

# Ion Exchange Resin for Assessing Phosphorus Availability in Soils

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Soil testing is an important tool for modern agriculture. It represents a link between a remarkable amount of research information on one side and the possibility to solve many plant nutrition problems for specific farmer sites on the other. To be effective, a soil test should give adequate evaluation of soil nutrient bioavailability. In this paper, research data are used to demonstrate that the ion exchange resin procedure is superior to other widely used methods to determine P in routine soil testing. In Brazil, ion exchange resin has been used since 1983 and about 100 laboratories have adopted the method.

Phosphorus has received considerable attention in the research of methods of soil analysis, but agreement on best methodology is lacking. Resin extractable P seems to be a superior method, but its adoption in routine soil testing is still limited worldwide.

When there is a choice between several methods of analysis, if results are not comparable, greenhouse experiments under controlled conditions are used to select the soil test that is more closely related with nutrient uptake. This is done in pot experiments with soils representing a wide range of attributes that affect P reactions. A test plant is grown under conditions of proper nutrient supply except for P. The linear correlations between P uptake by plant and soil P determined by different procedures allow the ranking of methods based on the quality of prediction of P availability in soils.

An example of such research for a pot experiment with flooded rice is shown in **Figure 1**. In this case, resin extractable P is compared with the Mehlich 1 extraction. The results of resin P presented a much better correlation with P absorbed by the rice plants than Mehlich 1.

Several studies comparing soil P determination methods have been carried out. The literature review by Silva and Raij (1999) included papers published with soils of different countries, in which P determined by different methods was correlated with plant P uptake. The data in **Table 1** indicate that the ion exchange resin method is better correlated with P uptake than the other methods and that it is suitable for all types of soils, both acidic and alkaline.

The pH of the extractant solution is important for the ion-exchange resin procedure as shown in **Table 2**. Phosphorus extraction was poor when the suspension pH was low. For soil #2, where no response to P was observed, a high value of extractable P (36 mg/dm<sup>3</sup>) was obtained when the suspension

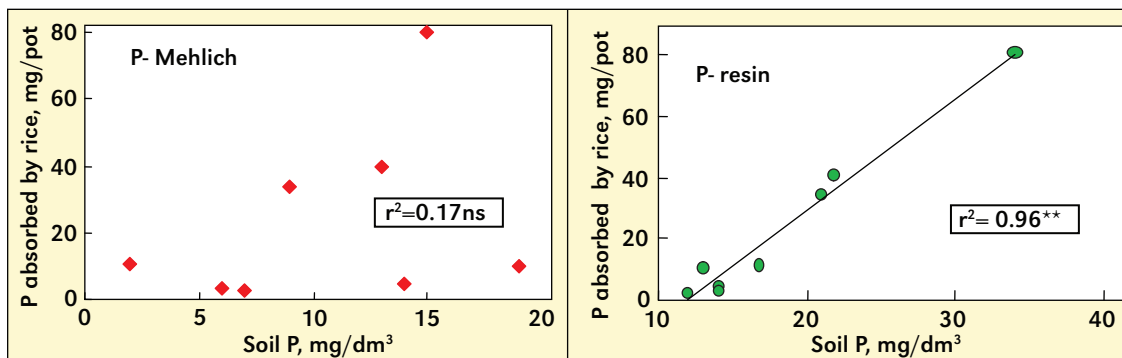
Table 1. Effectiveness of soil P extraction methods in predicting plant uptake based on data from 70 experiments reported in world literature.			
Method	Average coefficient of determination (100 r <sup>2</sup> ) for soils		
	Acid soils	Alkaline or neutral soils	Non specified soils
Resin	84	83	69
Olsen	47	52	58
Mehlich 1	56	39	41
Bray-1	53	25	48
Morgan	26	40	32

Source: Silva and Raij, 1999.

Table 2. Effect of pre-treatment <sup>1</sup> of the resin on pH of soil resin suspension and extractable P.				
Resin saturation	Soil 1		Soil 2	
	Suspension pH	Soil-P, mg/dm <sup>3</sup>	Suspension pH	Soil-P, mg/dm <sup>3</sup>
Resin-HCl	3.3	2	3.4	3
Resin-NaCl	5.3	1	5.6	5
Resin-NaHCO <sub>3</sub>	6.8	12	6.8	36

Soil 1- Cotton yield in kg/ha: control, 2,058; with P, 2,244.  
Soil 2- Cotton yield in kg/ha: control, 3,678; with P, 3,673.  
<sup>1</sup>Soils were shaken overnight in the soil-resin suspension.  
Source: Raij et al., 1986.

pH was 6.8 whereas at pH 5.6, soil P was only 5 mg/dm<sup>3</sup>. This can be explained in part because the availability of Fe and Al phosphates increase when pH increases. It also explains why acid extractants fail to remove P from soils high in Fe and Al



**Figure 1.** Relation of P uptake by flooded rice and P determined by resin and Mehlich 1 procedures. (Grande et al., 1986)

**Abbreviations and notes for this article:** P = phosphorus; HCl = hydrochloric acid; NaCl = sodium chloride; NaHCO<sub>3</sub> = sodium bicarbonate; Fe = iron; Al = aluminum; Ca = calcium; Mg = magnesium; K = potassium.

oxides containing sufficient available P. The presence of the bicarbonate ion saturating the resin is important because it buffers the medium, a factor that favors the stability of the results.

The equation below illustrates the system that has to be assessed by soil analysis. The method should extract P solution, which is very low, and obtain P labile from the labile forms. Non-labile P and undissolved fertilizer P should not be included in the results. Since resin extraction is done with a water suspension the ion exchange resin simulates more closely than the other methods the extraction by plant roots, acting as a sink for the elements absorbed from the solution. The negatively charged P ions in solution (mainly  $H_2PO_4^-$ ) are absorbed by the positive charges of the ion exchange resin, also promoting the dissolution of the labile P of the solid phase.

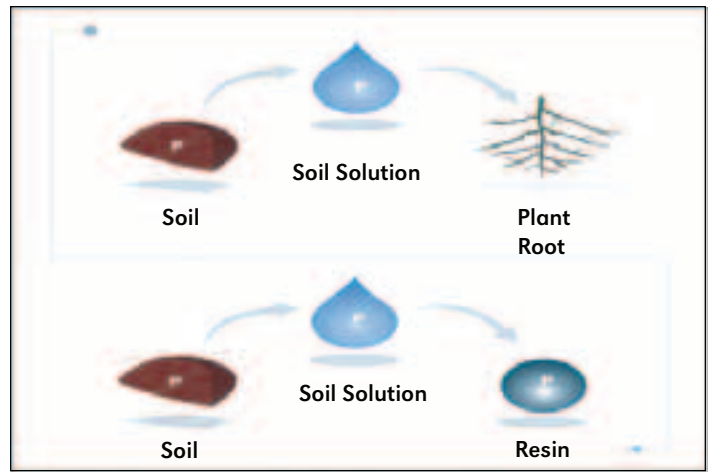


**Figure 2** shows a schematic representation on how the resin works, as compared with P uptake by plants. In this case, P moves through the soil solution to the roots creating a concentration gradient that promotes dissolution of the labile P in the solid phase and continuous movement to the roots by diffusion. Likewise, in the extraction procedure with the resin, P moves into solution, and is then adsorbed by the resin, a porous synthetic material with positive charges, mimicking what happens with roots. For soil extraction in the lab, the process is sped up by 16 hours of overnight shaking.

A soil test should extract mainly P solution and P labile. It should not remove slow release phosphates if they do not contribute for P uptake by plants. It should also not extract P from non-labile forms. The problem in practice is that most P extractants determine specific chemical forms of P, not necessarily bioavailable P. Thus, acid extracts, such as Mehlich 1, have preference for calcium phosphates and fluoride containing extractants, such as Bray 1, have specific action on Al phosphates.

In **Table 3** various aspects of the relationship between fertilizer P sources and methods for soil P determination are illustrated. Soils were treated with triple superphosphate (TSP), rock phosphate, and calcinated aluminum phosphate and cultivated with soybean in a pot experiment. Triple superphosphate was applied at seeding time and the three phosphates were applied 75 days prior to seeding. P uptake by soybean was measured and the soil samples were analyzed by resin, Mehlich 1, and Bray 1 methods.

The results presented in **Table 3** allow several observations. Comparing the results of superphosphate applied at seeding with those of the same fertilizer applied 75 days ahead, it can be seen that availability of P decreased with time of incubation, as shown by the reduction of P uptake by soybean from 4.3 mg/pot to 2.3 mg/pot. The decrease of P availability of water soluble phosphates with time is a well known effect; this tendency could be identified by resin, but not by Mehlich 1 or Bray 1.



**Figure 2.** Schematic demonstration of P extracted from soils by ion exchange resin.

Alvorada rock phosphate had low agronomic efficiency, with an uptake of only 1.1 mg/pot of P in excess of that of the control treatment. Results of resin and Bray 1 methods indicated this tendency, but Mehlich 1 extracted far too much P, as expected, for an acid extractant acting on a soil treated with apatite.

The calcinated aluminum phosphate, also of low agronomic efficiency, had low extractable values for resin and Mehlich 1, but Bray 1 overestimated the results because the fluoride in the extractant solution released P from the Al bond.

These examples show some of the limitations of the chemical extractants in assessing available P in soils.

It is commonly accepted or well known that pH values around 6 enhance P availability. Accordingly, in four field experiments in the State of São Paulo, a significant increase of P concentration in beans, sunflower, and soybean leaves was observed following limestone application (columns 2 and 3 in **Table 4**). The soil samples, collected 2 years after liming, presented puzzling results. The results of Mehlich 1 and Bray extractable P were not affected by liming, as seen in columns 4 and 5 in **Table 4**. Odd results were observed for the Olsen method since as soil pH increased, soil P decreased, thus moving in the opposite direction. The results obtained with P resin increased in the same direction as P in leaves. In conclusion,

**Table 3.** Phosphorus uptake by soybean with the application of three P sources, three different methodologies, and index ratios using TSP before seeding as a standard. The values represent the difference from the control treatment.

P evaluation	Fertilizers applied 75 days prior to seeding							
	Triple superphosphate applied at seeding		Triple superphosphate		Alvorada rock phosphate		Calcinated aluminum phosphate	
	Value	Index	Value	Index	Value	Index	Value	Index
Soybean, mg/pot	4.3	100	2.3	53	1.1	27	1.7	40
Resin P, mg/dm <sup>3</sup>	12.7	100	7.9	62	1.7	13	4.9	39
Bray 1 P, mg/dm <sup>3</sup>	37.9	100	39.6	105	7.9	21	39.4	104
Mehlich 1 P, mg/dm <sup>3</sup>	27.9	100	24.6	88	42.8	153	1.5	5

Source: Rajj and Diest, 1980.

Table 4. Relation between soil pH in CaCl <sub>2</sub> 0.01 M, leaf P content, and soil P – determined by four methods.						
Crop and soil	pH CaCl <sub>2</sub>	Leaf P g/kg	Soil P, mg/dm <sup>3</sup>			
			Mehlich 1	Bray 1	Olsen	Resin
Beans Organic soil	3.8 d <sup>1</sup>	2.44 b	17 a	20 a	41 a	33 b
	4.2 c	3.21 a	18 a	21 a	33 b	36 ab
	4.7 b	3.25 a	18 a	20 a	26 c	38 ab
	5.1 a	3.26 a	19 a	18 a	19 d	43 a
	5.2 a	3.25 a	20 a	19 a	21 d	43 a
Sunflower Ultisol	4.3 c	2.79 c	12 b	24 a	17 a	22 b
	4.6 c	3.27 b	12 b	22 a	17 a	26 ab
	5.3 b	3.81 a	16 a	25 a	16 a	33 ab
	5.5 ab	3.87 a	15 a	20 a	12 a	35 a
	5.7 a	3.80 a	16 a	20 a	12 a	37 a
Soybean Ultisol	4.3 a	1.85 c	6 a	15 a	10 a	13 c
	4.8 d	2.06 bc	7 a	16 a	11 a	16 c
	5.5 c	2.44 ab	5 a	13 a	7 a	17 bc
	6.1 b	2.26 a	7 a	17 a	8 a	22 ab
	6.4 a	2.55 a	7 a	15 a	8 a	27 a
Soybean Oxisol	4.5 d	2.35 b	9 a	20 a	18 a	16 c
	4.9 c	2.69 ab	8 a	22 a	15 ab	19 bc
	6.1 b	2.88 a	8 a	20 a	13 ab	23 b
	6.6 a	2.85 a	10 a	24 a	12 b	34 a

<sup>1</sup>Numbers followed by different letters in the same column are statically different at 5% level.  
Source: Raij and Quaggio, 1990.

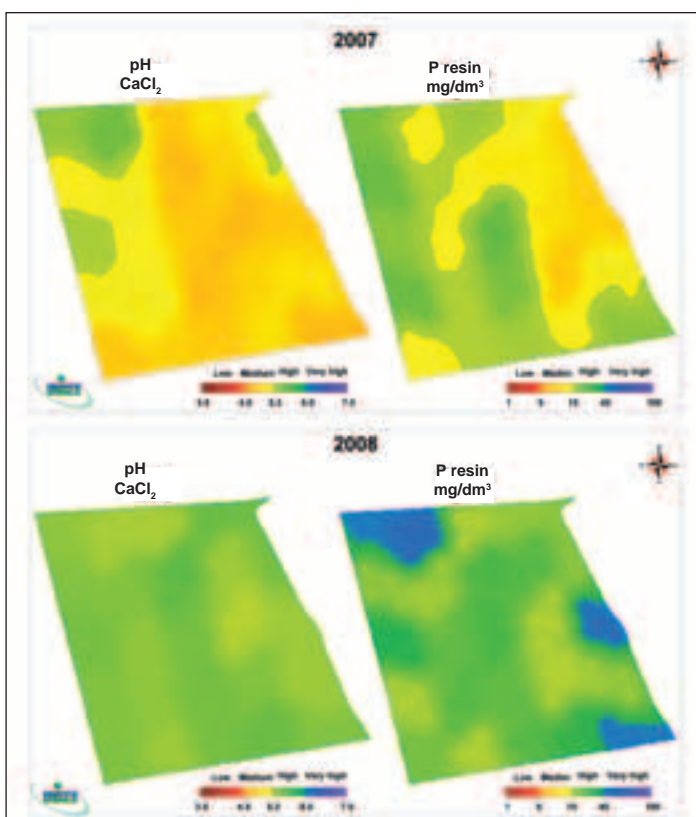



Figure 3. Images of precision agriculture showing pH in CaCl<sub>2</sub> and P resin before (2007) and after liming (2008).

the results showed that the resin procedure better evaluated the increase in P availability due to liming, while Mehlich 1 and Bray 1 were not sensitive to the changes caused by variation of soil pH. Olsen indicated a decrease in available P, which was inconsistent with leaf P concentration.

Another demonstration of the effect of liming on the increase of resin extractable P is shown in **Figure 3**, with maps prepared by precision agriculture technology, with pH and P resin values obtained before (2007) and after liming (2008). Reducing acidity by liming, as indicated by pH, resulted in increase of resin P. This is important because it has economical consequences, represented by a lower need to apply P fertilizers.

A soil test method is only good if it can be used in large scale soil testing. Although ion exchange resin has proven valid for the determination of available P in soils for more than 50 years, it was always considered a method not suitable for routine soil testing. However, the ion exchange resin has been used in Brazil since 1983 (Raij et al., 1986; Raij, 1999) and is now adopted by about 100 laboratories in that country. The ion-exchange resin procedure described by Raij et al. (1986) uses a mixture of cation and anion resins that enhances P extraction and also permits the determination of exchangeable Ca, Mg, and K in the same extract. Inexpensive time saving

equipment was developed by the IAC team (Raij et al., 2001) and is commercially produced by third parties, one important step to assure the adoption of the method.

Phosphorus extracted by ion exchange resin has been shown to be a sensitive index of P availability in soils. Having such a good alternative for P determination in soils could improve P fertilizer recommendations and advance fertilization technologies, such as precision agriculture. 

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### References

- Grande, M.A., N. Curi, and J.A. Quaggio. 1986. Rev. Bras. Ci. Solo. 10: 45-50.
- Raij, B. van. 1999. Commun. Soil Sci. Plant Anal. 29:1553-1570.
- Raij, B. van, J.C. Andrade, H. Cantarella, and J.A. Quaggio, eds. 2001. Chemical analysis for the evaluation of the fertility of tropical soils. Instituto Agronômico: Campinas. (in Portuguese).
- Raij, B. van and A. van Diest. 1980. Plant and Soil. 55:97-104.
- Raij, B. van and J.A. Quaggio. 1990. Commun. Soil Sci. Plant Anal. 21:1267-1267.
- Raij, B. van, J.A. Quaggio, and N.M. da Silva. 1986. Commun. Soil Sci. Plant Anal. 17: 547-566.
- Silva, F. C. da and B. van Raij. 1999. Pesq. Agrop. Bras. 34: 267-288.