SOIL AND PLANT NUTRITION - Article

Phosphorus fractions in apple orchards in southern Brazil

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ABSTRACT: Phosphorus (P) applications at dosages higher than the necessary may cause P buildup in the soil labile fractions and, consequently, pollution of water sources. This study aimed to assess accumulation of P fractions as well as the parameters of adsorption isotherms in soil profiles having a history of application of phosphate fertilizers and cultivated with apple trees. Soil samples were collected from an area with no history of cultivation and 2 apple orchards cultivated for 8 (P8) and 18 (P18) years, in the city of Urubici, Santa Catarina, southern Brazil. Soil samples were air dried, sieved in a 2-mm mesh, and subjected to chemical analyses (P adsorption) besides P chemical fractionation. Applications of phosphate fertilizers to the orchards, particularly P18, increased the inorganic and organic concentrations of P in all fractions. The distribution of P in organic and inorganic forms in the planted soils was similar to the distribution observed for the native vegetation soil. The highest inorganic labile P fraction, the lowest maximum P adsorption capacity, and the highest equilibrium concentration values at P18 are indicators of a higher environmental pollution risk of the orchards soils compared to the native soil.

Key words: apple orchard, phosphate fertilization, P chemical fractionation.

INTRODUCTION

The southern region of Brazil, especially the states of Rio Grande do Sul (RS) and Santa Catarina (SC), has climate characteristics that are favorable to the growing of apple trees (*Malus domestica*), with dominant humid mesothermal climate and mild summers (Cfb, according to Köppen-Geiger climate classification).

Santa Catarina has 17,604.00 ha of apple orchards, which is the largest area among the Brazilian states. Every year, 613,828 t of apples are grown, representing 46% of the national production (Goulart Junior 2015). Soils cultivated with apple trees are often shallow, with high potential acidity and low natural fertility (Nava et al. 2002). Therefore, before the introduction of apple seedlings, the soil acidity should be corrected with the application of lime to raise the pH levels in water to around 6.0. Additionally, fertilizers should be added to increase phosphorus (P), potassium (K) (CQFS-RS/SC 2004), and nitrogen (CQFS-RS/SC 2004) contents to the necessary levels for plant growth. Maintenance fertilization is performed when the plants start producing and is determined by a combined analysis of total nutrients in leaves, fruits, soil (every 3 years), and expected production (CQFS-RS/SC 2004). However, the fertilization in soils grown with fruit species is not always consistent with the recommended technical criteria, which may cause P buildup, particularly in the upper soil layers, and saturation of the adsorption sites of the soil reactive particles (Schmitt et al. 2013a).

The concentration of P in soil depends on the source material, pedogenesis, soil texture, and environmental factors. In addition, the rate and type of P applied as well as the cultivation history also affect P availability (Sharpley 2011). Numerous studies dealing with accumulation of P fractions in the soil have been conducted, based on the chemical fractionation method proposed by Hedley et al. (1982). This method uses, sequentially, chemical extractors that remove inorganic and organic P from the most available to the most stable fractions. Through the chemical fractionation of P, it has been observed the occurrence of inorganic and organic fractions of this nutrient in soils with a history of successive applications of phosphate fertilizers in annual crops (Ciampitti et al. 2011; Linquist et al. 2011; Tiecher et al. 2012a,b) as well as in fruit crops (Schmitt et al. 2013a,b; Brunetto et al.

2013; Schmitt et al. 2014). However, such accumulation is often more pronounced in the inorganic fractions. The adsorption of the applied P takes place in the most avid — and with the highest binding strength — sites first, and later the remaining P is redistributed into fractions with lower energy (Rheinheimer and Anghinoni 2001).

Thus, it is expected that, if regular applications of phosphate fertilizer in maintenance fertilization over the years are greater than the amounts required by the apple trees and the plants that coexist in the orchard lines, even the amount of P extracted from the fruits which are very low (1.5 to 3.0 g·kg^{-1}) (Nava 2012), P accumulation and redistribution into different organic and inorganic fractions will occur, with possible decrease in the maximum P adsorption capacity (MPAC) (Schmitt et al. 2013a). MPAC is an indicator of the soil capacity for P adsorption, which is highly associated with clay contents (Oliveira et al. 2014) and P application rates (Schmitt et al. 2013a). MPAC can be established by adsorption isotherms, adjusted by mathematical models, such as the one proposed by Koski-Vähälä and Hartikainen (2001). With this model, we can determine the decrease in MPAC of soils that have a history of frequent application of phosphate fertilizers, especially on the topsoil layers (Schmitt et al. 2013a).

This work aimed to assess P fractions and the parameters associated with P adsorption in the profile of soils cultivated with apple trees in southern Brazil, with historical application of phosphate fertilizers.

MATERIAL AND METHODS

Site description

Soil samples from 2 commercial apple orchards and 1 from a native area were collected in the city of Urubici (SC), southern region of Brazil (long 49°35′30″W, lat 28°0′5″S). Soils were classified as Humic Cambisol (Embrapa 2013). The climate in the region is humid mesothermal with mild summers (Cfb, Köppen's classification), with mean annual rainfall of 1,537 mm, mean temperature of 15.4 °C, with potential occurrences of 20 to 29 frosts over the year, and the accumulated chilling hours under 7.2 °C ranging from 642 to 847 h per year.

Orchard 1, 8 years old (P8), was implemented in 2003, with density of 4,444 plants per ha (4.5 m between rows

and 0.5 m between plants in the line). Orchard 2, 18 years old (P18), was implemented in 1993, with density of 1,482 plants per ha (4.5 m between rows and 1.5 m between plants in the line). The orchards have 2 commercial apple varieties, Gala and Fuji, corresponding to 70 and 30% of the plants, respectively. The chosen system consisted of the central leader. Plants of both orchards were grafted onto Marubakaido rootstocks, P8 with an M9 20-cm filter, and P18 with no filter. Before planting, the lime was applied at a dosage sufficient to raise pH in water to 6.0. It was applied to the surface and incorporated into approximately 0.20 m depth with 1 plowing and 1 harrowing pass. In the pre-planting fertilization stage, 33 kg of $K \cdot ha^{-1}$ and 130 kg of $P_2O_5 \cdot ha^{-1}$ were added to the orchard soils. Every year, approximately 91 kg of $N \cdot ha^{-1}$, 145 kg of $P_2O_5 \cdot ha^{-1}$, and 509 kg of $K_2O \cdot ha^{-1}$ were applied to the P8 orchard soil, as well as 64 kg of $N \cdot ha^{-1}$, 91 kg of $P_2O_5 \cdot ha^{-1}$, and 364 kg of $K_2O \cdot ha^{-1}$ were applied to the P18 orchard soil. N, P_2O_5, and K_2O were applied as urea, triple superphosphate, and potassium chloride, respectively. The fertilizers were applied only in the planting row soil (tree canopy projection), on the topsoil, and not incorporated into lower layers. On a yearly basis, the control of weeds within lines was made with the use of herbicides (glyphosate as active ingredient), whereas, between rows, the vegetation was mowed every 90 days, with residues disposed onto the soil surface. The predominant plants that grew spontaneously between the orchard rows were white clover (*Trifolium repens*), red clover (*Trifolium pratenses*), bahiagrass (*Paspalum notatum*), and *Chaptalia nutans*, a genus of the daisy family. The native field used as reference did not have a history of farming and fertilizer addition, consisting primarily of *Paspalum notatum* and *Desmodium* spp.

Soil collecting

In October 2011, 8 years after implementing orchard 1 (P8) and 18 years after implementing orchard 2 (P18), 6 trenches were opened in each orchard, measuring 0.3 × 0.5 × 0.5 m. The trenches were open in the rows. In the native area, 6 trenches were dug randomly in the same dimensions as for the orchards. Soil samples were collected from 0.0 – 0.025; 0.025 – 0.05; 0.05 – 0.10; 0.10 – 0.15; 0.15 – 0.20, and 0.20 – 0.40 m depths in each trench. The soil was air dried, sieved in a 2-mm mesh, and set aside for further analysis.

Physical and chemical characteristics of the soil

For the soil samples, the particle size distribution of the soil constituents was determined by the pipette method (Embrapa 1997) (Table 1). Soil organic carbon was calculated by the Walkley-Black (Embrapa 1997) method, and soil organic matter (SOM) by multiplying the total organic carbon content by 1.724 (Tedesco et al. 1995). Soil pH (in water) was measured using a soil:water suspension at 1:1 v/v, determined after 30 min of equilibrium. Subsequently, a SMP pH 7.5 buffer solution was added to the suspension, and the pH was measured again after 15 min. Available P and K were extracted with Mehlich-1 solution (0.05 $mol \cdot L^{-1}$ HCl + 0.0125 $mol \cdot L^{-1}$ H_2SO_4). P was determined by spectrophotometry, while K, by flame photometry. Exchangeable Ca, Mg, and Al levels were extracted with 1 $mol \cdot L^{-1}$ KCl. Ca and Mg concentrations were determined by atomic absorption spectrometry (AAS), and Al titration, with 0.025 $mol \cdot L^{-1}$ NaOH. Effective cation exchange capacity ($CEC_{effective}$) was calculated by the sum of the exchangeable cations Al + Ca + Mg + K. Cation exchange capacity at pH 7.0 ($CEC_{pH7.0}$) was calculated by the sum of exchangeable bases (Ca + Mg + K), plus H + Al, and estimated using the equation proposed by Kaminski et al. (2002), adopted by CQFS-RS/SC (2004) (Table 1).

Phosphorus chemical fractionation and phosphorus adsorption isotherms

P chemical fractionation was performed according to the method of Hedley et al. (1982), with modifications proposed by Condron and Goh (1989) and Gatiboni et al. (2013), briefly described as follows: 0.5 g of soil were subjected to sequential extraction with an anion exchange resin (Pi_{RTA}), removing labile inorganic P fraction; inorganic and organic P label forms extracted by 0.5 M $NaHCO_3$ (Pi_{bic} and Po_{bic}), which may contribute to the plants' nutrient supply; organic and inorganic P extracted by 0.1 M NaOH (Pi_{hid} and Po_{hid}) and inorganic and organic P extracted by 0.5 M NaOH (Pi_{hid05} and Po_{hid05}), representing the inorganic P on the oxides and silicate clays with intermediary binding energy and the moderate labile organic P fraction; and strongly adsorbed inorganic P extracted by 1 M HCl (Pi_{HCl}). After extractions, the remaining soil was oven-dried at 50 °C and digested with H_2SO_4 + H_2O_2 + $MgCl_2$ ($P_{residual}$),

Table 1. Chemical constituent levels of 6 layers of Humic Cambisol soils from a native area as well as from an 8-year-old (P8) and 18-year-old apple orchards (P18) grown in the plateau region of Santa Catarina, Brazil.

Site	Layer (m)	Clay[a]	Silt[a]	Sand[a]	pH-H$_2$O[b]	Organic matter[b]	P available[c]	Ca^{2+}[a]	Mg^{2+}[a]	CEC$_{pH\ 7.0}$ [d]	CEC$_{effective}$ [d]
		g·kg^{-1}				g·kg^{-1}		mg·kg^{-1}		cmol$_c$·dm^{-3}	
Native area	0.0 – 0.025	91	545	364	5.0	105.5	7.1	4.6	3.6	31.5	10.2
	0.025 – 0.05	106	560	334	4.0	73.1	3.9	2.4	2.4	32.9	7.2
	0.05 – 0.10	113	540	347	3.9	72.8	2.9	1.4	1.3	32.1	6.0
	0.10 – 0.15	111	537	352	3.8	69.8	1.9	0.8	1.0	38.4	5.6
	0.15 – 0.20	139	515	345	3.7	45.2	1.6	0.7	0.7	40.6	6.1
	0.20 – 0.40	151	483	366	3.7	41.5	0.6	0.5	0.6	33.6	5.7
P8	0.0 – 0.025	240	195	565	5.2	50.0	35.3	6.5	8.0	15.1	10.2
	0.025 – 0.05	257	182	561	6.1	47.1	19.7	6.8	3.1	12.8	10.3
	0.05 – 0.10	259	186	555	6.22	37.4	21.7	7.2	3.2	13.4	10.6
	0.10 – 0.15	272	171	557	6.4	38.1	8.6	6.0	4.5	13.5	10.7
	0.15 – 0.20	272	168	560	6.1	32.5	4.8	6.7	4.6	14.5	11.5
	0.20 – 0.40	213	192	595	5.3	13.2	1.5	5.4	3.7	14.4	9.4
P18	0.0 – 0.025	209	211	580	5.2	63.5	95.6	6.8	6.5	21.7	14.2
	0.025 – 0.05	216	199	585	4.9	55.4	95.3	7.7	2.4	18.7	10.5
	0.05 – 0.10	209	210	582	5.1	41.1	83.1	13.7	3.2	17.5	10.9
	0.10 – 0.15	212	201	587	5.4	27.1	83.3	8.2	3.1	16.7	11.7
	0.15 – 0.20	213	208	580	5.5	27.3	79.1	9.0	3.0	17.0	12.3
	0.20 – 0.40	241	185	574	5.5	29.6	51.8	6.7	3.4	14.3	10.4

[a]Embrapa (1997); [b]Tedesco et al. (1995); [c]Murphy and Riley (1962); [d]CQFS-RS/SC (2004).

which may contribute to plant nutrition in situations of extreme shortage in the soil.

The inorganic P of the alkaline extracts of NaHCO$_3$ and NaOH was determined by the method proposed by Dick and Tabatabai (1977). In such alkaline extracts, the total P was determined by autoclave digestion with ammonium persulfate + sulfuric acid; in turn, the organic P was determined by the difference between the total and the inorganic P. The concentration of P in the acid extracts was determined according to Murphy and Riley (1962). P fractions from the Hedley fractionation were grouped into total P inorganic and P organic fractions (Cross and Schlesinger 1995). The total P inorganic fraction was determined by the sum of the inorganic fractions (anion exchange resin + 0.5 M NaHCO$_3$ + 0.1 M NaOH + 0.5 M NaOH + 1 M HCl), while the total P organic fraction, by the sum of the organic fractions (0.5 M NaHCO$_3$ + 0.1 M NaOH + 0.5 M NaOH).

The remaining soil samples from the 0.0 – 0.025 and 0.15 – 0.20 m layers were subjected to determination of P adsorption isotherm parameters, as described by Koski-Vähälä and Hartikainen (2001). For that, 1.0 g of dried soil was added to 15-mL Falcon tubes. Next, 10 mL of a 0.001 mol·L^{-1} CaCl$_2$ solution were added, containing 10 different P concentrations (0.0; 0.5; 1.0; 2.5; 5.0; 7.0; 10.0; 25.0; 50.0 and 75.0 mg·L^{-1}), corresponding to 0, 5, 10, 25, 50, 70, 100; 250; 500 and 750 mg of P·kg^{-1} of soil, respectively. Soon afterwards, the tubes underwent continuous stirring for 16 h in 33-rpm end-over-end, at a temperature of ±25 °C. Later on, the samples were centrifuged at 2,510 g for 10 min, and, in the extract, the remaining P level in solution was determined by the method proposed by Murphy and Riley (1962). The absorbed P was estimated by the difference between the amount added and the amount recovered in the equilibrium solution. Subsequently, the data were adjusted by the mathematical model (Eq.1) proposed by Koski-Vähälä and Hartikainen (2001):

$$P_{sorbed} = (MPAC \times P_{solution} / km +\ _{Psolution}) - Q_0 \tag{1}$$

where: $P_{solution}$ is the concentration of P in the equilibrium solution; km is the concentration of P in the solution that allows for half of the maximum P adsorption; Q_o is the amount of P desorbed in distilled water.

The equilibrium phosphorus concentration (EPC) was determined by adjusting the data via the mathematical model proposed by Koski-Vähälä and Hartikainen (2001). These authors introduced the amount of P desorbed in distilled water (Q_o) that is visually represented by the intersection of lines in the ordinate axis and the EPC, by the intersection of the *x* axis (Eq. 1).

Statistical treatment of the data

P concentrations in the different soil layers in the same site, or within the same layer between the orchards and the native area, were subjected to analysis of variance (ANOVA). P content was used as a dependent variable, while soil layer and site, as independent variables. The results of all analyses were verified by F-test, and when ANOVA was significant, means were separated according to Tukey's test (p ≤ 0.05).

RESULTS AND DISCUSSION

Continuous applications of phosphate fertilizers in apple tree orchards in southern Brazil increased the levels of inorganic P in all fractions assessed (Table 2). Pi_{RTA} and Pi_{bic} fractions were higher in apple-grown soils, especially P18. Levels of Pi_{RTA} (mg·kg^{-1}) at the 20-cm layer (weighted mean) were 20.95 for the native area, 69.73 for P8, and 286.31 for P18. Such contents are considered high (over 20 mg·kg^{-1}) for a native soil and very high (over 40 mg·kg^{-1}) for cultivated (P8 and P18) soils (CQFS-RS/SC 2004). Nonetheless, average contents of available P extracted by Mehlich-1 in the same soil fraction were 3.0; 15.6 and 85.2 mg·kg^{-1} for the native, P8, and P18 soils, respectively (Table 1). These contents are considered very low (≤ 3 mg·kg^{-1} for native area soil), high (12.1 – 24 mg·kg^{-1} for P8), and very high (> 24 mg·kg^{-1} for P18) for such soils (CQFS-RS/SC 2004). These values indicate appropriate P contents in the P8 soil and above the recommended levels in the P18 one. The latter shows no production increases when

Table 2. Fractions of inorganic and residual P (P$_{residual}$) extracted by anion exchange resin (Pi$_{RTA}$), 0.5 mol·L^{-1} NaHCO$_3$ (Pi$_{bic}$), 0.1 mol·L^{-1} NaOH (Pi$_{hid}$), 1 mol·L^{-1} HCl (Pi$_{HCl}$), and 0.5 mol·L^{-1} NaOH (Pi$_{hid05}$) of Humic Cambisol soils from a native area as well as from an 8-year-old (P8) and 18-year-old apple orchards (P18) grown in the plateau region of Santa Catarina, Brazil.

Site	Layer (m)	P fractions (mg·kg^{-1})					
		P$_{iRTA}$	P$_{ibic}$	P$_{ihid}$	P$_{iHCl}$	P$_{ihid05}$	P$_{residual}$
Native area	0.0 – 0.025	8.5 aC*	62.1 aB	17.7 aC	4.4 aC	82.8 abB	132.4 aC
	0.025 – 0.05	25.4 aC	42.1 abB	14.3 abC	3.4 aC	95.0 aB	106.3 bcC
	0.05 – 0.10	24.8 aC	37.1 bcB	13.4 abC	2.4 aC	106.4 aB	110.0 bC
	0.10 – 0.15	25.2 aC	25.2 cB	12.7 abB	0.7 aC	48.5 bcC	96.2 bcdC
	0.15 – 0.20	16.9 aB	24.1 cB	7.6 bB	0.9 aC	38.8 cC	91.6 cdC
	0.20 – 0.40	7.1 aB	26.7 cB	8.6 bB	0.2 aB	37.9 cB	85.3 cC
P8	0.0 – 0.025	159.32 aB	67.3 aB	52.9 aB	37.2 aB	101.1 aB	160.8 aB
	0.025 – 0.05	73.6 bcB	48.8 bB	21.1 bcB	21.0 abcB	88.9 abB	154.0 aB
	0.05 – 0.10	88.7 bB	43.0 bB	26.2 bB	24.9 abB	104.9 aB	154.5 aB
	0.10 – 0.15	54.2 cB	26.0 cB	15.4 cdB	14.5 bcdB	101.7 aB	131.8 bB
	0.15 – 0.20	19.6 dB	22.1 adB	11.4 deB	7.2 cdB	78.6 abB	155.1 aB
	0.20 – 0.40	8.9 dB	9.1 dC	6.9 eB	2.1 dB	57.9 bB	129.4 bB
P18	0.0 – 0.025	285.0 bA	144.5 aA	74.7 bA	254.4 aA	228.8 aA	219.2 abA
	0.025 – 0.05	315.7 aA	113.9 bcA	88.0 aA	214.7 bA	227.9 abA	190.1 cA
	0.05 – 0.10	314.5 aA	128.0 bA	85.8 aA	219.8 bA	221.3 abA	222.7 aA
	0.10 – 0.15	277.1 bA	104.8 cA	64.0 cA	210.2 bA	220.4 abA	206.6 bA
	0.15 – 0.20	253.3 cA	84.6 dA	67.0 bcA	218.9 bA	229.3 aA	211.7 abA
	0.20 – 0.40	167.2 dA	104.6 cA	48.2 dA	118.9 cA	186.9 bA	169.5 dA

*Means followed by the same lower case letter between layers of the same site and means followed by the same upper case letter in the column within the same layer between sites are not significantly different by Tukey's test at 5% probability level.

compared to the former; it only increases the risk for environmental contamination (CQFS-RS/SC 2004; Bai et al. 2013). Gatiboni et al. (2014) conducted a study in soils from Santa Catarina state to assess the potential of P released to water as a function of clay contents in the soil, as well as the contents of available P determined by Mehlich-1. These authors recommend that the limit of P contents in the soil is reached when the available P extracted by Mehlich-1 exceeds the percentage of clay plus 40. Therefore, for P18, which has 21% of clay, the P critical limit is 61 mg·kg^{-1}. Above this threshold, the amount of P desorbed in water would increase dramatically. In the P18 soil, Mehlich-1 resulted in 85.2 mg P·kg^{-1}, indicating high potential of P transfer to water. It can be seen that, for P18, the amount of P applied in maintenance fertilization during crop cycles is probably higher than the amount of P required by the soil and the trees; therefore, it can explain the high contents of Pi_{RTA} and Pi_{bic} (Table 2).

Results for the Pi_{hid} and Pi_{hid05} showed similar tendencies as for the Pi_{RTA} and Pi_{bic} fractions, with higher P contents in the upper surface layers and orchard areas, particularly P18 (Table 2). The P fraction obtained with NaOH extracts mainly the P linked to Fe and Al oxyhydroxides (Cross and Schlesinger1995). Such P levels are proportional to the amount of oxides present in the clay fraction of the soil (Rheinheimer et al. 2008), as well as the previous addition of phosphate fertilizers to the soil (Ciampitti et al. 2011). Pi_{HCl} contents were higher at the topsoil, particularly in the P8 and P18 apple orchards. In the soil of the native area, Pi_{HCl} levels were lower and considered consistent with the weathered soils found in southern Brazil (Rheinheimer et al. 2008; Schmitt et al. 2013b; Schmitt et al. 2014), where apatite is nearly absent. The highest Pi_{HCl} levels found in the P8 and P18 soils are results of the combined action of phosphate fertilizer additions, the raise in soil pH, and the addition of Ca from liming, conditions that are conducive to the neo-formation of Ca phosphate, which is solubilized by 1 mol·L^{-1} HCl. Rheinheimer and Anghinoni (2001) comment that, in no-tillage soils in southern Brazil, an increase in Ca-bound P fractions may occur in soils under continuous application of topsoil phosphate fertilizers. Therefore, a similar phenomenon has likely occurred in the soils of both orchards, because apple growers usually do not define the need and dosage of P based on technical

standards for the crop, such as soil and tissue analysis and expected crop yields. Therefore, fertilizers are generally applied in dosages above the crop needs. In addition, P transport within the plant is low, usually 6 kg P·ha^{-1} year^{-1} in orchards that have an average production of 60 t·ha^{-1} (Nachtigall et al. 2004). The contents of $P_{residual}$ extracted by $H_2SO_4 + H_2O_2 + MgCl_2$ were higher in the P18 soil. This portion represents recalcitrant P, to which plants have difficult access. It may contribute to the plants nutrition only when there is extreme lack of this nutrient in the soil (Schmitt et al. 2013a). Some studies have shown that, in numerous soils from southern Brazil, most of the available P is found in the residual fraction (Rheinheimer et al. 2008; Gonçalves and Meurer 2009). However, after the addition of phosphate fertilizers, a rearrangement of P in the soil and P buildup in all fractions may occur. The event magnitude depends on the P application rate and transport.

Similarly to the concentrations of inorganic P, there was an increase in organic P in all fractions of the soils cultivated with apple trees (Table 3). The highest concentrations of Po_{bic} were found in the P18 soil, except in the 0.05 – 0.10 m layer, where the concentrations were similar to those of the P8 soil. This organic P fraction can be easily mineralized by soil microorganisms (Cross and Schlesinger 1995) and so it can contribute to the inorganic P, especially in soils with low contents of available P, such as that of the native area. The concentrations of Po_{hid} and Po_{hid05} were similar to those of Po_{bic}, higher in the P18 soil. Such higher contents can be explained by the application of fertilizers and lime, which improves the chemical conditions of the soil. Thus, there was an increased production of understory plants that coexist in the orchards, added to the deposition of apple senescent leaves and pruned branches on the soil surface. Following the decomposition of plant debris and thinnest senescent roots in the upper layers of the soil, part of the P present in those tissues may be transported to the soil, cycling the nutrient and incrementing its fractions in the soil (Brunetto et al. 2011).

The results for the total inorganic and organic P show that pre-planting phosphate fertilization and maintenance phosphate fertilization along cycles exceed the levels of P extracted by plants, causing accumulation of inorganic and organic P in the soil (Table 4). Cumulative organic P can be due to the re-establishment of part of the Pi

Table 3. Fractions of organic P extracted by 0.5 mol·L⁻¹ NaHCO₃ (Pi$_{bic}$), 0.1 mol·L⁻¹ NaOH (Po$_{hid}$), and 0.5 mol·L⁻¹ NaOH (Po$_{hid05}$) of Humic Cambisol soils from a native area as well as from an 8-year-old (P8) and 18-year-old apple orchards (P18) grown in the plateau region of Santa Catarina, Brazil.

Site		P fractions		
	Layer (m)	Po$_{bic}$ (mg·kg⁻¹)	Po$_{hid}$ (mg·kg⁻¹)	Po$_{hid05}$ (mg·kg⁻¹)
Native area	0.0 – 0.025	73.2 aC*	195.2 aC	82.8 abB
	0.025 – 0.05	54.9 abC	161.8 bC	95.0 aB
	0.05 – 0.10	59.4 abB	118.1 cC	106.4 aB
	0.10 – 0.15	45.3 abC	107.5 cdC	48.5 bcC
	0.15 – 0.20	34.2 bcC	89.6 dC	38.8 cC
	0.20 – 0.40	8.9 cC	56.2 eC	37.9 cB
P8	0.0 – 0.025	435.5 aB	338.9 aB	101.1 aB
	0.025 – 0.05	224.3 cB	214.4 cB	88.9 abB
	0.05 – 0.10	277.0 bA	248.5 bB	104.9 aB
	0.10 – 0.15	196.8 cB	200.4 cB	101.7 aB
	0.15 – 0.20	149.1 dB	145.5 dB	78.56 abB
	0.20 – 0.40	78.0 eB	120.9 dB	57.9 bB
P18	0.0 – 0.025	549.1 aA	565.2 bA	228.8 aA
	0.025 – 0.05	358.6 bA	630.2 aA	227.9 abA
	0.05 – 0.10	301.8 cA	528.2 cA	221.3 abA
	0.10 – 0.15	302.3 cA	499.7 dA	220.4 abA
	0.15 – 0.20	293.7 cA	433.5 eA	229.3 aA
	0.20 – 0.40	291.5 cA	272.8 fA	186.9 bA

*Means followed by the same lower case letter between layers of the same site and means followed by the same upper case letter in the column within the same layer between sites are not significantly different by Tukey's test at 5% probability level.

Table 4. Total inorganic and total organic P of Humic Cambisol soils from a native area as well as from an 8-year-old (P8) and 18-year-old apple orchards (P18) grown in the plateau region of Santa Catarina, Brazil.

P fractions	Layer (m)	NA	P8	Increase in relation to the NA	P18	Increase in relation to the NA
			mg·kg⁻¹	times	mg·kg⁻¹	times
Total inorganic P[a]	0.0 – 0.025	175.4 aC*	417.8 aB	1.1	987.5 aA	1.5
	0.025 – 0.05	180.2 aC	253.4 cB	0.9	960.2 aA	1.3
	0.05 – 0.10	184.1 aC	287.6 bB	0.8	970.4 aA	1.1
	0.10 – 0.15	112.3 bC	211.9 cB	1.0	877.5 bA	1.5
	0.15 – 0.20	88.4 bC	139.9 dB	0.9	853.2 bA	1.6
	0.20 – 0.40	80.4 bB	84.8 eB	0.6	625.8 cA	1.3
	CV%			1.9		
Total organic P[b]	0.0 – 0.025	358.8 aC	841.8 aB	1.1	1,244.7 aA	0.9
	0.025 – 0.05	272.2 bC	481.5 cB	1.1	1,240.2 aA	1.1
	0.05 – 0.10	197.1 cC	558.2 bB	1.4	1,063.6 bA	1.2
	0.10 – 0.15	183.3 cC	426.5 cB	1.2	976.7 cA	1.0
	0.15 – 0.20	154.5 cC	315.7 dB	1.1	904.1 dA	1.0
	0.20 – 0.40	81.4 dC	216.8 eB	1.5	667.6 eA	1.4

[a]Total inorganic P, sum of inorganic fractions; [b]Total organic P, sum of organic fractions. *Means followed by the same lower case letter in the column and means followed by the same upper case letter in the row are not significantly different according to Tukey's test at 5% probability level. NA = Native area.

into Po by higher biomass production, particularly by the understory opportunistic plants coexisting with the apple trees. Furthermore, studies show that additions of inorganic P above the plants extraction capacity cause accumulation of organic fractions (Ciampitti et al. 2011; Schmitt et al. 2014). Thus, plants and microorganisms have sufficient amounts of nutrients for development without the need to mineralize the organic sources. On the other hand, in the native soil, which shows low levels of P, plants and microorganisms must have adaptive strategies, such as exudation of phosphatases, to obtain the required amount of P (Schen et al. 2011).

Distribution of P in organic and inorganic forms in soils cultivated with apple trees was very similar to that found in the native area (Table 4). This shows that phosphate buildup by applications of fertilizers occurs in both organic and inorganic forms, contrasting the studies conducted by Brunetto et al. (2013) and Couto et al. (2014), who showed a preferential P accumulation in the inorganic forms, previously present in the soil. These results may be explained by the high concentrations of organic matter (> 5%; CQFS-RS/SC 2004), both in the native and in the orchards soils, caused by the higher altitude and, consequently, the lower atmosphere and soil temperature (Oliveira et al. 2014). In such conditions, there seems to be a higher conversion of P added via fertilization to organic forms, corroborating the results obtained by Tiecher et al. (2012a,b) for a 23-year-old no-tillage Latosol cultivated with different crop rotations in southern Paraná, Brazil.

Parameters for the phosphorus adsorption isotherms

The highest MPAC values were found in the 0.15 – 0.20 m layer in relation to the 0.0 – 0.025 m one for all soils (Table 5). The soil of the native area and the P8 showed higher MPAC values in the 0.0 – 0.025 m layer. In the 0.15 – 0.20 m depths, the highest MPAC levels were found in the native area, followed by P8 and P18. These higher values in the soil of the native area are likely to be due to a lower saturation of the soil sorption sites. The lowest MPAC values in the P18 soil can be explained by the long history (over 18 years of cultivation) of phosphate fertilizers application, which favored the occupation of the sorption sites by that element, especially those located in the soil inorganic reactive particles (Nwoke et al. 2003). P concentration in the solution that allows for half of the maximum P adsorption (km) was higher in the P18 soil (24.02 mg·L^{-1}), followed by the P8 (8.95 mg·L^{-1}), and the native area soil (1.83 mg·L^{-1}). These results show that, in the native area, the shape of the curve is indicative of higher adsorption, whereas, in the fertilized areas, the isotherm curve is not as accentuated. However, the highest concentrations of P desorbed in water (Qo) were found in the 0.0 – 0.025 m layer of the P8 and P18 soils and in the 0.15 – 0.20 m layer of the native soil (Table 5).

Regarding the equilibrium phosphorus concentration (EPC) parameter, the highest values were found in the 0.0 – 0.025 m layer in relation to the 0.15 – 0.20 m one

Table 5. Parameters related to the adsorption isotherms adjusted by Koski-Vähälä and Hartikainen equation in the 0.0 – 0.025 and 0.15 – 0.20 m depths of Humic Cambisol soils from a native area as well as from an 8-year-old (P8) and 18-year-old apple orchards (P18) grown in the plateau region of Santa Catarina, Brazil.

Site	MPAC[a]	km[b]	Q$_o$[c]	EPC[d]
	mg·kg^{-1}	mg·L^{-1}		
0.0 – 0.025 m				
Native area	524.53 bB*	3.39 cA	54.06 bB	0.39 cA
P8	517.57 bB	9.93 bA	83.44 aA	1.89 bA
P18	425.63 aB	25.54 aA	71.31 aA	5.13 aA
0.15 – 0.20 m				
Native area	839.73 aA	0.28 cA	73.59 aA	0.03 cB
P8	580.10 bA	7.96 bA	36.26 bB	0.53 bB
P18	475.83 cA	22.51 aA	70.40 aA	4.93 aA

[a] Maximum phosphate adsorption capacity; [b] Equilibrium P concentration in the solution that allows for half the maximum P adsorption; [c] Amount of P desorbed in water; [d] Equilibrium P concentration; *Means followed by the same lower case letter in the column and in the same depth and upper case letters in the same treatment, but between depths, are not significantly different by Tukey's test (a = 5%). MPAC = Maximum P adsorption capacity; km = Concentration of P in the solution that allows for half of the maximum P adsorption; Q$_o$ = is the amount of P desorbed in distilled water; EPC = Equilibrium phosphorus concentration.

in the soils of the native and P8 areas. This was expected, once the highest concentrations of available P, Pi_{RTA}, and Pi_{bic} were found in the topsoil, particularly in the P8 and P18 (Table 1). The highest EPC values were observed in the P18, followed by the P8 soil (Table 5). EPC is a key theoretical parameter in the study of potential soil contamination, because it indicates that, in the case of erosion of a P-rich soil (sediment) carried to a water body, the potential release of this element to the water will occur every time that the concentration of P soluble in the water body is lower than the EPC. Thus, regarding the highest EPC values, the km, and MPAC, the P18 orchard soil presented higher potential risk for P contamination in water bodies, mainly from surface runoffs.

CONCLUSION

Successive applications of phosphate fertilizers in apple orchards in the highland regions of Santa Catarina state increase P concentrations in all forms assessed by the Hedley fractionation method. Such increase is higher in older orchards and more pronounced in the soil upper layers.

Distribution of P in organic and inorganic forms in the soils planted with apple trees was similar to the distribution of P observed in the soil with native vegetation, indicating that the accumulation of phosphate via fertilizer occurs proportionally in the P forms previously present in the soil.

The combined assessment of P chemical fractionation with parameters of P adsorption isotherms in the soil indicates that the indiscriminate application of phosphate fertilizers onto the soils of apple orchards in the highland regions of Santa Catarina state is transforming such areas into critical environments, posing a great risk of phosphate contamination to water bodies due to surface runoffs.

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