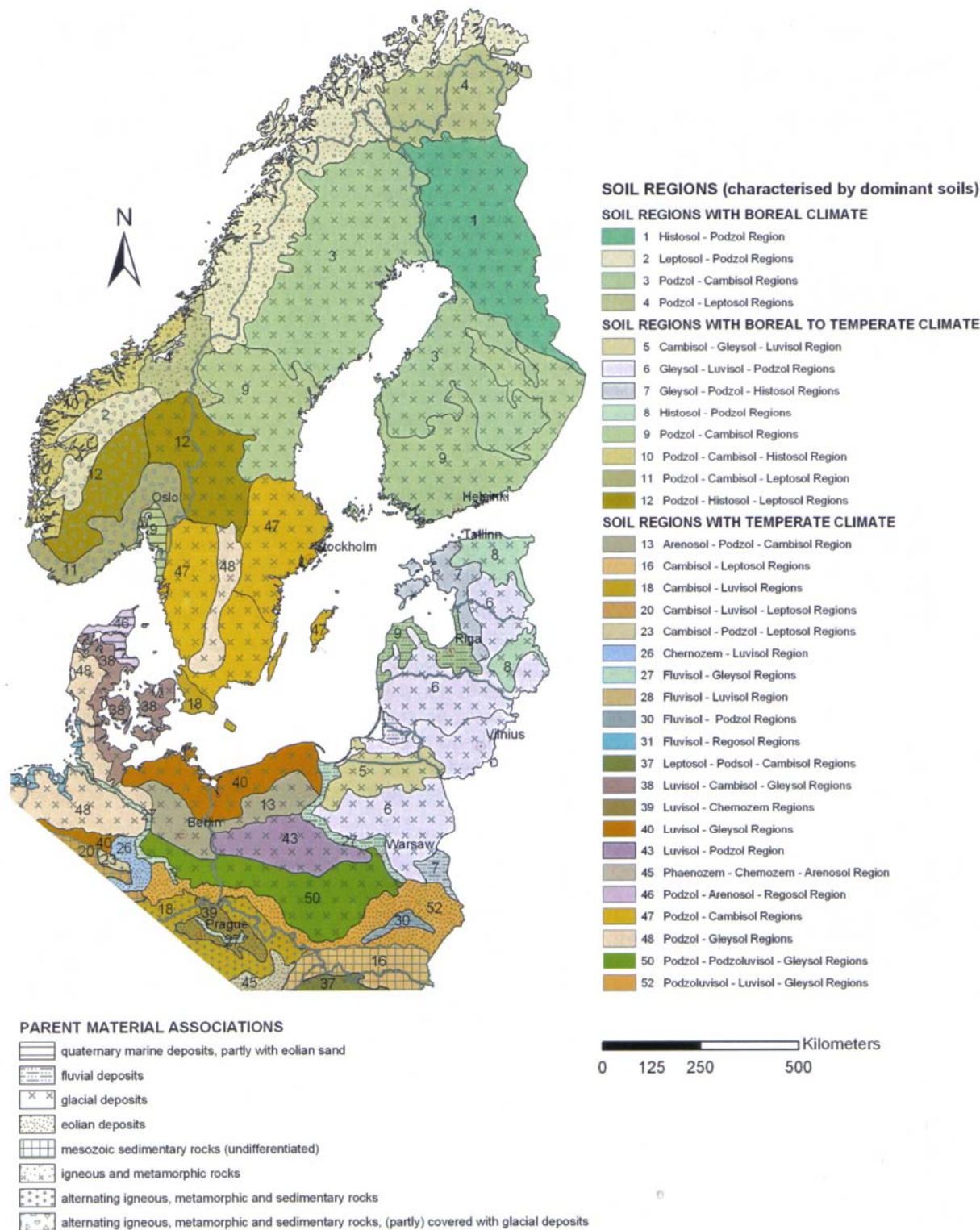


Figure 2. Map of soil regions and parent material in countries around the Baltic Sea, except from Russia and Belarus (Reimann et al., 2003). Used with permission (BZ.8 – schub/jb) from Bundesanstalt für Geowissenschaften und Rohstoffe, © 2003 BGR, Hannover.

Table 2. Country, site, number of samples (n), soil type, area, amount of arable land and distance to the Baltic Sea

Country	Site	n (ae.)	Soil type	Size (km ²)	Amount of arable land (%)	Distance to Baltic Sea (km)
Estonia	Tonga	11	Heavy clay ¹	9.7 ¹	85 ¹	0.2 ¹
	Ragina	1	Silty clay loam ¹	21.3 ¹	53 ¹	11 ¹
	Kuusiku	6	Clay loam ²			
	Tartu field trial	10	Fine sand loam ³			
Latvia	Vecauce	28	Sandy loam ⁴	0.6 ⁵	80 ⁵	
Lithuania	Graisupis	13	57% loam, 40% sandy loam ⁶	14.2 ⁶		170 ³
Sweden	E23/Östergötland	30	Clay ⁷	7.6 ⁷	53 ⁷	30 ⁸

¹) Iital *et al.*, 2003

²) Petersen *et al.*,

³) A. Toomsoo, *pers. com.* 2009

⁴) Knapp Haraldsen *et al.*, 1997

⁵) Jansons *et al.*, 2002

⁶) Sigitas Sileika *et al.*, 2005a

⁷) Kyllmar, 2006

⁸) B. Ulén, *pers. com.*, 2009

A number of soil parameters that could affect the amount of P extracted were measured (Table 4). The pH was measured in a 1:5 soil:water suspension. Calcium (Ca), Fe and Al content were analysed after AL extraction (Egnér *et al.*, 1960; Svensk Standard 1993, 1995). The Ca content was determined by Atomic Adsorption Spectrophotometry (AAS) and the Fe and Al content by ICP spectrometry. The C and N content was measured by a high temperature induction furnace combustion method using LECO CN2000 (LECO Cooperation, 2003). Clay content was determined according to Eriksson *et al.* (2005) and Phosphorus Sorption Index (PSI) according to Börling *et al.* (2001). Complete descriptions of the different methods are found in Appendix 1 and detailed general soil characteristics for individual soil samples in Appendix 2.

Table 3. Extraction agent, abbreviation, P analysis method and country in which it is used

Extraction agent		P analysis method	Country
Ammonium lactate ¹	P-AL	Colorimetric	Lithuania
Ammonium lactate ¹	P-AL	ICP	Sweden, Norway
Double lactate ²	P-DL	Colorimetric	Latvia, Poland e.g.
Mehlich 3 ³	P-M3	Colorimetric	Estonia since 2004
Olsen ⁴	Olsen-P	ICP	Denmark e.g.

¹) Egnér *et al.*, 1960

²) Riehm, 1943

³) Mehlich, 1984

⁴) Olsen *et al.*, 1954

Table 4. Average soil concentrations of nitrogen (N), carbon (C), calcium (Ca-AL), iron (Fe-AL) and aluminium (Al-AL) together with soil pH and phosphorus sorption index (PSI) at the seven different sites

Site	N (%)	C (%)	Ca-AL (mg kg ⁻¹)	Fe-AL (mg kg ⁻¹)	Al-AL (mg kg ⁻¹)	pH H ₂ O	PSI
Tonga	0.24	2.89	3862	480	952	6.8	6.3
Ragina	0.18	2.64	20664	138	356	7.8	3.0
Kuusiku	0.14	2.15	7180	228	396	7.7	3.1
Tartu field trial	0.10	1.15	1709	293	234	7.2	2.0
Vecauce	0.23	3.08	9784	178	421	7.4	2.7
Graisupis	0.21	3.01	9943	223	318	7.5	3.0
E23/Östrgötland	0.23	2.51	3492	765	426	6.7	4.6

P extraction methods

The ammonium lactate method (P-AL) according to Egnér *et al.* (1960) and Swedish standard SS 02 8310 (Svensk Standard, 1993, 1995) is used in Sweden and Lithuania. In the present study, 5 g air-dried soil were weighed and placed in a 200 mL shaker bottle together with 100 mL extract solution (0.01 M ammonium lactate (NH₄CH₃CH(OH)COO) and 0.40 M acetic acid (CH₃COOH)). The samples were shaken by end-over-end rotation and the extract was filtered (OOH-filter) and analysed colorimetrically for P. The same extraction method was used in a commercial laboratory and the extract was analysed for P by ICP spectrometry.

The double lactate (P-DL) method was performed according to Riehm (1943) and Thun & Herrmann (1953). Two grams of air-dried fine soil were placed in a 200 mL shaker bottle with 100 mL extract solution (0.02 M calcium lactate (Ca[CH₃CH(OH)COO]₂) and 0.02 M HCl). The samples were shaken by end-over-end rotation and the extract was filtered (OOH-filter) and analysed colorimetrically for P.

The Mehlich 3 method is commonly used in some parts of the U.S. and in 2004 it was adopted in Estonia. The procedure according to Mehlich (1984) and Sims (2000) was used in the present study. Two grams of air-dried soil were placed in Erlenmeyer flasks with 20 mL extract solution (0.2 M acetic acid (CH₃COOH), 0.25 M ammonium nitrate (NH₄NO₃), 0.015 M ammonium fluoride ([NH₄]F), 0.013 M HNO₃ and 0.001 M EDTA). Flasks were shaken on a shaking table and the extracts were then filtered (OOH-filter) and analysed colorimetrically for P.

The Olsen-P method was performed according to Olsen *et al.* (1954). One gram of air-dried soil and 20 mL extraction solution (0.5 M NaHCO₃) (pH 8.5) were mixed by shaking at 200 or more vibrations per min for 30 min. The suspension was filtered (OOH-filter) and analysed for P by ICP. Extraction and analysis were carried out at a commercial laboratory.

The main cation, its concentration and the pH in the different extracts varied as shown in Table 5.

Table 5. Extraction method, main cation in soil extract, soil:solution ratio, pH in extraction solution, vibrations/revolutions per min and duration of shaking

Extraction method	Main cat ion, concentration		Ratio soil:solution	pH	Vibrations/ revolutions per min	Shacking/turn duration
	(mol/L)	(g:mL)				
P-AL ⁽¹⁾	NH ₄ ⁺	0.01	1:20	3.75 ± 0.05	<35	90
P-DL ⁽²⁾	Ca ²⁺	0.02	1:50	3.60 ± 0.10		90
P-M3 ⁽³⁾	NH ₄ ⁺	0.035	1:10	2.45 ± 0.05	>200	5
Olsen-P ⁽⁴⁾	Na ⁺	0.5	1:20	8.50	>200	30

¹⁾ Egnér *et al.*, 1960; SIS, 1993; SIS, 1995

²⁾ Riehm, 1943; Thun & Herrmann, 1953

³⁾ Mehlich, 1984

⁴⁾ Olsen *et. al.*, 1954

P analysis methods

In the colorimetric method for analysis of the amount of P in the extract solution, 5 mL filtrate were transferred into a 50 mL calibrated flask together with 8 mL mixed reagent according to Murphy & Riley (1962) containing 1.25 M sulphuric acid (H₂SO₄), 0.03 M ammonium molybdate ((NH₄)₂MoO₄), 0.01 M ascorbic acid (C₆H₈O₆) and 0.0002 M potassium antimony tartrate (C₄H₄O₇SbK). The volume of solution in the flask was made up to 50 mL with deionised water. The reagent formed a molybdate blue complex together with orthophosphates, also called molybdate reactive P (MRP), giving an intense pure blue colour, which was analysed on a spectrophotometer (904 nm) after 1 h. The series with standard solutions was prepared with extraction solutions.

With ICP spectrometry, the solution is converted at a very high temperature into an aerosol, or plasma, where the atoms exist in an ionised state. Ions in this state emit light, which is converted into an electronic signal that can be measured quantitatively by a photomultimeter, which measures the intensity of light of a specific wavelength (Bradford & Cook, 1997).

Calculations

Degree of P saturation (DSP) has been used in environmental risk assessments of P leaching from agriculture fields in the Netherlands. DSP is calculated according to the following equation (Schoumans & Groenedijk, 2000), which originally also included an empirically determined coefficient (1/0.5):

$$DSP = 100 \cdot \frac{P_{ox}}{PSC}$$

where P_{ox} = oxalate-extractable P (mmol kg⁻¹) and PSC = total P sorption capacity. In the present study, the sum of Al and Fe (Al-AL and Fe-AL) in the AL extract (mmol kg⁻¹) was used as an indicator of the P sorption capacity.

To measure the sorption of P in soil (PSI), 1 g of air-dried soil was shaken with a 0.01 M CaCl₂ and 0.002 M KH₂PO₄ solution for 20 h (detailed description in Appendix 1). PSI was calculated according to the following equation (Bache & Williams, 1971; Börling *et al.*, 2001):

$$PSI = \frac{X}{\log C}$$

where X is the amount of P adsorbed by the soil (mol kg⁻¹ soil) and C is the concentration in the solution (mmol L⁻¹).

Statistics

Comparisons between the different extraction methods were made by one-way ANOVA and paired t-test. In comparing differences between extraction methods and between different laboratories, paired t-test and Wilcoxon's test were used. Results from extraction methods and analysis methods were compared pair-wise by regression analysis and by determination of the correlation coefficient (Pearson r). Step-wise regression was used to compare any impact from soil characteristics. All statistical analyses was made in MINITAB 15 and EXCEL, where the risk of rejecting a true hypothesis was set at 5% ($\alpha=0.05$).

Results

P analysis by colorimetry and ICP spectrometry

There was a statistically significant difference between the two methods of P analysis ($t_{0.975, 99}=12.00$; $p<0.001$) (Figure 3a). The P concentration based on ICP spectrometry was higher than the corresponding value based on colorimetry, almost without exception (98%). The average difference was found to be 19% higher for ICP. The difference was most clear at low P-AL levels (Figure 3b), where an almost exponential decrease was found for P-AL ICP compared with P-AL col.

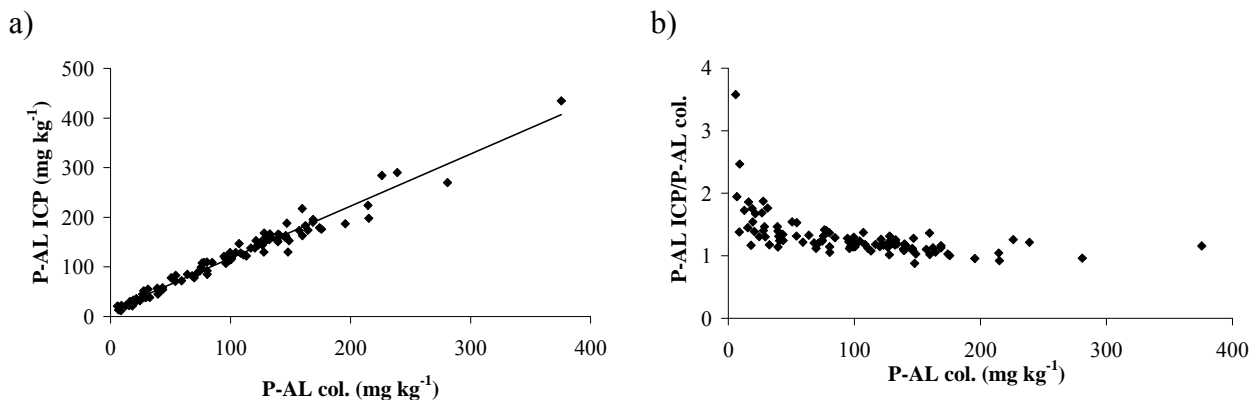


Figure 3. a) Concentration of P in AL extract based on ICP spectroscopy compared with colorimetric analysis. The regression equation is $P\text{-AL ICP} = 1.0494P\text{-AL col.} + 1.2657$ ($r^2 = 0.966$; $p < 0.001$). b) Ratio between the two different methods of analysis in relation to P in the soil test (measured colorimetrically).

Comparisons of the amount of P extracted with the P-DL method and analysed colorimetrically in Sweden and Latvia revealed a significantly higher ($t_{0.975, 28}=2.67$; $p=0.013$) amount of extracted P in the laboratory in Sweden, based on t-tests (Figure 4a). The Swedish laboratory obtained on average 10% higher values. A similar significant difference was also found between the laboratory in Sweden and that in Lithuania (average difference 6%) ($t_{0.95, 15}=1.47$) (Figure 4b), based on Wilcoxon tests. However, these general differences between the laboratories are within the general uncertainty for soil P method, which is set at 20% for the largest Swedish commercial laboratory (Gustavsson, pers. comm. 2009).

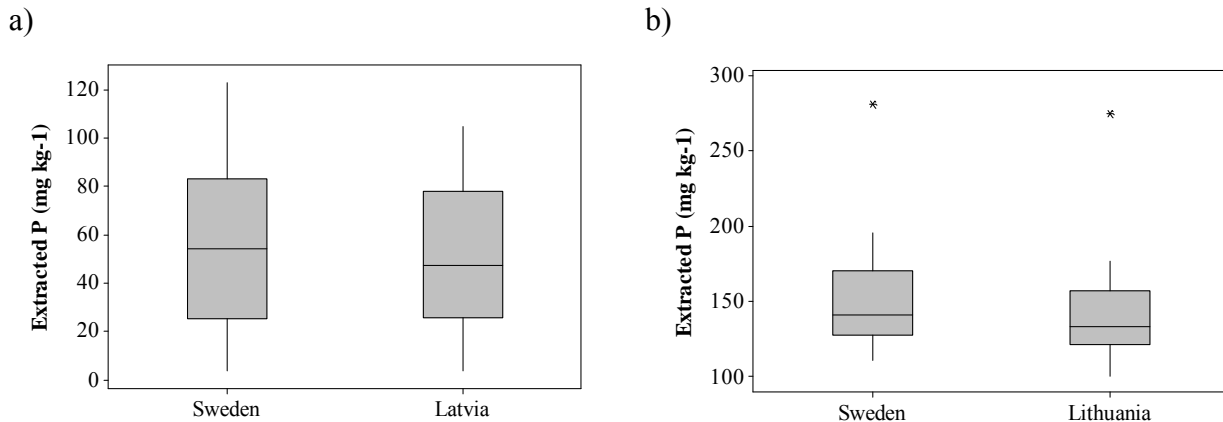


Figure 4. Plant-available P measured colorimetrically after extraction by a) the P-DL method in a research laboratory in Sweden and one in Latvia; b) the P-AL method in a research laboratory in Sweden and one in Lithuania.

Comparison of different extraction methods

Based on one-way ANOVA ($n=99$), there were small but statistically significant differences (ANOVA $F_{(0.95; 2, 198)}=8.93$; $p<0.001$) between the amounts of P extracted by the three extraction methods that involved colorimetric analysis (P-AL, P-M3 and P-DL). The amount of P extracted increased in the order $P-DL \leq P-M3 < P-AL$ (Figure 5a) and the paired t-test revealed significantly higher values for P-AL compared with P-DL ($t_{0.975, 98}=14.13$; $p<0.001$) and for P-AL compared with P-M3 ($t_{0.975, 98}=7.75$; $p<0.001$). A significantly lower amount of P was extracted by the Olsen-P method compared with P-AL ($t_{0.975, 98}=16.16$; $p<0.001$) (Figure 5b), P-M3 ($t_{0.975, 98}=9.52$; $p<0.001$) and P-DL ($t_{0.975, 98}=10.67$; $p<0.001$). In the comparison with P-AL, where the Olsen-P values were on average 24% of the P-AL values, all samples were analysed with ICP spectrometry. Thus the real differences between Olsen-P and the P-DL and P-M3 methods may be even larger, since the latter two were only analysed colorimetrically. Based on the comparisons of the two P analysis methods in the present study, colorimetry might have resulted in approx. 19% lower P-DL and P-M3 values. Consequently, the generally efficiency of P extraction between the methods appeared to increase in the following order: Olsen-P < P-DL \leq P-M3 < P-AL (Figure 5) (equation for the regression line, determination coefficient (r^2) and correlation (r) in Appendix 4).

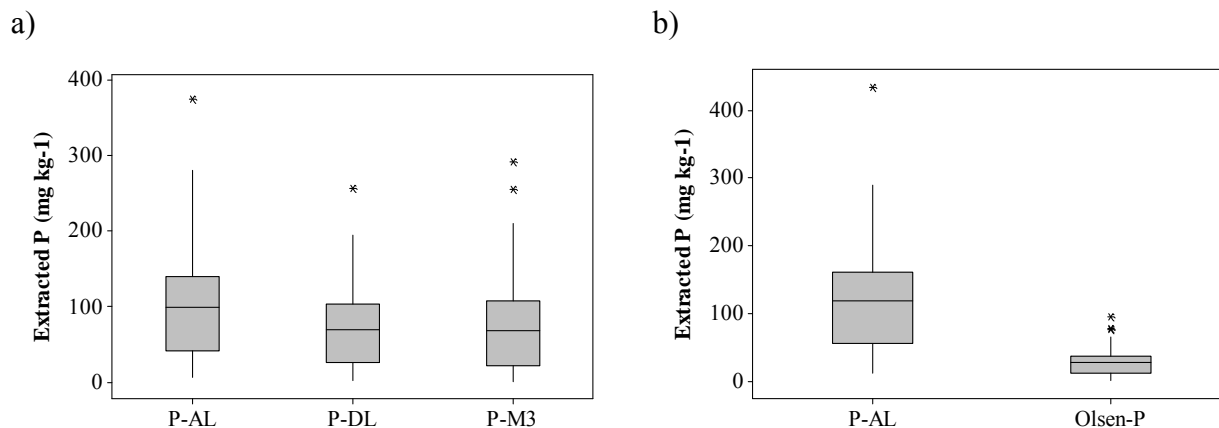


Figure 5. Amount of plant-available P extracted from soil (mg kg^{-1}) a) based on the P-AL, P-DL and P-M3 methods and analysed colorimetrically; and b) based on the P-AL- and Olsen-P methods and analysed by ICP spectrometry.

The relationships between the different extraction methods varied slightly from site to site (Figure 6a-d). In the Estonian long-term field trial Kuusiku, comparatively more P was extracted with the P-AL method than with the P-DL method, in contrast to the other sites. The same pattern for this site was observed between the P-AL and P-M3 methods, and between the P-AL and the Olsen-P methods. Opposite, the amounts of P extracted with the P-M3 compared with P-DL and P-AL methods were lower in the Estonian field trial area Tartu.

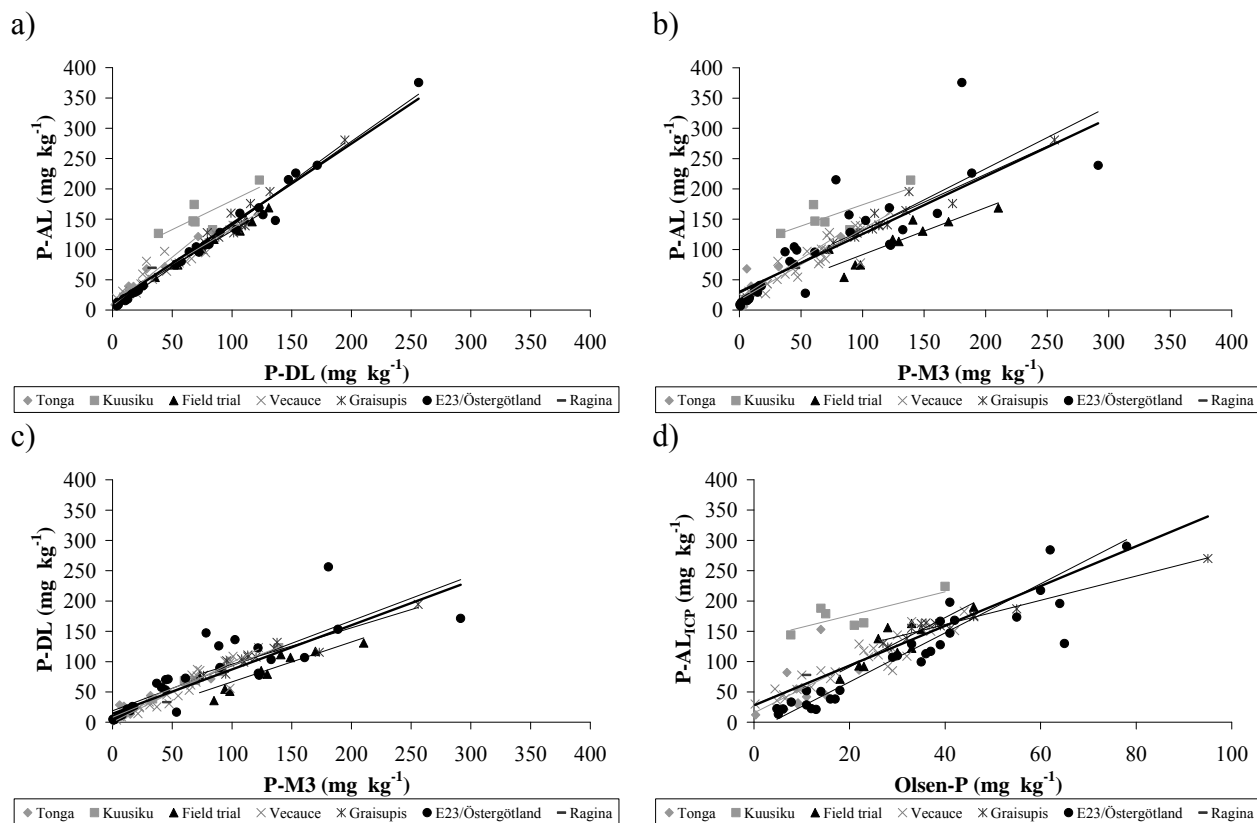


Figure 6. Linear regression between a) P-AL and P-DL; b) P-AL and P-M3; c) P-DL and P-M3; and d) P-AL and Olsen-P, where the thick line represents the overall regression and the thinner regression lines represent the different sites. Amounts of P are given in mg kg^{-1} .

Taking into consideration some general soil characteristics, even stronger relationships between the extraction methods were estimated. The concentration of Al-AL and Fe-AL in the AL extract generally had a high impact on the P concentration, but there were also correlations with pH and with the concentrations of soil C and Ca-AL (Appendix 7).

In the Estonian field trial Tartu, the Latvian catchment Vecauce and the Swedish catchment E23/Östergötland, the differences in amount of P extracted were more closely related to soil concentration of C than in the other areas. In contrast, in the Estonian catchment Tonga and field trial Kuusiku, the C concentration only seemed to have a minor effect of the amount of P extracted, while the soil cation concentration seemed to have more impact. For the Swedish clay-dominated catchment E23/Östergötland, more P was extracted by the P-M3 method than from the coarser soils from the Baltic sites, based on a very rough determination of the clay content (Figure 7).

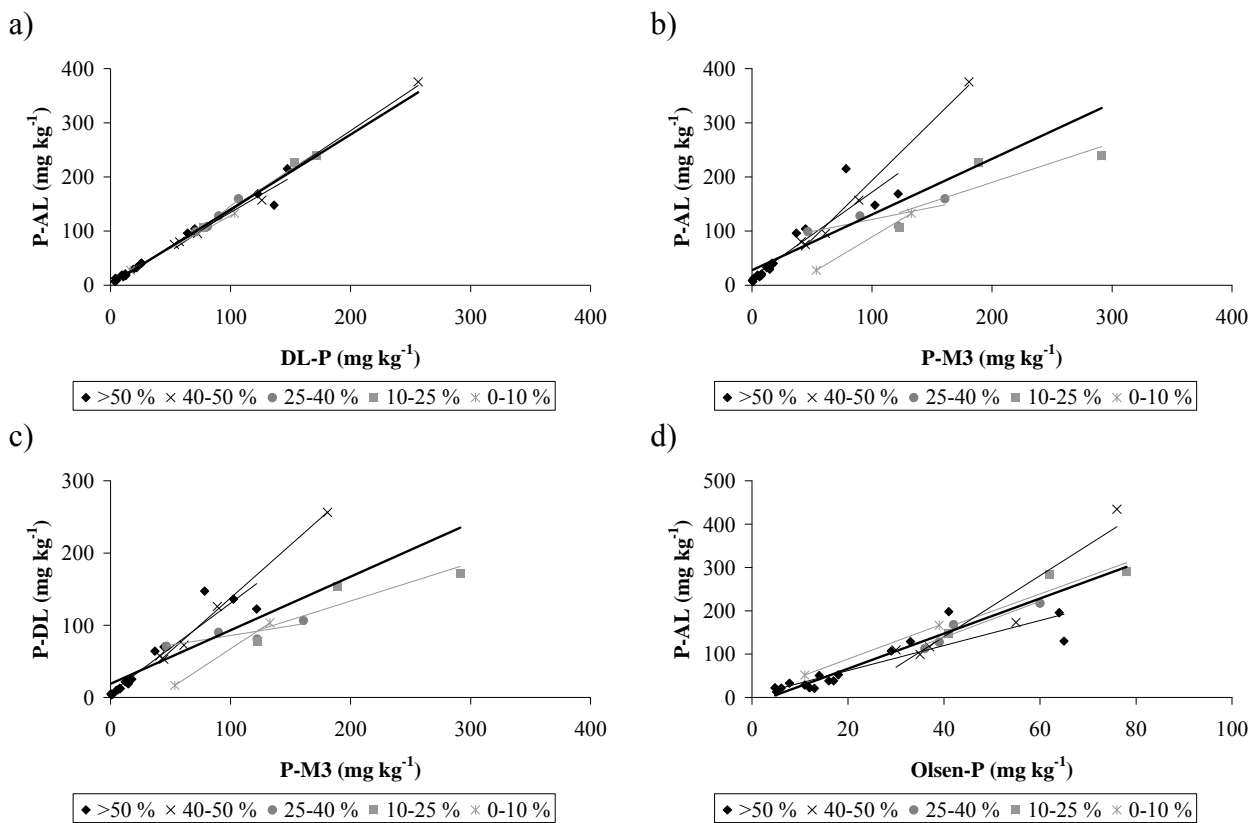


Figure 7. Linear regression between a) P-AL and P-DL; b) P-AL and P-M3; c) P-DL and P-M3; and d) P-AL and Olsen-P for soils with different clay contents, where the thin lines represent regression lines for different clay classes and the thick line represents the average for the group.

Soil P characterisation as environmental index

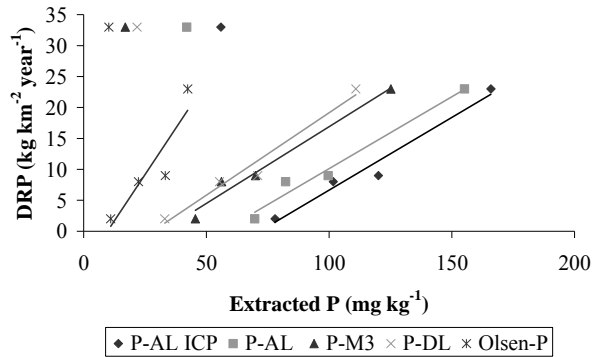


Figure 8. *DRP (kg km⁻²year⁻¹) compared against P extracted by the different methods (mg kg⁻¹).*

catchments having soils with a high capacity to sorb P either indicated by a high molar ratio of [P/(Al+Fe)] in the AL extract or a high value of PSI. Only when two calcareous catchments (Tonga and Ragina) were excluded soil extracted P, especially Olsen-P, seemed to be a reasonable predictor for DRP-concentration in stream water (Table 6).

There was a correlation between results from all extraction methods and P losses as DRP (kg km⁻² year⁻¹) from the sites (Figure 8) except for soils from the Estonian catchment Tonga. This catchment had high losses of DRP in relation to P extracted from the soil samples.

However, the DRP concentration in stream water from all catchments was poorly correlated to the P extracted from the soil, taking all catchments in account (Table 6).

DRP concentration was even higher from the

Table 6. *Site, average flow-weight concentration of dissolved reactive phosphorus (DRP) in stream water, number of samples (n), median value of soil content of P-AL ICP, P-DL, P-M3, Olsen-P P saturation in AL solution AL[P/(Al+Fe)] (DPS), PSI and the sum of Fe-AL+Al-Al in the studied catchments*

Site	DRP (mg L ⁻¹)	n	P-AL ICP	P-DL (mmol kg ⁻¹)	P-M3	Olsen- P ICP	DPS	PSI	AL[(Al+Fe)]
Tonga	0.180	11	1.45	0.43	0.31	0.34	4.1	6.60	43
Ragina	0.006	1	2.52	1.06	1.45	0.31	15.7	2.97	16
Vecaue	0.024	28	3.50	1.75	2.10	0.72	19.9	2.55	18
E23/Östergötland	0.058	30	3.59	1.47	2.17	1.07	11.5	2.82	14
Graisupis	0.100	15	5.26	3.47	3.66	1.36	36.6	4.56	41

The correlation between PSI and two or three soil parameters was usually found to be strong (Table 7). In clay soils, PSI seemed to be related to cation concentration and in coarser soil to C concentration of the soil samples.

Table 7. *Regression equation for PSI in terms of other soil characteristics. The units used in the regression are Al (mmol kg⁻¹); Ca (mmol kg⁻¹); Fe (mmol kg⁻¹); C (%)*

Site	Regression equation	Adj. determination coefficient (r ²)	Significance level (p)
Tonga	$PSI = 0.929 + 0.599Fe_{AL} + 0.00814Ca_{AL} + 0.0273Al$	0.921	<0.001
Kuusiku	$PSI = -1.28 + 0.731Fe_{AL} + 0.0938Al_{AL}$	0.922	0.010
Tartu field trial	$PSI = 0.01 + 0.370Fe_{AL}$	0.236	0.010
Vecaue	$PSI = 1.30 + 0.235C + 0.0433Al_{AL}$	0.828	<0.001
Graisupis	$PSI = 1.97 + 0.0879Al_{AL}$	0.613	0.002
E23/Östergötland	$PSI = 0.562 + 0.000701 Ca_{AL} + 0.00376 A_{AL} - Al_{AL}$	0.636	<0.001

Discussion

P analysis and local adaptation of soil P test

As in the present investigation, higher P concentrations in AL soil extracts (on average 19%) for ICP determination compared with colorimetric determination have been reported in the south of Sweden (Ulén, 2006). Even higher differences (on average + 36%) have been reported for P-M3 extracts of grassland soils in Québec, Canada (Ziadi *et al.*, 2009). These differences were concluded to be the result of high concentrations of organic material and of organic-bound P in the grassland soils in the Canadian study. The ability to include organically bound P during the very high temperature analysis with ICP could be a major explanation for the higher amount of P found using ICP spectrometry compared with the colorimetric method. In addition, precipitation of P and extracted cations may cause salt errors with colorimetric determination, which only measures orthophosphates (Murphy & Riley, 1962).

The present study revealed small differences in results between the Latvian and Swedish laboratory (10%) and between the Lithuanian and Swedish laboratory (7%) compared with the 8-51% (calculated from mean values) variations found in much more extended intercalibration between several European laboratories using the same methods (Neyroud & Lischer, 2003). The authors concluded that it is hard to make any comparison between the values obtained using the different methods because of these variations between laboratories.

Extraction methods

In soils Fe and Al are elements known to adsorb and fix P, the latter through *e.g.* binding to sesquioxides (White, 2006). In addition, organic matter, Ca-, Fe- and Al complexes and Fe and Al compounds in the amorphous state may take part in P sorption and binding processes (Brady & Weil, 2002). P will adsorb to different compounds depending on soil pH (White, 2006). In acid soils, reactions between P and Al- or Fe- oxides or hydroxides are most common and P may precipitate and bind as outer- or inner-sphere complexes on Al- or Fe- oxides. In alkaline soils, P binding to Ca is quite common.

The composition of active elements in the extraction solution is probably the main reason for the large variations observed in amount of P extracted with the different methods. Different ratios of soil:solution and different rates of shaking are other factors. The components in P-AL and P-DL extracts have a good capacity to chelate cations and to desorb P from Al- and Fe- oxides (Vanderdeelen, 1994). In the P-M3 method additional agents, including EDTA, are used to adapt the extraction for a range of elements such as copper (Cu), while NH_3F is included for extracting adsorbed P (Mehlich, 1984). According to Mehlich (1978), NH_3F is not efficient in extracting P from Ca-phosphates, but very efficient in extracting P from Al- and Fe- oxides, which could result in an underestimation of available P in Ca-oxides and an overestimation of available P in Al- and Fe- oxides. Olsen-P extraction uses the relationship between solubility of Ca-phosphates, pH and Ca activity to form CaCO_3 and thereby release P from Ca-oxides (Olsen *et al.*, 1954).

The P-AL method seems more efficient at extracting P than the P-DL method. According to Murphy & Riley (1962), the colorimetric method of analysis measures only free orthophosphates, and therefore P precipitated to Ca-ions, which is a major component in DL extraction solution,

will not be analysed. The P-DL:P-AL ratio and Ca were poorly correlated (Figure 9), but based on measurements in the AL-extract, higher Ca-AL concentrations were indicated to result in a lower ratio of extracted P with the P-DL method than lower Ca-AL concentrations. This might be a result of more precipitation with Ca with higher concentrations of Ca in the DL solution.

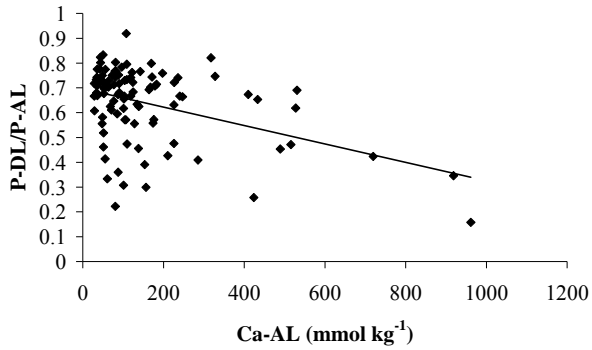


Figure 9. Relationship between P-DL/P-AL and Ca-AL
All values given in mmol kg^{-1} ($r=0.424$)

The cation NH_4^+ was present in two of the extraction solutions (Table 5). According to Barrow & Shaw (1979), NH_4^+ ions result in higher desorption of P in solution than Ca ions, which was probably the main reason for the higher amount of P extracted in the P-AL method compared with P-DL. The Mehlich extraction solution contains a higher concentration of NH_4^+ but a very short period of shaking may reduce the amount of P extracted, compared with the P-AL method.

Different extraction methods have different components aimed at lowering the pH, which could also have an effect on the amount of P extracted. Both P-AL and P-M3 use acetic acid as a pH lowering substance, which might affect the amount of P extracted due to its mild chelating properties.

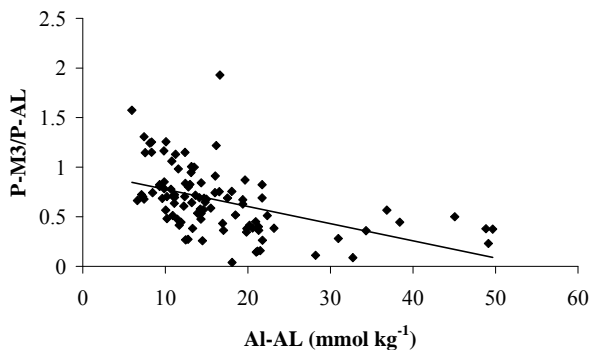


Figure 10. Relationship between P-M3/P-AL and Al-AL
All values given in mmol kg^{-1} ($r=0.479$)

Mehlich (1987) found P-M3 to be efficient in extracting P from Al compounds but in the present investigation only a moderate correlation was found between the P-M3:P-AL ratio and Al-AL concentration (Figure 10). This showed that P-AL was more efficient in extracting P from soils with a higher Al-AL content than those with a lower content. The ratio between P-M3 and P-AL was also relatively higher for sites with coarser texture, in contrast to the P-DL:P-M3 ratio. Coarser soil is probably more dependent on organic matter to adsorb P than soils of finer texture,

which might explain the different results obtained with P-M3. Since coarser soils from Latvia and Lithuania generally had a higher C content than the finer soils in the present investigation (Table 4), this explains the generally high efficiency of extraction obtained by the P-M3 method for these sites.

For the Estonian field trial Tartu, step-wise regression revealed no strong relationships between P-AL on the one hand, and the P-DL and P-M3 methods on the other, based on the Fe-AL content. This was in contrast to the findings for most of the other sites (Appendix 7). It was also observed that increasing C content of the soil strengthened the correlations between the P-DL and P-M3 methods and, to a lesser degree, between the P-AL and P-M3 methods. The soils of this field experiment had a high ratio of P-M3 to Fe-AL (0.78) compared with the other sites (0.33)

based on values in mmol kg^{-1} . This might indicate that the P-M3 method is quite efficient in extracting P from Fe-phosphates at the actual site.

In the present investigation, the soils with high C content (Tonga, Vecauce, Graisupis and E23/Östergötland) generally had higher Olsen-P values than Estonian field trials. This might be an effect of the higher pH in the Olsen extraction, which probably resulted in a higher amount of P being extracted P from organic material, in agreement with Otabbong *et al.* (2004).

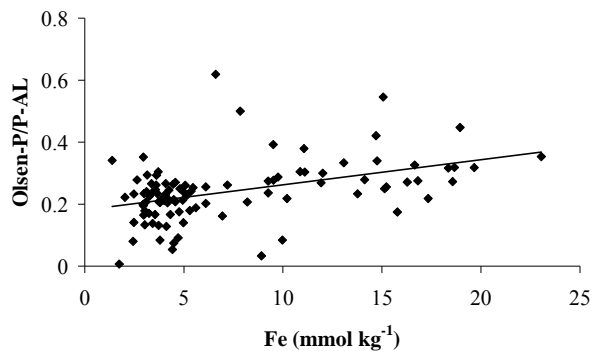


Figure 11. Relationship between Olsen-P/P-AL and Fe-AL ($r=0.435$)

Olsen-P mainly extracts the water-extractable P and some P found in Ca-phosphates (Olsen *et al.*, 1954), which explains the very low outcome from this method in the present study. Observed differences between P-AL and Olsen-P were explained by soil pH, Ca-AL, Fe-AL and Al-AL content in the present study. However the efficiency of Olsen-P increased only very weakly with *e.g.* Fe-AL concentration (Figure 11). In some studies, Olsen-P has been suggested as a more reliable indicator of plant-available P in calcareous soils compared with the P-M3 method (Mallarino, 1995; Zbiral & Němec, 2002).

Environmental P index

In order to compare the present results with results reported in the literature, the ‘critical values’ for leaching and P-M3 extraction in the present study were increased by 19% to produce a probable level based on the ICP analysis. The suggested critical value for Olsen-P of 60 mg kg^{-1} (Hesketh & Brookes, 2000) was exceeded by three soil samples in the present study, two of which were found in the Swedish catchment. In addition, three soil samples exceeded the critical value for P-M3 of 240 mg kg^{-1} (Sims *et al.*, 2002), two of which were the soil samples that also exceeded the Olsen-P critical value.

Extractable Al-AL and Fe-AL from acid soils of coarser texture have been assumed to correspond to PSC in such soils (Schoumans & Groenedijk, 2000; Sims *et al.*, 2002). Ulén (2006) calculated the P-AL:PSI ratio and found that a high ratio indicated a high risk of leaching of DRP. It was also found that that AL $[P/(Al+Fe)]$ was correlated with DRP in drainage water from clay topsoils and sandy subsoils. However, the present study revealed an effect of other soil characteristics, such as Ca and organic material (C content), on sorption of P measured as PSI (Table 7). This shows that it is not only Al and Fe that affect P sorption, but also Ca and organic matter content. Due to the large variation in pH and Ca in the soils around the Baltic Sea, any simplified environmental P index has to be used with care.

Finer soils often contain more cations, including Fe and Al, than coarser soils. However in stream water in the catchment Tonga, with soils which had a high PSI but quite low soil P results,

relatively high concentrations of DRP were monitored. Rapid water flow in macropores and a high connectivity to the stream might be an explanation. In contrast, in the catchment Vecauce, soils with high soil test P were frequently found, but low DRP concentration in stream water. This again shows the importance of water transport and the connectivity between the fields and the stream for the overall P losses.

Just a few areas were used in this study and more samples and sites would be needed to draw reliable conclusions. However, the study showed that the large variations in soils around the Baltic Sea raise questions about the use of simplifying models applied successfully in *e.g.* the Netherlands and U.S. in the Baltic area. In order to estimate the risk of high DRP leaching around the Baltic Sea, a common soil-P test is needed. Although it is possible to compare the results of different extraction methods against each other, significant differences were observed between some fields as a result of other soil characteristics.

High DRP leaching was measured just from some catchments with a high environmental index. One should keep in mind that the extraction methods discussed here were originally developed for measuring plant-available P for crop production purposes and not for environmental assessment. It would be very valuable to have a common soil test developed specifically for environmental assessment purposes around the Baltic Sea but that could also be used for plant production purposes.

Conclusions

Significant differences were found between the different P extraction methods studied. At the present time, the results obtained by these different methods are often compared without considering these differences. The problem can be solved by intercalibration between the methods using a process that also considers the other soil characteristics affecting P desorption, or by the development of a common method to extract P, which could be used in both environmental and soil fertility assessments. The results also showed that it is important to use a single method of P analysis, since some methods measure only orthophosphates while others also include other P forms. In order to compare data and ultimately deal with the problem of diffuse P losses from agricultural land to the Baltic Sea, there is an urgent need for a unified environmental monitoring procedure that considers all the factors affecting P sorption in the heterogeneous soils around the Baltic Sea and the water flow in macropores.

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Appendix 1

Methods for measuring soil characteristics

pH

The soil acidity (pH-value) determined by mixing 5 mL air-dried soil with 25 mL water and shaking for 5 min., standing for 16 h, brief shaking again and leaving to settle so that the particles could sediment out. The pH was then determined using a pH-meter in the water phase.

Calcium

Calcium was determined in the ammonium lactate extract (for extraction method see 'AL-method'). The filtrate was diluted 1:10 in the extraction solution before being diluted five times with 1.25% lanthanum solution. The mixture was analysed by AAS (atomic absorption spectrophotometry; 422.7 nm). For samples with calcium content higher than 5 ppm, the 1:10 filtrate was diluted again in the extraction solution to reach a concentration in the range of the standards.

Carbon and nitrogen

The amount of carbon and nitrogen was measured by heating 980-990 mg dry soil to 1050°C for 5 min and using a LECO CN2000 analyser to measure the percentage of carbon and nitrogen in the vapour (LECO Cooperation, 2003).

Iron and aluminium

Iron and aluminum content was determined in the AL-solution whith ICP analyze in a commercial another laboratory.

Phosphorus sorption index

The soil P sorption capacity was determined based on Bache & Williams (1971) and Börling *et al.* (2001). One gram of air-dried soil was weighed into a 50 mL centrifuge tube containing 1 drop of toluene and 10 mL of 0.01 M CaCl₂ and 0.002 M KH₂PO₄ solution. The samples were shaken backwards and forwards for 20 h, then centrifuged for 10 min at 3 000 rpm and filtered (OOH-filter). The P concentration in the solution was analysed using the colorimetric method given above. Phosphorus sorption index was calculated using the equation:

$$PSI = \frac{X}{\log C}$$

where X is the amount of phosphorus adsorbed by the soil (mol kg⁻¹ soil) and C is the concentration in the solution (mmol L⁻¹).

Clay content

The clay content was determined by a field method where a 1-2 cm² piece of wet soil that had been stored in a refrigerator was rewetted and rolled to a thin sting until it broke. The clay content was defined by the thickness of the string according to Eriksson *et al.* (2005). The clay content was also defined by rolling the soil into a 7 mm string, bending it and assessing the clay content.

Appendix 2

Soil concentrations of nitrogen (N), carbon (C), calcium (Ca), iron (Fe) and aluminium (Al) together with soil pH and phosphorus sorption index (PSI) in the different soil samples

Soil sample	N (%)	C (%)	Ca-AL (mg kg ⁻¹)	Fe-AL (mg kg ⁻¹)	Al-AL (mg kg ⁻¹)	pH H ₂ O	PSI
Tonga							
1	0.285	3.099	2017	671	1216	6.03	8.89
2	0.160	1.717	3225	498	761	6.79	7.33
3	0.216	2.770	2435	388	625	6.50	4.77
4	0.186	2.156	2049	266	926	6.27	4.24
5	0.317	3.517	2726	620	1340	6.24	8.31
6	0.199	2.392	2839	341	1036	7.02	5.26
7	0.251	3.349	3416	263	200	7.21	2.93
8	0.225	2.562	2219	402	1318	6.17	6.13
9	0.209	2.369	3507	545	835	6.97	6.68
10	0.275	3.524	9618	730	1326	7.57	7.67
11	0.316	4.287	8435	557	883	7.50	6.60
Kuusiku							
1	0.094	1.658	6148	212	535	7.71	3.40
2	0.199	2.883	9041	278	404	7.74	3.67
3	0.071	1.295	7053	169	400	7.76	2.19
4	0.205	3.107	6271	247	336	7.46	3.18
5	0.143	2.137	5523	251	315	7.66	3.09
6	0.108	1.825	9044	208	386	7.78	2.95
Ragina							
1	0.179	2.643	20664	138	356	7.75	2.97
Tartu Field trial							
1	0.091	1.072	1368	281	200	7.01	1.86
2	0.116	1.359	1426	300	219	6.93	1.49
3	0.102	1.220	1761	341	265	7.32	2.18
4	0.091	0.971	1337	268	225	7.10	1.87
5	0.091	1.160	2000	313	291	7.42	2.45
6	0.094	1.072	1387	255	225	7.08	1.60
7	0.099	1.154	1386	283	192	7.15	1.87
8	0.091	1.007	1132	305	160	7.02	2.01
9	0.105	1.271	3545	288	354	7.53	2.17
10	0.110	1.254	1747	296	204	7.31	2.02

Soil sample	N (%)	C (%)	Ca (mg kg ⁻¹)	Fe (mg kg ⁻¹)	Al (mg kg ⁻¹)	pH H ₂ O	PSI
Vecauce							
1	0.181	2.668	9456	147	295	7.69	2.48
2	0.119	1.524	4888	207	350	7.62	2.25
3	0.270	3.435	9077	164	523	7.47	2.77
4	0.166	2.430	9894	199	394	7.64	2.55
5	0.187	2.419	6965	172	603	7.59	3.05
6	0.114	1.189	1145	202	272	6.44	1.45
7	0.252	2.942	12730	192	300	7.57	3.19
8	0.247	4.506	28833	113	523	7.70	3.22
9	0.170	1.816	2139	166	196	7.17	1.88
10	0.324	4.565	16980	136	391	7.55	3.23
11	0.186	2.121	3194	182	432	7.34	2.24
12	0.190	3.098	19612	167	994	7.75	4.12
13	0.144	1.959	7164	209	384	7.57	2.72
14	0.127	1.891	11435	169	344	7.70	2.83
15	0.139	1.443	1960	241	387	7.18	2.61
16	0.112	1.453	6569	165	178	7.59	1.61
17	0.196	2.116	1916	233	530	6.52	2.28
18	0.199	2.359	2104	223	387	6.35	2.21
19	0.138	1.622	2058	191	288	7.30	2.17
20	0.113	1.475	7320	198	375	7.66	2.91
21	0.200	2.513	3069	230	330	7.21	2.93
22	0.112	1.379	1678	188	586	6.92	2.08
23	0.046	2.916	38535	97	580	8.09	2.39
24	0.197	2.488	3198	212	368	7.34	2.54
25	0.226	3.139	13137	138	381	7.59	2.36
26	1.460	19.850	36818	77	359	7.58	6.52
27	0.388	4.880	4163	181	586	7.27	3.08
28	0.160	2.129	7915	174	446	7.55	2.07

Soil sample	N (%)	C (%)	Ca-AL (mg kg ⁻¹)	Fe-AL (mg kg ⁻¹)	Al-AL (mg kg ⁻¹)	pH H ₂ O	PSI
Graisupis							
1	0.200	2.603	6870	249	251	7.59	3.02
2	0.179	2.215	4040	255	228	7.41	2.69
3	0.278	4.229	16423	176	333	7.67	3.17
4	0.164	3.315	21134	205	396	7.88	3.25
5	0.160	2.940	17370	201	312	7.83	2.96
6	0.155	2.136	6805	228	254	7.64	2.64
7	0.192	2.578	5699	232	345	7.41	3.08
8	0.219	2.717	3867	237	251	7.29	2.67
9	0.266	3.179	4757	227	266	7.16	2.73
10	0.246	3.222	6725	227	260	7.42	3.34
11	0.196	2.430	3298	251	266	7.27	2.45
12	0.324	5.115	21269	165	433	7.58	3.37
13	0.198	2.467	4356	276	487	7.57	3.56

Soil sample	N (%)	C (%)	Ca-AL (mg kg ⁻¹)	Fe-AL (mg kg ⁻¹)	Al-AL (mg kg ⁻¹)	pH H ₂ O	PSI
E23/Östergötland							
1	0.294	3.415	4962	369	321	7.12	7.95
2	0.241	2.668	4168	618	536	6.96	6.28
3	0.347	3.617	5124	570	488	6.46	6.27
4	0.274	2.905	4085	821	499	6.64	6.42
5	0.217	2.252	3495	850	457	6.91	4.70
6	0.280	2.811	4754	909	555	6.88	6.06
7	0.327	3.467	4995	458	575	6.51	5.33
8	0.269	2.825	4045	532	571	6.68	5.72
9	0.273	2.875	4267	531	567	6.75	6.11
10	0.296	3.105	4368	841	574	6.52	6.42
11	0.276	2.776	5377	517	545	7.01	5.38
12	0.291	3.066	5559	824	565	6.78	5.20
13	0.236	2.470	3077	1037	294	6.60	3.80
14	0.163	1.755	2556	930	300	6.71	2.98
15	0.182	1.997	2542	845	275	6.83	2.95
16	0.256	2.810	3627	881	275	6.75	2.75
17	0.286	2.801	4305	438	473	7.01	4.06
18	0.267	2.648	4391	517	587	7.06	5.58
19	0.230	2.386	4122	1058	460	6.98	6.13
20	0.162	1.869	1940	607	303	6.65	2.94
21	0.186	2.205	2230	769	364	6.78	3.33
22	0.238	2.701	2171	666	436	6.43	3.27
23	0.237	2.562	3600	1042	309	6.84	4.42
24	0.202	2.077	3249	1098	271	7.17	3.38
25	0.180	1.930	2897	1025	299	6.81	3.37
26	0.176	1.929	1721	789	334	6.37	3.25
27	0.149	1.687	1442	939	355	5.94	3.10
28	0.203	2.268	2444	1287	418	6.37	5.07
29	0.095	1.264	1150	224	448	6.73	3.08
30	0.203	2.277	2097	968	335	6.47	3.15

Appendix 3

Soil concentrations of phosphorus determined by different extraction and analysis methods $P\text{-AL}_{col}$, $P\text{-DL}_{col}$, $P\text{-M3}_{col}$, $P\text{-AL}_{ICP}$, $Olsen\text{-P}_{ICP}$ in the different soil samples given in mg kg^{-1}

Soil sample	$P\text{-AL}_{colorom.}$ (mg kg^{-1})	$P\text{-DL}_{colorom.}$ (mg kg^{-1})	$P\text{-M3}_{colorom.}$ (mg kg^{-1})	$P\text{-AL}_{ICP}$ (mg kg^{-1})	$Olsen\text{-P}_{ICP}$ (mg kg^{-1})
Tonga					
1	6	5	3	21	6.3
2	9	2	1	12	0.4
3	39	13	15	55	8.9
4	39	18	14	57	10
5	16	10	6	30	9.1
6	72	44	32	86	22
7	121	72	82	153	14
8	29	12	11	42	11
9	25	9	7	32	9.2
10	39	26	9	45	15
11	68	29	6	82	6.9
Kuusiku					
1	174	68	60	179	15
2	133	84	90	164	23
3	215	123	139	224	40
4	127	38	34	144	7.7
5	147	67	61	188	14
6	145	69	69	160	21
Ragina					
1	70	33	45	78	11
Tartu field trial					
1	75	51	98	93	22
2	169	131	210	190	46
3	146	117	170	163	33
4	75	55	94	92	23
5	117	85	124	138	26
6	113	80	130	122	33
7	101	75	73	115	30
8	54	36	85	71	18
9	149	112	141	153	35
10	130	107	149	156	28

Soil sample	P-AL _{colorom.} (mg kg ⁻¹)	P-DL _{colorom.} (mg kg ⁻¹)	P-M3 _{colorom.} (mg kg ⁻¹)	P-AL _{ICP} (mg kg ⁻¹)	Olsen-P _{ICP} (mg kg ⁻¹)
Vecauce					
1	139	103	98	151	42
2	80	61	66	92	28
3	140	101	94	166	33
4	128	85	73	150	37
5	43	24	22	58	12
6	78	56	98	109	32
7	95	78	66	121	29
8	59	25	37	72	16
9	64	45	45	85	14
10	31	8	8	55	4.4
11	132	98	98	155	35
12	97	44	55	111	26
13	123	87	71	144	30
14	22	9	6	36	4.8
15	43	25	23	54	9
16	101	70	67	118	23
17	54	30	47	83	17
18	76	53	64	108	24
19	27	14	21	45	6.2
20	28	20	15	39	6.5
21	51	33	31	78	10
22	85	66	70	109	29
23	19	3	3	30	0.2
24	99	76	71	122	25
25	146	109	101	159	37
26	81	28	31	85	29
27	100	73	69	129	22
28	162	123	122	183	44

Soil sample	P-AL _{colorom.} (mg kg ⁻¹)	P-DL _{colorom.} (mg kg ⁻¹)	P-M3 _{colorom.} (mg kg ⁻¹)	P-AL _{ICP} (mg kg ⁻¹)	Olsen-P _{ICP} (mg kg ⁻¹)
Graisupis					
1	164	122	135	174	46
2	128	79	95	130	27
3	196	132	138	187	55
4	160	99	110	163	38
5	176	115	173	176	46
6	139	111	113	154	41
7	141	108	113	164	36
8	134	105	108	159	39
9	120	89	94	138	32
10	111	78	76	124	28
11	141	108	120	163	35
12	281	194	256	270	95
13	127	101	96	155	33

Soil sample	P-AL _{colorom.} (mg kg ⁻¹)	P-DL _{colorom.} (mg kg ⁻¹)	P-M3 _{colorom.} (mg kg ⁻¹)	P-AL _{ICP} (mg kg ⁻¹)	Olsen-P _{ICP} (mg kg ⁻¹)
E23/Östergötland					
1	18	13	8	21	13
2	21	12	8	29	11
3	9	5	0.4	22	4.8
4	29	19	15	38	16
5	104	70	45	129	33
6	96	64	37	107	29
7	215	147	78	198	41
8	13	4	2	22	6.1
9	7	4	1	13	5.1
10	15	11	6	22	12
11	41	26	17	51	14
12	40	25	18	53	18
13	80	57	41	110	30
14	169	123	122	196	64
15	128	90	90	168	42
16	376	256	181	435	76
17	148	136	102	130	65
18	19	9	5	33	7.8
19	33	22	12	38	17
20	108	81	122	128	39
21	133	103	133	167	39
22	239	171	291	290	78
23	99	71	47	113	36
24	157	126	89	173	55
25	96	72	61	117	37
26	107	78	123	147	41
27	160	107	161	218	60
28	75	53	44	99	35
29	28	17	54	52	11
30	226	153	189	284	62

Appendix 4

Analysis method, equation for regression line between the methods, determination coefficient, correlation and significance level. Extracted amount of phosphorus given in mg kg⁻¹

Methods	Analyze method	Equation for regression line	Determination coefficient (r ²)	Correlation (r)	Significance level (p)
P-AL and P-DL	Colorimetric	$P-AL=1.3183P-DL+11.029$	0.923	0.966	p<0.001
P-AL and P-M3	Colorimetric	$P-AL=0.9545P-M3+30.136$	0.726	0.852	p<0.001
P-DL and P-M3	Colorimetric	$P-DL=0.7295P-M3+14.069$	0.790	0.889	p<0.001
P-AL and Olsen-P	ICP	$P-AL=3.2788Olsen-P+27.855$	0.713	0.846	p<0.001

Regression equations between P-AL and P-DL for different sites. All factors given in mg kg⁻¹

Site	Equation for regression line	Determination coefficient (r ²)	Correlation (r)	Significance level (p)
Tonga	$P-AL=1.5995P-DL+7.241$	0.945	0.972	<0.001
Kuusiku	$P-AL=0.9577P-DL+84.85$	0.659	0.812	<0.001
Tartu field trial	$P-AL=1.1697P-DL+13.647$	0.985	0.993	<0.001
Vecauce	$P-AL=1.1715P-DL+17.426$	0.939	0.969	<0.001
Graisupis	$P-AL=1.4443P-DL+4.99$	0.916	0.957	<0.001
E23/Östergötland	$P-AL=1.3844P-DL+1.467$	0.985	0.992	<0.001

Regression equations between P-AL and P-M3 for different sites. All factors is given in mg kg⁻¹.

Site	Equation for regression line	Determination coefficient (r ²)	Correlation (r)	Significance level (p)
Tonga	$P-AL=1.2869P-M3+20.245$	0.781	0.884	<0.001
Kuusiku	$P-AL=0.7007P-M3+103.74$	0.593	0.770	0.073
Tartu field trial	$P-AL=0.7743P-M3+14.099$	0.779	0.883	<0.001
Vecauce	$P-AL=1.1686P-M3+16.653$	0.855	0.925	<0.001
Graisupis	$P-AL=0.9223P-M3+39.736$	0.917	0.958	<0.001
E23/Östergötland	$P-AL=1.0291P-M3+27.57$	0.712	0.844	<0.001

Regression equations between P-DL and P-M3 for different sites. All factors is given in mg kg⁻¹.

Site	Equation for regression line	Determination coefficient (r ²)	Correlation (r)	Significance level (p)
Tonga	$P-DL=0.8138P-M3+7.972$	0.846	0.920	<0.001
Kuusiku	$P-DL=0.7651P-M3+17.193$	0.984	0.992	<0.001
Tartu field trial	$P-DL=0.6583P-M3+0.856$	0.782	0.884	<0.001
Vecauce	$P-DL=0.9893P-M3+0.192$	0.896	0.946	<0.001
Graisupis	$P-DL=0.601P-M3+35.669$	0.887	0.942	<0.001
E23/Östergötland	$P-DL=0.7424P-M3+18.923$	0.721	0.849	<0.001

Regression equations between P-DL and P-M3 for different sites. All factors is given in mg kg⁻¹.

Site	Equation for regression line	Determination coefficient (r ²)	Correlation (r)	Significance level (p)
Tonga	$P-AL = 3.9306Olsen-P + 15.621$	0.299	0.547	0.082
Kuusiku	$P-AL = 1.9515Olsen-P + 137.24$	0.611	0.782	0.066
Tartu field trial	$P-AL = 4.0737Olsen-P + 9.5325$	0.758	0.870	0.001
Vecauce	$P-AL = 3.2729Olsen-P + 28.607$	0.865	0.930	<0.001
Graisupis	$P-AL = 2.0001Olsen-P + 81.151$	0.954	0.997	<0.001
E23/Östergötland	$P-AL = 4.0491Olsen-P - 14.604$	0.831	0.912	<0.001

Ratio between different extraction methods for sites in the present study, ranked in order of increasingly coarse soil texture

Soil type	Site	P-M3/P-AL col.	P-DL/P-M3 col.	P-DL/P-AL col.	Olsen-P/P-AL ICP
Heavy clay	Tonga	0.25	1.39	0.34	0.21
Clay	E23/Östergötland	0.70	0.68	0.47	0.31
Clay loam	Kuusiku	0.45	0.95	0.47	0.10
Loamy sand	Graisupis	0.81	0.95	0.76	0.24
Sandy loam	Vecauce	0.80	0.83	0.67	0.23
Fine sandy loam	Tartu	1.11	0.65	0.71	0.22

Appendix 5

Plant-available P content in soil from the Latvian site Vecauce extracted with P-DL and analysed by a Swedish laboratory and a Latvian Laboratory.

Soil sample	P-DL (mg kg⁻¹)	
Vecauce	Swedish laboratory	Latvian laboratory
1	103	103
2	61	55
3	101	53
4	85	94
5	24	25
6	56	48
7	78	80
8	25	26
9	45	35
10	8	10
11	98	91
12	44	46
13	87	80
14	9	10
15	25	18
16	70	55
17	30	28
18	53	43
19	14	15
20	20	16
21	33	33
22	66	53
23	3	3
24	76	60
25	109	100
26	28	38
27	73	72
28	123	105

Appendix 6

Plant-available P content in soil from the Lithuanian site Graisupis extracted with P-AL and analysed by a Swedish laboratory and a Lithuanian laboratory

Soil sample	P-AL (mg kg⁻¹)	
Graisupis	Swedish laboratory	Lithuanian laboratory
1	164	133
2	128	100
3	196	177
4	160	148
5	176	166
6	139	131
7	141	133
8	134	124
9	120	118
10	111	113
11	141	140
12	281	275
13	127	124

Appendix 7

Regression equation between amount of P extracted by different methods and other soil characteristics tested. The following units were used in the regression: P-AL (mg kg⁻¹); P-DL (mg kg⁻¹); P-M3 (mg kg⁻¹); Al (mg kg⁻¹); Ca (mg kg⁻¹); Fe (mg kg⁻¹); C (%); pH (pH units)

Methods	Analyze method	Equation for regression line	Determination coefficient (r ² _{adj})	Significance level (p)
P-AL and P- DL	Col.	$P-AL=2.70 + 1.33P-DL + 0.000833Ca -AL + 0.00450Al-AL$	0.939	<0.001
P-AL and P-M3	Col.	$P-AL = - 250 + 0.979 P-M3 + 34.7 pH + 0.0454 Fe-AL + 2.66 C + 0.0120 Al-AL$	0.763	<0.001
P-DL and P-M3	Col.	$P-DL = - 142 + 0.732 P-M3 + 0.0344 Fe-AL + 19.7 pH + 0.00308 Al-AL$	0.813	<0.001
P-AL and Olsen-P	ICP	$P-AL = - 144 + 3.29 Olsen-P + 27.0 pH - 0.00152 Ca-AL - 0.0166 Fe-AL - 0.0116 Al-AL$	0.748	<0.001

Regression equations between P-AL and P-DL for different areas. The following units were used in the regression: P-AL (mg kg⁻¹); P-DL (mg kg⁻¹); P-M3 (mg kg⁻¹); Al (mg kg⁻¹); Ca (mg kg⁻¹); Fe (mg kg⁻¹); pH (pH units)

Site	Equation for regression line	Determination coefficient (r ²)	Significance level (p)
Tonga	$P-AL = 23.9 + 1.47 P-DL - 0.0145 Al$	0.952	<0.001
Kuusiku	$P-AL = 208 + 0.718 P-DL - 0.370 Fe - 0.00681 Ca + 0.0699 Al$	0.996	0.043
Tartu			
Vecauce	$P-AL = - 2.88 + 1.22 P-DL + 1.56 C + 0.0248 Al + 0.000220 Ca$	0.974	<0.001
Graisupis	$P-AL = 7.29 + 1.17 P-DL + 0.00194 Ca$	0.967	<0.001
E23/Östergötland	$P-AL = 99.6 + 1.37 P-DL - 14.5 pH$	0.986	<0.001

Regression equations between P-AL and P-M3 for different areas. The following units were used in the regression: P-AL (mg kg⁻¹); P-DL (mg kg⁻¹); P-M3 (mg kg⁻¹); Al (mg kg⁻¹); Ca (mg kg⁻¹); Fe (mg kg⁻¹); pH (pH units)

Site	Equation for regression line	Determination coefficient (r ²)	Significance level (p)
Tonga	$P-AL = - 72 + 1.22 P-M3 + 12.8 pH + 0.00186 Ca$	0.844	0.001
Kuusiku	$P-AL = 248 + 0.390 P-M3 - 0.530 Fe$	0.783	0.043
Tartu	$P-AL = - 153 + 0.334 P-M3 + 158 C + 0.138 Al + 1.2 pH$	0.908	0.002
Vecauce	$P-AL = - 183 + 1.24 P-M3 + 26.6 pH - 0.0036 Fe$	0.911	<0.001
Graisupis	$P-AL = -136 + 0.695 P-M3 + 15.1 C + 21.1 pH$	0.956	<0.001
E23/Östergötland	$P-AL = 13.5 + 1.25 P-M3 + 0.0398 Ca - 0.188 Al - 24.0 C$	0.777	<0.001

Regression equations between P-DL and P-M3 for different areas. Following units is used in the regression P-AL (mg kg⁻¹); P-DL (mg kg⁻¹); P-M3 (mg kg⁻¹); Al (mg kg⁻¹); Ca (mg kg⁻¹); Fe (mg kg⁻¹); pH (pH units)

Site	Equation for regression line	Determination coefficient (r ²)	Significance level (p)
Tonga	$P-DL = -1.992 + 0.844 P-M3 + 0.00245 Ca$	0.927	<0.001
Kuusiku			
Tartu	$P-DL = -309 + 0.341 P-M3 + 128 C + 28.3 pH$	0.920	<0.001
Vecauce	$P-DL = 1.6 + 0.994 P-M3 + 0.000047 Ca - 0.124 C - 0.012 Fe$	0.878	<0.001
Graisupis			
E23/Östergötland	$P-DL = 15.3 + 0.907P-M3 + 0.0311 Ca - 0.147 Al - 21.4 C$	0.800	<0.001

Regression equations between P-DL and P-M3 for different areas. The following units were used in the regression: P-AL (mg kg⁻¹); P-DL (mg kg⁻¹); P-M3 (mg kg⁻¹); Al (mg kg⁻¹); Ca (mg kg⁻¹); Fe (mg kg⁻¹); pH (pH units)

Site	Equation for regression line	Determination coefficient (r ²)	Significance level (p)
Tonga	$P-AL = 23.6 + 3.43 Olsen-P - 0.0480 Al + 33.8 C - 0.117 Fe - 0.1 pH$	0.913	0.006
Kuusiku	$P-AL = -417 + 2.02 Olsen-P - 0.0134 Ca + 84.4 pH$	0.979	0.013
Tartu	$P-AL = -178 + 1.94 Olsen-P + 163 C + 0.212 Fe$	0.887	0.001
Vecauce	$P-AL = 32.4 + 3.32 Olsen-P - 1.61 C$	0.855	<0.001
Graisupis	$P-AL = 75.9 + 2.13 Olsen-P + 0.0607Al - 6.43 C$	0.964	<0.001
E23/Östergötland			

Appendix 8

Clay content in soil samples from E23/Östergötland

Soil sample	Clay content (%)
E23/Östergötland	
1	>50
2	>50
3	>50
4	>50
5	>50
6	>50
7	>50
8	>50
9	>50
10	>50
11	>50
12	40-50
13	>50
14	25-40
15	40-50
16	>50
17	>50
18	>50
19	25-40
20	0-10
21	10-25
22	25-40
23	40-50
24	40-50
25	10-25
26	25-40
27	40-50
28	0-10
29	10-25
30	>50