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ZIEMĀJU LABĪBU PIESĀTINĀJUMS AUGU SEKAS STRUKTŪRĀ: EFEKTIVITĀTE UN ILGTSPĒJĪBA

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Lietuvas Zemkopības institūta Joniškēļu izmēģinājumu stacijā laika periodā no 1998.-2002. gadam māla augsnēs *Gleyic Cambisol* tika veikti sekojoši pētījumi: A. Augu sekas ar dažādām ziemāju un vasarāju kultūru proporcijām (1. Bez ziemāju kultūraugiem; 2. 25% ziemāju kultūraugu; 3. 50% ziemāju kultūraugu; 4. 75% ziemāju kultūraugu; 5. 100% ziemāju kultūraugu), audzējot viengadīgos un daudzgadīgos zālaugus, vasaras un ziemas kviešus, tritikāli un miežus; B. Augsnes apstrādes sistēmas (1. Konvencionālā – aršana; 2. Ilgtspējīgā – aršana pēc zālaugiem, bezaršanas apstrāde pēc labībām). Pētījuma rezultāti parādīja, ka ziemāju labību proporcijas palielināšana augu sekas struktūrā samazina augsnes sablīvēšanās pakāpi, uztur produktīvākas mitruma rezerves, uzlabo ūdens-gaisa attiecību un humifikācijas procesu augsnē, samazina daudzgadīgo nezāļu daudzumu un paaugstina augu sekas produktivitāti. Samazinātas apstrādes izmantošana ilgtspējīgajā sistēmā noteica organisko vielu mineralizācijas pazemināšanos un humusa daudzuma palielināšanos augsnē. Salīdzinot ar vasarāju labībām, ziemāju labības bija tolerantākas pret samazinātu augsnes apstrādi.

COMPARISON OF METHODS FOR THE DETERMINATION OF PHOSPHORUS IN CARBONATIC SOILS

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Abstract

Plant available phosphorus determination by the Egner–Riehm (DL) method (LV ST ZM 82-97) is provided for use in the agrochemical research of sod-podzolic and other soils. However, the method is not suited for characterizing resources of the available phosphorus in carbonatic soils. The research goal was to develop methods for estimating the available phosphorus supply in calcareous soils. By the standard method (Egner-Riehm) the obtained results of phosphorus content was compared with those presented by the Olsen and Mehlich-3 method. The analysis of correlation and regression were employed for comparing the data of available phosphorus content in soil samples determined by different methods, as well as t-test was used for determining phosphorus content change. When analysing Paired Samples T Test (n=145) the most significant correlation ($r=0.95$) was determined between the amounts of phosphorus obtained by the Egner-Riehm and Olsen methods. Changes in the results obtained by the Egner-Riehm and Olsen methods revealed that in alkaline (pH.7.5) soils with CaCO_3 content above 5%, a certain amount of available phosphorus does not pass into calcium lactate extraction. The Olsen method is the most suited method for phosphorus extraction in carbonatic soils using NaHCO_3 as an extracting agent.

Key words: available phosphorus, Olsen, Mehlich-3, Egner-Riehm

Introduction

Zemgale region, the “granary” of Latvia, is called so mainly because of the fertile carbonatic (sod-calcareous soils, gley soils), suitable for obtaining high yields. In order to maintain and improve the fertility of these soils, it is important to estimate correctly their provision with plant available nutrient resources. The necessary information is provided by the data of soil analysis which enable one to set the

rates of fertilization on economic and ecological grounds. In calcareous soils particularly important is the physically-chemical and chemical immobilization and the mobilization of phosphorus. Conversion of phosphates into the plant unavailable form takes place both on the surface of carbonates and in the soil solution, where the concentration of calcium ions is comparatively high, as well as in the adsorption complex of the soil (Braschi *et al.*, 2003). The binding of the available phosphorus to plants into insoluble compounds is influenced by the soil reaction, the content of organic matter and the clay in the soil, the presence of iron compounds and moisture (Holford and Mattingly, 1975; Castro and Torrent, 1995; Carreira and Lajtha, 1997; Samadi and Gilkes, 1999; Zhou and Li, 2001). Up to now in the agrochemical research carried out in our country plant available phosphorus determination in soils was carried out by the Egner-Riehm (DL) method where calcium lactate extraction (pH 3.5 – 3.7) was used as the phosphate extracting agent. This standard method (LV ST ZM 82-97) is used for the agrochemical research of sod-podzolic and other soils. Although, as experience and research in other countries proves, this particular method is not suitable for the characterization of plant available phosphorus resources in carbonates containing soils. Carrying out the analysis by DL method carbonates and other alkaline compounds neutralize hydrochloric acid of the extracting agent by reducing its ability to dissolve potential plant available phosphates, consequently false information is obtained about the rate of phosphorus provided to plants (Zbiral, 2000). To determine the available phosphorus in carbonatic soils the most common is the Olsen method (Olsen *et al.*, 1954; Watanabe and Olsen, 1965), where a solution of 0.5 M sodium hydrogencarbonate (pH 8.5) is used as the extracting agent. The ions HCO_3^- , CO_3^{2-} and OH^- of the extracting agents reduce the amount of Ca^{2+} ions in the solution by sediment of CaCO_3 , as well as the ions Al^{3+} and Fe^{3+} - in the form of hydroxides, thus increasing the content of unbind phosphates in the solution. Another suitable extracting agent for such soils is ammonium hydrogencarbonate, which is the base of movable phosphorus determination in carbonatic soils according to Machigin (ГОСТ 26205 – 84). Ammonium carbonate together with DTPA (diethylenetriaminopentacetic acid) in several western states of the USA is used not only for plant available phosphorus determination, but also for the simultaneous determination of several other plants nutritive macro- and microelements (Soltanpour and Schwab, 1977). Mehlich-3 method ((Mehlich, 1984) is based on plant available compounds extraction in weak acid solutions (0.2 M CH_3COOH and 0.013 M HNO_3), to which ammonium fluoride NH_4F , ammonium nitrate NH_4NO_3 and ethylene diamine tetraacetic acid (EDTA) are added. It is known that this extraction possesses a better buffer ability, it is less neutralized by the carbonates of the soil and thus the results of this analysis better characterize the relationship with the plant available phosphorus amount of carbonatic soils (Tran *et al.*, 1990; Mallarino, 1997; Pierzynski, 2000). However the phosphorus determination results obtained by this method in the presence of carbonates frequently are considerably higher (Mallarino and Sawyer, 1999). Application possibilities of Mehlich-3 method were tested recently in many European countries including Latvia by comparing them with the existing standard methods for the determination of plant available macro- and microelements (Zbiral, 2000; Fotyma and Shepherd, 2000; Loide *et al.*, 2005; Timbare *et al.*, 2006).

Carbonatic soils comprise only a small part of the areas used for agriculture, therefore up to now when carrying out agrochemical research, they were not considered as a specific group and diverse methods of plant available phosphorus extraction was not applied to them. The aim of the research, on the basis of the Soil and Plant Research Institute crop rotation stationary archive collection of farmland soil monitoring and soil standard profile samples, was to establish the most suitable extraction method for the estimation of plant available phosphorus in carbonates-containing soils.

Materials and Methods

There are 145 soil samples from Latvia University of Agriculture Soil and Plant Research Institute crop rotation stationary for different rate treatments of phosphorus fertilizers, the archive collection of farmland soil monitoring and soil standard profile samples with soil reaction pH_{KCl} 6.05 – 8.67, carbonate content from 0.08 to 18.2 %, organic matter content from 0.7 to 95.5 g kg^{-1} , with clay fraction content from 1.86 to 44.1 %, used in the research. The plant available phosphorus content of all samples was determined by the following methods: 1) Egner-Riehm method (LV ST ZM 82-97), where 0.04 M calcium lactate extraction is used as an extracting agent being acidified by hydrochloric acid up to pH 3.5 – 3.7; 2) Olsen method (LVS ISO 11263:2002) – extracting agent 0.5 M sodium hydrogencarbonate solution, its reaction with sodium hydroxide reaches the precision of pH 8.5; 3) Mehlich-3 method where solution of 0.2 M acetic acid + 0.015 M ammonium fluoride + 0.013 M nitric acid + 0.25 M ammonium

nitrate + 0.001M EDTA is used as an extracting agent. The phosphorus in soil extract is measured photometrically by the molybdate – ascorbic acid method.

Mathematical processing of obtained results from soil analysis is carried out. Statistic indices of the results of plant available phosphorus analysis are determined for the sample. With different phosphorus extraction methods for the comparison of obtained data, correlation and regression analysis is used, as well as t-test for testing phosphorus content changes.

Results and Discussion

For the research of the methods comparison in the selected soil samples the plant available phosphorus content was different. The main statistic indices of determined phosphorus content for extracting agents by the Egner-Riehm (DL), Mehlich-3 and Olsen, as well as differences in methods by analyzing the whole sample are shown in Table 1. The average amount of phosphorus extracted from the soil by calcium lactate extraction (DL-P) was 79.6 mg kg⁻¹, by Mehlich-3 extracting agent (M-P) - 76.5 mg kg⁻¹, but only 30.6 mg kg⁻¹ P passed into sodium hydrogencarbonate (Ols-P). The median value by the DL-P and Ols-P results were next to average indices, but by the M-P results the median was slightly deviated (70.2 mg kg⁻¹ P) in the direction of lower value. So DL-P and M-P with quite close average content indices, the maximum value were 267.3 and 418.9 mg kg⁻¹ P respectively. Differences in the extracted phosphorus amount by mutually comparing Egner-Riehm, Mehlich-3 and Olsen extracting agents prove that, when analyzing soil samples with sharply different properties, the obtained results vary markedly both in soils with a low and high content of movable phosphorus. The boundary of three standard deviations by the correlation DL-P/Ols-P was exceeded in 3 cases, by the correlation DL/M-P – in 1 case, by the correlation M-P/Ols-P – in 3 cases. In the research when carrying out analysis of methods that affect factors, the results of these samples were not included in the analysis.

Table 1. Statistic indices of phosphorus determination results for the analyzed samples

	DL-P, mg kg ⁻¹	Ols-P, mg kg ⁻¹	M-P, mg kg ⁻¹	Difference, mg kg ⁻¹		Correlation	
				DL-P – Ols-P	DL-P – M-P	DL-P / Ols-P	DL-P / M-P
Average	79.6	30.6	76.5	48.9	3.03	2.89	1.39
Median	80.8	29.3	70.2	50.7	7.8	2.59	1.12
Minimum	0	0.81	0	-4.5	-213.7	0	0
Maximum	267.3	117.9	418.9	150.1	97.5	20.97	149.3

By carrying out results assessment of soil sample chemical analysis, the mutual relationships between phosphorus extraction methods are determined. Close linear relationship are found between phosphorus amounts measured by the Egner-Riehm and Olsen methods, as well as the Egner-Riehm and Mehlich methods (Fig. 1).

The relationship between Egner-Riehm and Olsen methods had the highest correlation coefficient (r = 0.95) there was a slightly lower relationship between Egner-Riehm and Mehlich methods (r = 0.91) and the Mehlich and Olsen methods (r = 0.89). There is little data in literature about the relationship between the Egner-Riehm and Olsen methods, but similar linear correlation between the Egner-Riehm and Mehlich-3 methods is recorded also in research in Estonia, where depending on the humus content in the soil the correlation coefficient has been found to be from r = 0.821 to 0.867 (Loide *et al.*, 2005). But in the researches carried out at the Centre of Agrochemical Researches, it is found that correlation between the phosphorus determination results obtained by the Egner-Riehm and Mehlich-3 methods is only average tight (r = 0.61 – 0.62) (Timbare *et al.*, 2006).

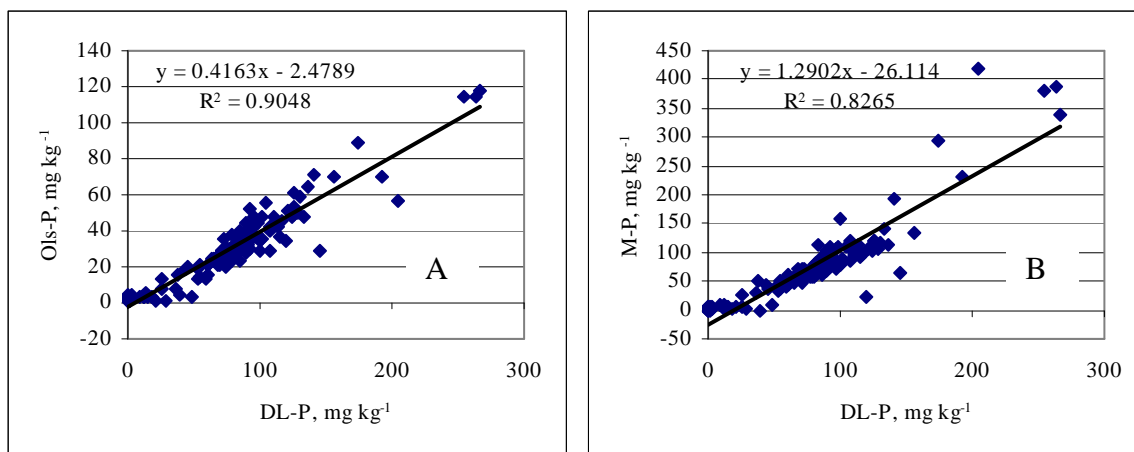


Figure 1. Mutual coherence of plant available phosphorus content determined by the Egner-Riehm and Olsen (A) and Egner-Riehm and Mehlich-3 (B) methods.

In order to find out which of the tested phosphorus determination methods mutually differ by the influence of different soil properties, the assessment of coherence changes of the determined P amount by the Egner-Riehm and Olsen was carried out for separate parts of the sample; taking into consideration agrochemical characterization of the samples. The obtained results proved that phosphorus extraction methods tested in the research show a good mutual correlation in weak acid and neutral soil reaction. The quantities of the highest correlation coefficient for the relationship between Egner-Riehm and Olsen methods ($r = 0.96 - 0.97$) are determined in the exchange acidity interval $\text{pH}_{\text{KCl}} 6.6 - 7.5$. By the increase of soil acidity up to $\text{pH}_{\text{KCl}} 6$, the coherence between phosphorus amounts extracted by applying these methods, shows little tendency to reduce, which could be related to the fact, that the Olsen method can be applied for phosphorus determination in neutral and alkaline soils, but is not suitable for phosphorus determination in acid soils (Mallarino, Sawyer, 1999). Also in alkaline soils $\text{pH}_{\text{KCl}} 7.5 - 8.6$, the coherence between Egner-Riehm and Olsen methods becomes weaker ($r = 0.81$), therefore it could be assumed, that the phosphorus amount, determined by the Egner-Riehm in calcium lactate extraction, does not adequately characterize plant available phosphorus in the soil. These relationships could get more convincing confirmation by analyzing soil sample of greater volume in a wider pH interval.

By comparing plant available phosphorus amounts determined by the Egner-Riehm and Mehlich-3, it is evident, that in the pH interval from 6 to 7.5 correlation coefficient ($r = 0.92 - 0.94$) is lower than for the coherence between the Egner-Riehm and Olsen methods, which matches with the obtained coherence also for the whole soil Paired Sample analyzed. However, with soil alkalinity becoming higher, the coherence between the phosphorus amount determined by the Egner-Riehm and Mehlich-3, markedly becomes weaker ($r = 0.50$). This makes us think that the Mehlich-3 method is still less suited for phosphorus determination in alkaline soils than the Egner-Riehm method. For soils with a reaction above $\text{pH}_{\text{KCl}} 7.5$, the coherence between Mehlich-3 and Olsen is very weak ($r = 0.29$). For weak acid and neutral soils the correlative relationship between phosphorus amounts determined by these methods is tight ($r = 0.96 - 0.98$). Our obtained results are confirmed also by research mentioned in the scientific literature. For example, in the Czech Republic (Zbiral, 2000) it was determined that in soils with the pH_{KCl} higher than 7.1, the amount of extracted phosphorus, measured by the Mehlich-3 method, depends on soil reaction and exchange calcium content. The plant available phosphorus amount, extracted from the soil by the Egner-Riehm, Olsen and Mehlich-3 methods, was affected also by the carbonate content. With the carbonate content not exceeding 5%, there was a close correlative coherence between the tested methods. The highest correlation coefficient ($r = 0.95$) is found between the phosphorus amount which has passed into calcium lactate extraction and sodium hydrogencarbonate extraction. In soil samples, in which the carbonate content exceeded 5%, the coherence between the methods was

considerably weaker. The correlation coefficient for the coherence between the Egner-Riehm and Olsen methods was 0.44, but between the Egner-Riehm and Mehlich-3 methods – 0.49.

The correlation of phosphorus determination results, which in the Egner-Riehm and Olsen case (correlation DL-P/Ols-P) for the analyzed soil Paired Sample was 2.35 on average, but by the Egner-Riehm and Mehlich-3 methods (correlation DL-P/M-P) – 1.17, with changing soil exchange acidity, decreased. This tendency is more typical for the correlation between the phosphorus determination results ($r = 0.53$) shown the by Egner-Riehm and Olsen methods, when, with the increase of soil alkalinity, in calcium lactate extraction (Egner-Riehm method) the passed phosphorus amount decreased (Fig. 2). The correlation of results by the Egner-Riehm and Mehlich-3 methods varied from 0 to 5.51 not depending on soil reaction. For soil samples with a diverse carbonate content the most essential changes are found between the results of the Egner-Riehm and Olsen methods. With the increase of carbonate content, the DL-P/Ols-P correlation decreases ($r = 0.71$). This proves that in alkaline soils, rich in carbonates, a certain part of the potential plant available phosphorus amount does not pass into calcium lactate extraction.

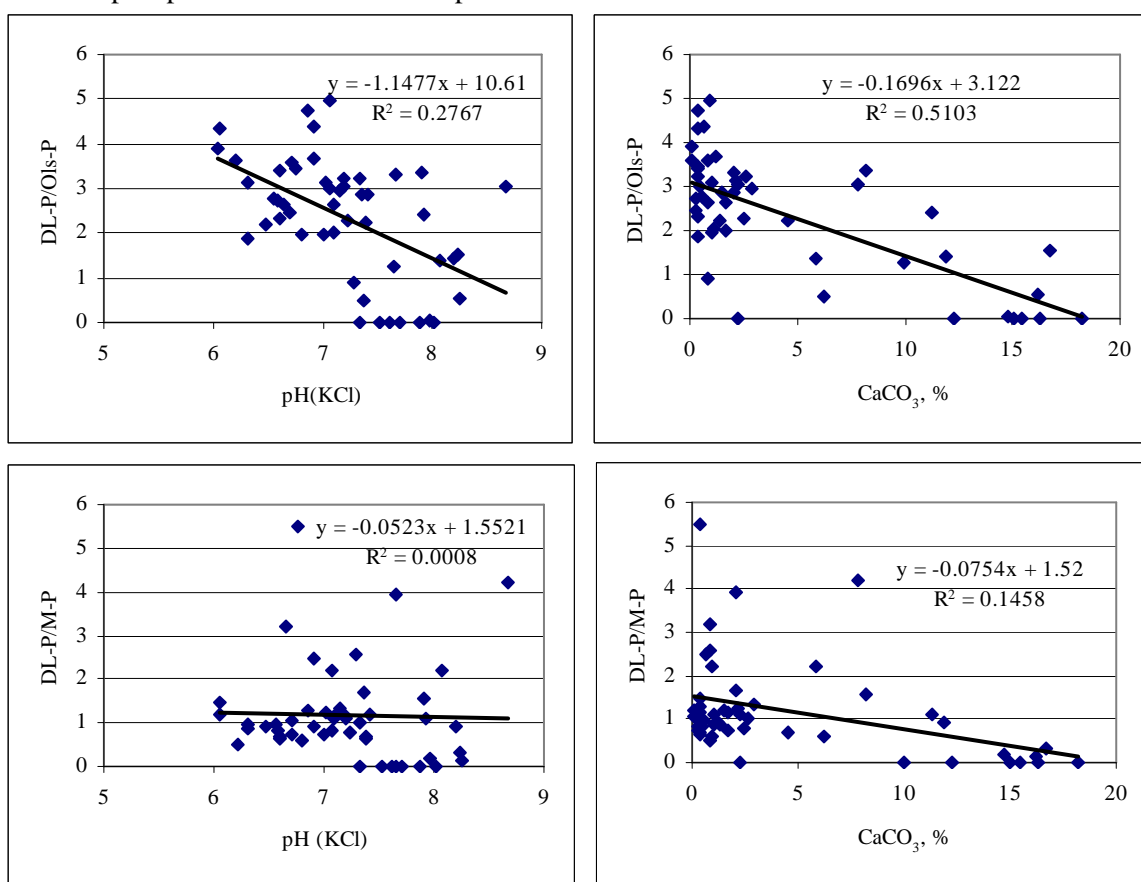


Figure 2. Influence of soil reaction and carbonate content on correlations of phosphorus determination results by the Egner-Riehm and Olsen method (DL-P/Ols-P) and the results by the Egner-Riehm and Mehlich-3 method (DL-P/M-P).

The obtained relationship prove that up to now the Egner-Riehm standard method used in agrochemical research of soils in Latvia incompletely characterises the sufficiency of plant available phosphorus in carbonatic soils with a alkaline reaction. According to the results of the research carried out and the data of literature, it is obvious that in calcareous soils the Olsen method would be more suitable. Types of phosphorus compounds, their transformations and binding mechanisms in these soils are different from soils where the dominate binding of phosphates in aluminium and iron compounds and in anion adsorption complex. Consequently, the use of one and the same plant available phosphorus determination methods in acid and neutral, as well as in alkaline carbonatic soils actually is not reasonable. The same way, depending on the soil reaction and carbonate content, sufficiency levels of soil phosphorus also should be differentiated.

Conclusions

Close correlative coherence ($r = 0.89 - 0.95$) is determined among plant available phosphorus determination results obtained from the soil sample ($n=145$), analyzing these samples by the Egner-Riehm, Olsen and Mehlich-3 methods. In alkaline soils, rich in carbonates, the relationship between the results by the Egner-Riehm and Olsen, as well as between the Egner-Riehm and Mehlich-3 methods become weaker. The correlation of phosphorus content results determined by the Egner-Riehm and Olsen method with the increase of soil alkalinity essentially decreases, which proves that extraction of potential plant available phosphorus resources with calcium lactate extraction is insufficient. Similar relationship between the correlation by the Egner-Riehm and Mehlich-3 results was poorly expressed. For the determination of plant available phosphorus in alkaline carbonatic soils the most suitable is the Olsen method.

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FOSFORA NOTEIKŠANAS METOŽU SALĪDZINĀJUMS KARBONĀTUS SATUROŠĀS AUGSNĒS

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LLU LF Augsnes un augu zinātniskajā institūtā veikti augsnes pētījumi augu sekas stacionāra atšķirīgu fosfora mēslošanas normu variantiem, lauksaimniecībā izmantojamo zemju augsnes monitoringa un augšņu etalonprofilu paraugu arhīva kolekcijai. Visiem paraugiem noteikts augiem viegli izmantojamā fosfora saturs pēc: 1) Egnera-Rīma metodē (LV ST ZM 82-97), kā ekstrāģentu lietojot 0.04 M kalcija laktāta šķīdumu, kas paskābināts ar sālsskābi līdz pH 3.5 – 3.7; 2) Olsena metodi (LVS ISO 11263:2002) – ekstrāģents 0.5 M nātrija hidroģēnkarbonāta šķīdums, kura reakcija ar nātrija hidroksīdu precizēta līdz pH 8.5; 3) Mēliha-3 metodi kā ekstrāģentu izmanto 0.2 M etiķskābes + 0.015 M amonija fluorīda + 0.013 M slāpekļskābes + 0.25 M amonija nitrāta + 0.001M EDTA šķīdumu. Fosfors augsnes izvilkumos noteikts fotometriski pēc molibdāta – askorbīnskābes metodes.

Noteikta cieša korelatīva sakarība ($r = 0.89 - 0.95$) starp augiem viegli izmantojamā fosfora noteikšanas rezultātiem, kas iegūti augsnes paraugu kopai ($n=145$), analizējot šos paraugus pēc Egnera-Rīma, Olsena un Mēliha-3 metodēm. Bāziskās, ar karbonātiem bagātās augsnēs, sakarība starp Egnera-Rīma un Olsena, kā arī starp Egnera-Rīma un Mēliha-3 metožu rezultātiem pavājinās. Pēc Egnera-Rīma un Olsena metodes noteiktā fosfora satura rezultātu attiecība, pieaugot augsnes bāziskumam, būtiski samazinās, kas liecina par nepilnīgu augiem potenciāli izmantojamo fosfora resursu ekstrakciju ar kalcija laktāta šķīdumu. Egnera-Rīma un Mēliha-3 rezultātu attiecībai līdzīga sakarība bija vāji izteikta. Augiem viegli izmantojamā fosfora noteikšanai bāziskās karbonātus saturošās augsnēs vairāk piemērota ir Olsena metode.