Soil available phosphorus by Mehlich-1, Mehlich-3 and anion exchange resin and its sensitivity to soil clay content

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Abstract
Mehlich-1 is the most used chemical method to determine soil available P in Brazil, but its efficacy is affected by variations in clay contents due to the exhaustion of the extractants and readsorption of P by the soil particles. Thus, other methods have been tested in Southern Brazil to replace the Mehlich-1. The objective of this work was to evaluate the ability of Mehlich-1 (M1), Mehlich-3 (M3), and anion exchange resins in strip (AERst) or in sphere (AERsp) forms, to extract P from soils with a wide range of clay contents. Samples were collected from the B horizon of a Brazilian Oxisol were mixed with different amounts of sand in order to get artificial soil samples containing 200, 400 and 600 g/kg of clay, in addition to a pure sand (with no clay) and a pure soil (800 g/kg of clay). Phosphorus rates (0, 100, 200, 400 and 600 mg/kg) were applied to each one of these experimental soils that were subsequently incubated for 1, 30, 90 or 180 days. After each incubation period, available P was quantified by the four methods. All methods, extracted less P as the clay content of the samples increased. The amount of P extracted also decreased with increases on the incubation time. Thus, the evaluation of soil P availability to plants determined by all tested methods need to take into consideration the amount of clay.

Key Words
Phosphorus, soil analysis, availability, Mehlich, resin.

Introduction
Plants take up nutrients only from soil solution. However, soil nutrient availability depends on the relationship between ions in liquid and solid phases since the latter form replace the nutrients in the soil solution as their uptake by plants proceeds. The ability of the solid forms to resist changes in the concentration of a given ion in the solution represents the soil buffer capacity, which is controlled by the binding energy of the nutrient with the soil particles and by its diffusivity to the soil solution. Thus, chemical methods used to estimate nutrient availability from the soil must detect the amounts that can readily go to soil solution. Mehlich-1 is the official method used in Southern Brazil to evaluate soil available P. In this method, labile P is extracted by acid dissolution, which preferentially attacks P pools associated with calcium compounds and, to a less extent with aluminum and iron compounds. This method has the inconvenience of detecting decreasing amounts of P as the content of soil clay increases, due to extractant exhaustion and the readsorption of P on inorganic colloids that takes place in clayey soils following the extraction but before the determination. To overcome this problem, other methods are being evaluated in Southern Brazil to replace Mehlich-1, such as Mehlich-3 and anion exchange resin. The objective of this study was to evaluate the efficacy of Mehlich-1, Mehlich-3, and two forms of anion exchange resin (in strips and in sphere) to extract P from samples of the same soil mixed or not with sand in order to get a wide range of clay contents.

Methods
This work was carried out in the Soil Fertility Laboratory at Santa Catarina State University, in Lages, Southern Brazil. Treatments consisted of a factorial including samples of the same soil containing various amount of clay (0, 200, 400, 600 and 800 g/kg) that received increasing rates of P (0, 100, 200, 400 and 600 mg/kg). Phosphorus was determined in all these samples by four chemical methods [Mehlich-1,M1, Mehlich-3,M3, (Mehlich, 1984) and anion exchange resin in strips (AERst) or in spheres (AERsp) forms, according to Raij et al. 2001)]. The soil sample was collected in the subsurface horizon of an Oxisol. It had 800 g/kg of clay with predominance of kaolinite and iron oxides. To get the variations on clay contents, the natural soil samples were mixed with different amounts of sand, in addition to a pure sand (with no clay) and a pure soil (800 g/kg of clay). The sand used had particle size between 0.5 to 1.0 mm and was previously washed sequentially with HCl 0.1 mol/L and distilled water, several times. The prepared samples were moistened in order to attain 80% of the soil water retained at field capacity and subsequently incubated for

30 days for physical and chemical properties stabilization. Subsequently, $CaCO_3$ was applied to raise the pH-H_2O of each individual sample to 6.0, an a new incubation period of 30 days was performed. At this time, samples were dried, sieved and the P adsorption capacity was determined, through adsorption isotherms adjusted by using the Langmuir model. Then, P rates were applied, as KH_2PO_4, and quadruplicate samples were incubated for 1, 30, 90 and 180 days. During this time, distilled water was added at two weeks interval to keep moisture near 80% of the water retained at field capacity. After each period of incubation, samples were dried at 60 º C, sieved to pass a 2.0 mm sieve, and analyzed for P. It was used a completely randomized design with four replications. Results were submitted to analysis of variance and means were compared by the Bonferroni test. The percentage of recovery of P added was calculated by the following equation:

$$\%Prec = (Pext – Pnill/Padd)*100 \tag{1}$$

where %Prec = P recovery (%); Pext = P extracted from a treatment with P application; Pnill = P extracted from the treatment without P application; Padd = quantity of P applied.

Results
The increase in the clay content of the samples increased the adsorption of P and decreased its recovery by all four chemical methods (Table 1). This is because in sandy soils the number of sites for specific adsorption of phosphates is small, which limits this process and allows P to remain in more available forms. Moreover, raising the clay content increases the adsorption of P and decreases its availability. In fact, all methods tested extracted less P with increases of clay content due mainly to an increase of P sorption. The amount of P extracted by all methods dramatically dropped with increases in the percentage of clay in the samples, showing that these methods are similarly sensitive to variations in soil buffer capacity. For the treatment that did not receive phosphate, all methods showed similar P values regardless of the clay content in the samples (Table 1).
As the rate of P applied increased, the methods also detected higher levels of available P. However, for samples containing the highest clay content (800 g/kg), this occurred only where it was added the highest P rate (600 mg/kg), demonstrating the extremely high sorption capacity of this soil. M1 and AERsp generally extracted more phosphorus than M3 and AERsp, probably due to the acidity of the M1, which causes an aggressive extraction from the colloid surfaces. The higher ability of AERsp to extract P relatively to AERst was probably a consequence of a larger exchange surface area of the former kind of resin. After 24 hours of incubation, the recovery of added phosphorus from the samples with no clay (pure sand) ranged from 80 to 106% (Table 2) while from the pure soil sample (800 g/kg of clay) the P recovered ranged from only 1.1 to 5.8%, which demonstrates the strong effect of clay on P adsorption. In most situations, a slight decrease in P extracted occurred with increases in incubation time probably as the result of increases in the energy of P adsorption by the soil particles. These results show that the time elapsed following the application of phosphate until its extraction from the soil must be considered.

Conclusion
All chemical methods were sensitive to the soil buffer capacity, because they extracted less P as the amount of clay in the samples increased. They also detected a decrease on phosphorus availability with increases in incubation time following P addition. Thus, to correctly interpret P availability to plants soils must be segregated in categories according to clay content regardless of the chemical method used.

References
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Table 1. Phosphorus determined by Mehlich-1 (M1), by Mehlich-3 (M3), and by two forms of anion exchange resin, in strips (AERst) or in spheres (AERsp), from soil samples with different clay contents as affected by the rate of P applied and by the incubation time following P addition.

Clay (g/kg)	Methods	0 mg P/kg				100 mg P/kg				200 mg P/kg				400 mg P/kg				600 mg P/kg			
		1d	30d	90d	180d	1d	30d	90d	180d	1d	30d	90d	180d	1d	30d	90d	180d	1d	30d	90d	180d
		--- Available P (mg/kg) ---																			
0	M1	1,7 a	1,7 a	1,7 a	1,2 a	110,7 a	106,4 a	99,5 a	80,7 a	218,8 a	189,4 a	195,5 a	156,8 a	426,5 a	414,0 a	358,3 a	318,9 b	594,6 a	576,6 a	526,5 a	502,2 a
	M3	1,2 a	1,3 a	0,6 b	1,0 ab	98,1 b	75,9 c	69,1 c	84,1 a	155,1 b	138,2 c	118,5 d	152,7 a	439,5 a	422,5 a	266,9 b	375,8 a	600,8 a	581,8 a	519,1 a	525,1 a
	AERst	0,4 b	0,5 b	0,5 b	0,5 b	78,2 c	75,2 c	72,6 bc	68,1 c	153,2 b	149,8 b	144,4 c	125,9 b	370,5 b	326,2 b	285,8 b	245,3 c	451,3 b	418,3 c	452,0 b	401,7 b
	AERsp	1,1 a	0,3 b	0,4 b	0,3 b	82,0 c	81,1 b	77,2 b	73,6 b	154,7 b	154,6 b	168,8 b	133,3 b	362,2 b	330,3 b	362,1 a	254,6 c	459,2 b	470,8 b	530,4 a	409,9 b
200	M1	1,3 a	1,3 a	1,2 a	1,1 a	14,6 a	14,7 a	13,3 a	9,8 a	28,1 ns	29,9 ns	25,0 ab	25,2 ns	101,3 b	87,1 b	78,7 c	75,2 c	202,8 a	204,5 ab	197,5 ab	145,0 b
	M3	1,3 a	1,2 a	0,7 ab	0,9 ab	10,1 ab	8,3 b	5,1 b	6,7 ab	33,2	27,8	19,4 b	23,5	88,6 b	81,8 b	80,8 c	103,6 b	144,0 b	112,2 c	140,6 c	168,4 b
	AERst	0,6 b	0,4 b	0,5 b	0,3 b	6,7 b	6,3 b	6,0 b	3,9 b	23,3	20,2	31,0 a	20,0	108,9 b	77,9 b	111,5 b	93,0 bc	179,0 ab	161,4 b	155,6 bc	139,9 b
	AERsp	1,4 a	0,6 b	1,3 a	0,9 ab	9,6 ab	8,2 b	6,8 b	8,3 ab	24,4	22,5	20,6 b	26,8	159,1 a	118,5 a	149,2 a	156,1 a	223,7 a	226,9 a	222,9 a	234,7 a
400	M1	1,5 a	1,5 b	1,4 a	1,1 a	7,6 a	6,6 ns	6,3 ns	4,6 ns	16,5 a	12,2 ns	11,2 ns	10,5 ns	49,1 b	44,4 ab	31,8 b	26,7 b	80,9 bc	73,1 bc	72,2 bc	59,4 bc
	M3	0,6 bc	0,5 c	0,3 c	0,3 b	3,0 ab	3,0	1,5	2,4	14,2 ab	9,6	4,7	6,3	36,0 b	27,2 b	23,8 b	26,6 b	38,3 c	54,6 c	53,3 c	41,6 c
	AERst	0,4 c	0,3 c	0,5 bc	0,4 ab	1,7 b	1,7	1,3	1,2	4,3 b	3,8	4,4	2,2	31,0 b	28,8 b	34,3 b	15,3 b	105,3 ab	114,1 b	110,2 b	89,0 ab
	AERsp	1,3 ab	2,8 a	1,1 ab	0,4 ab	6,3 ab	4,3	2,5	2,7	15,1 a	13,8	9,0	9,0	76,3 a	60,3 a	72,7 a	55,6 a	144,7 a	164,6 a	163,3 a	134,9 a
600	M1	1,4 a	1,3 a	1,3 a	1,0 ns	6,5 a	4,8 ns	4,7 ns	3,3 ns	14,1 ns	11,0 ns	10,1 ns	9,8 ns	41,3 a	31,0 ns	28,9 ns	20,9 ns	72,9 b	59,4 ns	51,9 ab	44,9 b
	M3	0,8 ab	0,7 ab	0,5 b	0,6	1,8 ab	1,2	1,0	0,7	4,5	2,9	2,2	2,2	19,0 ab	13,6	5,8	12,0	34,9 b	26,0	21,0 b	26,9 b
	AERst	0,3 b	0,2 b	0,3 b	0,7	1,1 b	0,8	0,8	0,7	4,3	2,4	1,2	2,0	10,7 b	16,2	8,4	6,4	50,6 b	41,4	26,1 b	17,8 b
	AERsp	0,7 ab	0,7 ab	0,6 ab	0,4	4,4 ab	3,5	2,5	2,8	9,3	7,6	5,3	9,4	26,8 ab	17,5	18,7	22,7	124,9 a	62,1	79,9 a	95,9 a
800	M1	1,3 a	1,1 a	1,1 a	2,2 ns	4,4 ns	4,0 ns	3,5 ns	3,4 ns	9,6 ns	6,2 ns	4,4 ns	5,9 ns	24,5 ns	20,4 ns	18,1 ns	11,7 ns	61,5 ns	32,2 ns	25,2 ns	24,4 ns
	M3	0,8 ab	0,7 ab	0,4 b	1,5	0,9	0,7	0,3	0,3	1,9	1,0	0,9	0,7	5,2	4,1	2,7	2,7	16,7	7,0	5,3	6,7
	AERst	0,5 b	0,4 b	0,6 ab	0,5	1,0	0,6	0,7	0,8	2,1	1,9	1,1	1,4	3,4	3,4	2,4	2,5	23,4	7,3	6,3	6,5
	AERsp	0,6 ab	0,3 b	0,8 ab	0,5	3,5	2,5	2,8	2,9	9,0	2,8	5,6	5,5	24,7	21,4	15,7	17,9	59,6	28,5	46,0	41,3

Similar letters in the column, for each clay content, do not differ by the Bonferroni test (P<0.05); ns = not significant.

Table 2. Recovery of added phosphorus by Mehlich 1 (M1), by Mehlich 3 (M3), and by anion exchange resin, in strips (AERst) or in spheres (AERsp), samples with different clay contents that received increasing rates of P and were incubated from 1 to 180 days. (Average of all of P doses)

Clay (g/kg)	Method	Incubation time			
		1d	30d	90d	180d
		-------------------- P recovery (%) ---------------------			
0	**M1**	105.7	99.4	92.8	80.1
	M3	95.8	86.3	70.1	85.0
	AERst	80.5	75.1	72.7	64.6
	AERsp	81.2	79.8	85.0	68.0
200	**M1**	21.3	20.8	19.0	15.8
	M3	17.6	14.7	14.3	17.7
	AERst	18.6	15.5	18.6	15.0
	AERsp	24.4	21.5	22.5	24.7
400	**M1**	9.7	8.3	7.3	6.2
	M3	6.1	5.7	4.5	4.6
	AERst	7.1	7.3	7.4	5.1
	AERsp	13.9	12.1	12.7	10.8
600	**M1**	8.4	6.4	5.8	4.7
	M3	3.3	2.2	1.7	1.9
	AERst	3.4	3.1	1.8	1.2
	AERsp	8.8	5.2	5.5	7.2
800	**M1**	5.8	3.8	3.1	2.7
	M3	1.1	0.5	0.4	0.0
	AERst	1.5	0.7	0.5	0.5
	AERsp	5.7	3.3	3.9	4.1

P recovery calculated by equation (1)