Alterations of chemical attributes in soils under different years of *Vitis vinifera* L. cultivation

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Abstract

Among the problems related to over fertilization in vineyards is the indiscriminate use of N, P and K and Cu- and Zn-based pesticides, which result which may lead to degradation of soil chemical attributes and in nutritional imbalance to plants. This study aimed to evaluate changes in chemical attributes of soils with different years of cultivation of *Vitis vinifera* L. cv. Pinot Noir. Soils with different cultivation periods (4, 9 and 16 years) and at different depths (0-10, 10-20, 20-30, 30-40, 40-50 and 50-60 cm) were analyzed. The following soil chemical attributes were evaluated: pH$_{\text{H}_2\text{O}}$, H+Al, OM, available phosphorus and potassium, exchangeable calcium, magnesium and aluminum, manganese, copper, zinc and boron, besides cation exchange capacity (CEC), base saturation and aluminum saturation. The experimental design was randomized blocks in split plots, considering three times after planting (4, 9 and 16 years) and six depths (0-10, 10-20, 20-30, 30-40, 40-50 and 50-60 cm), with three replicates. Soil chemical attributes were subjected to analysis of variance and means were compared by Tukey test (p<0.05). There was significant variation in the macro and micronutrient contents in relation to both the areas and the depths. Areas with 9 and 16 years had higher macronutrients and micronutrients contents, mainly in the first 10 cm depth, due to the successive uses during the years of vineyard management after the planting of the vines.

*Keywords:* Nutrient availability, grapes, soil fertility.

Alterações de atributos químicos em solos sob diferentes anos de cultivo de *Vitis vinifera* L.

Resumo

Entre os problemas relacionados à super fertilização nas vinhas, está o uso indiscriminado de N, P e K e de pesticidas à base Cu e Zn, que podem resultar na degradação dos atributos químicos do solo e no desequilíbrio nutricional das plantas. Este estudo teve como objetivo avaliar alterações nos atributos químicos de solos com diferentes anos de cultivo de *Vitis vinifera* L. cv. Pinot Noir. Foram analisados solos com diferentes períodos de cultivo (4, 9 e 16 anos) e em diferentes profundidades (0-10, 10-20, 20-30, 30-40, 40-50 e 50-60 cm). Foram avaliados os seguintes atributos químicos do solo: pH$_{\text{H}_2\text{O}}$, H + Al, MO, fósforo e potássio disponíveis, cálcio, magnésio e aluminio trocáveis, manganês, cobre, zinco e boro, além da Capacidade de troca de cátions (CTC), saturação por bases e saturação por alumínio. O delineamento experimental foi de blocos casualizados em parcelas subdivididas, considerando três períodos de cultivo (4, 9 e 16 anos) e seis profundidades (0-10, 10-20, 20-30, 30-40, 40-50 e 50-60 cm), com três repetições. Os atributos químicos do solo foram submetidos à análise de variância e as médias foram comparadas pelo teste de Tukey (p < 0.05). Houve variação significativa nos teores de macronutrientes e micronutrientes em relação às áreas e profundidades. Áreas com 9 e 16 anos apresentaram maiores teores de macronutrientes e micronutrientes, principalmente nos primeiros 10 cm de profundidade, devido aos usos sucessivos durante os anos de manejo da vinha após o plantio das vinhas.

Palavras-chave: Disponibilidade de nutrientes, videiras, fertilidade do solo.

Introduction

In the last decades, the expansion of viticulture in Rio Grande do Sul, Brazil, has been basically due to the exploitation of other regions with satisfactory Terroir for the production of wine grapes intended for the manufacture of fine wines, such as sparkling wines. The Southeastern highlands of Rio Grande do Sul, with predominance of granitic rocks, have soils which are naturally acidic and with low natural fertility, which is the reason why careful soil correction and fertilization become necessary (Brunetto, 2008; Giovannini & Marin, 2009).

The vine adapts to a wide variety of soils, with nitrogen, potassium and phosphorus, at moderate contents, being the essential elements for its development. Magnesium, manganese, iron, zinc, copper and boron are required at residual contents, with pH ranging from 5.0 to 6.0 and with
organics matter content of at least 20 g dm-3. Therefore, the soil must have nutrients that contribute to the increase of cation exchange capacity (CEC) and consequently to base saturation (V%), besides altering the availability of micronutrients and reducing the levels of exchangeable Al and Mn (Cafres, 2004).

However, liming and fertilization performed in vineyards in southern Brazil often do not use prediction criteria based on soil analysis. Among the problems related to over fertilization in vineyards is the indiscriminate use of N, P and K and Cu- and Zn-based pesticides, which result in nutritional imbalance to plants.

Excess N makes the grapevine very vigorous, prolonging the vegetative growth period and delaying fruit ripening (Hibert et al., 2003). This situation leads to the formation of water, soft berries, reduction in bud fertility and greater shading, forming smaller bunches with higher acidity. Excess P causes increase in must acidity, reduces juice content in pulp and may induce deficiency of Fe and Zn (Fregoni, 1980). In regard to K, its excess leads to rachis drying, due to lower absorption of Ca, early entry in vegetative rest and delayed resumption of vegetative activity by the plant in the next cycle, besides causing Mg deficiency (Tagliavini, Scudellazi, Marangoni, & Toselli, 1996).

Vineyards in Southern Brazil require a large amount of copper- and/or zinc-based fungicides, because plants are very sensitive to the high levels of rainfall, relative air humidity and temperatures found in this region, especially during the production cycle (Jermini, Blaise, & Gessler, 2010; Couto et al., 2015; Ambrosini et al., 2016). Thus, over the years Cu and Zn contents may increase, especially in the most superficial soil layers, because normally the soil is not turned, and Cu and Zn are complexed with the functional groups of the organic matter and also adsorbed to the functional groups of clay minerals (Casali et al., 2008; Nogueiro, Alleoni, Nachtigall, & Melo, 2010; Fernández-Calviño, Pateiro-Moure, & Nóvoa-Muñoz, 2012).

When in excess in the soil, Cu and Zn can cause modifications in root morphology and anatomy, leading to reduction in nutrient absorption, causing nutritional deficiency in the plants, which can be diagnosed by the analysis of leaf tissues (Pavlikova et al., 2008; Kopittke, Asher, Blamey, & Menzies, 2009; Toselli et al., 2009; Chen, Lee, Chen, & Juang, 2013).

This study aimed to evaluate changes in chemical attributes of soils with different years of cultivation of V. vinifera L. cv. Pinot Noir. Soils with different cultivation periods (4, 9 and 16 years) and at different depths (0-10, 10-20, 20-30, 30-40, 40-50 and 50-60 cm) were analyzed.

**Material and Methods**

**Study area**

The study was carried out in a vineyard located in the municipality of Encruzilhada do Sul at 30° 43’ 12.74” of latitude South and 52° 37’ 54.23” of longitude West of Greenwich at 361 m of altitude, with rainfall and mean annual temperature of 1,541 mm and 17.1 °C, respectively, and relief predominantly formed by gentle hills (Cunha, Pires, Pasinato, & Dalmago, 2005). Soil samplings were carried out in three areas with different years of cultivation after the seedlings were planted. Table 1 presents the textural characteristics of the studied areas, where soils range from silty loam to silty clay loam.

The number of plants, soil type and location of each region studied (according to cultivation time) were:

- 4 years of planting: total area of 6.10 ha, with 118,788 plants grown in a Cambissolo Háplico Tb Distrófico latossólico (Inceptisol), located at 30° 43’ 01.48” S and 52° 37’ 42.74” W of Greenwich, at 346 m of altitude.
- 9 years of planting: total area of 5.13 ha, with 15,800 plants, grown in an Argissolo Vermelho Distrófico úmbrico (Ultisol), located at 30° 43’ 16.25” S and 52° 37’ 44.64” W of Greenwich, at 353 m of altitude.
- 16 years of planting: total area of 5.76 ha, with 17,850 plants, grown in an Argissolo Vermelho Distrófico típico (Ultisol), located at 30° 42’ 29.48” S and 52° 37’ 54.79” W of Greenwich, at 335 m of altitude.

**Table 1. Granulometric distribution (g kg⁻¹), textural classification and particle density (Dp, g cm⁻³) of the areas with different years cultivation after grapevine planting and different depth (cm).**

| Depth | Total | Silt | Clay | Textural Classification | Dp  |
|-------|-------|------|------|-------------------------|-----|
|       | Sand  |      |      |                         |     |
| 4 years |
| 0-10  | 167   | 704  | 123  | Silty loam              | 2.50|
| 10-20 | 196   | 647  | 157  | Silty loam              | 2.49|
| 20-30 | 231   | 575  | 193  | Silty loam              | 2.53|
| 30-40 | 107   | 596  | 297  | Silty clay loam         | 2.50|
| 40-50 | 109   | 547  | 343  | Silty clay loam         | 2.53|
| 50-60 | 145   | 418  | 437  | Silty clay              | 2.54|
| 9 years |
| 0-10  | 139   | 651  | 210  | Silty loam              | 2.47|
| 10-20 | 147   | 633  | 220  | Silty loam              | 2.51|
| 20-30 | 104   | 656  | 240  | Silty loam              | 2.48|
| 30-40 | 125   | 618  | 257  | Silty clay loam         | 2.53|
| 40-50 | 87    | 516  | 397  | Silty clay              | 2.50|
| 50-60 | 78    | 462  | 460  | Silty clay              | 2.46|
| 16 years |
| 0-10  | 202   | 711  | 87   | Silty loam              | 2.47|
| 10-20 | 226   | 677  | 97   | Silty loam              | 2.52|
| 20-30 | 213   | 597  | 190  | Silty loam              | 2.52|
| 30-40 | 253   | 554  | 193  | Silty loam              | 2.55|
| 40-50 | 234   | 496  | 270  | Clay loam               | 2.55|
| 50-60 | 102   | 575  | 323  | Silty clay loam         | 2.52|

The soil acidity correction is performed with the use of dolomitic limestone, with an average of 10 to 12 t ha⁻¹ per application. Two to three applications of this dosage are performed at pre-planting and incorporated, aiming to maintain the pH at 6.5, recommended for vines (CQPS - RS/SC, 2004), with annual application followed by incorporation. After planting, the limestone applications were

Acta Brasiliensis 3(3): 116-123, 2019

117
carried out using pelleted FIDAGRAN formulation. Fertilization with N, P and K, with annual application, occurred in the plant rows, with approximately 7 kg ha⁻¹ of N, 63 kg ha⁻¹ of P₂O₅ and 63 kg ha⁻¹ of K₂O.

Fertilization with nitrogen is carried out by observing the vegetative development of the plants; when it is low, N is applied at 10, 40 and 70 days after sprouting, whereas phosphorus and potassium are applied 10 days before winter pruning and 10 days after pruning, according to the fertilization recommendation for the crop (CQFS - RS/SC, 2004). Ca, Mg, Mn, Cu, Zn, S and B are applied to the soil along with NPK fertilizers. Ca and B are also applied through the leaves at the pre-flowering stage. Zn, Mn and Cu sprays occur indirectly, as they are in the composition of many fungicides such as Dithane, Kocide, Ellect, Garra B. Complementary application is also made via soil, in some cases Mg, usually foliarily applied 5 to 7 times per cycle.

Sample collection and analysis

Disturbed soil samples were collected in the layers of 0-10, 10-20, 20-30, 30-40, 40-50 and 50-60 cm, with three replicates, in each of the three vineyard areas with different times of cultivation after planting the seedlings. Samples were collected from the planting row up to the middle of the interrow.

The samples were air dried and sieved through a 2-mm mesh for the analysis of soil chemical attributes, according to Tedesco, Gianello, Bissani, Bohnen, and Volkweiss (1995). Active soil acidity was determined in water (pH₂O₂) and potential acidity (H⁺-Al), by titration, after extraction with 0.5 mol L⁻¹ calcium acetate solution. Organic matter (OM) was estimated based on the content of organic carbon (OC), determined by the modified Walkley-Black wet combustion method (Tedesco et al., 1995).

Available phosphorus (H₃PO₄) and potassium (K⁺) were determined with 3 g of soil and 30 mL of Mehlich-1 extraction solution, which were kept on a horizontal shaker for 2 hours, followed by a 15-hour rest period for soil decantation, and then the absorbance reading was taken on the spectrophotometer. Exchangeable calcium (Ca²⁺), magnesium (Mg²⁺) and aluminum (Al³⁺) were determined by extraction with potassium chloride (0.1 mol L⁻¹ KCl). Manganese (Mn), copper (Cu²⁺) and zinc (Zn²⁺) with 10 g of soil, were determined by extraction with 0.1 mol L⁻¹ HCl (pH 1.2) in the 1:4 soil:solution ratio, shaken for 30 minutes on a horizontal shaker, later decanted for 16 hours, and read in Atomic Absorption Spectrophotometer (Perkin Elmer, 2380). Boron (B) was obtained by extraction with hot water and determined by colorimetry. CEC was determined based on the sum of exchangeable cations of the soil (Na⁺, K⁺, Cu²⁺, Mg²⁺) displaced by ammonia ions at buffered pH 7.0 (Tedesco et al., 1995). Base saturation was determined considering the ratio between the exchangeable bases and CEC at pH 7.0, and aluminum saturation was determined based on the ratio between Al³⁺ and effective CEC (Tedesco et al., 1995).

Statistical analysis

The experimental design was randomized blocks in a split-plot scheme, considering the three years of management after grapevine planting as main plots (4, 9 and 16 years) and six depths as subplots (0-10, 10-20, 20-30, 30-40, 40-50 and 50-60 cm), with three replicates, totaling 54 samples. Soil chemical attributes were subjected to analysis of variance and means were compared by Tukey test (p<0.05).

Results and Discussion

In general, there were increased contents of exchangeable calcium (Ca²⁺exc) and exchangeable magnesium (Mg²⁺exc), especially in the younger areas, 4 and 9 years, compared with the older area, 16 years of cultivation (Table 2), regardless of depth.

The contents observed after the three periods of management were considered as high (CQFS - RS/SC, 2004), corroborating the results found by Cassol (2008) and Mafra (2009) in vineyards with the cv. Cabernet Sauvignon at the Santa Catarina Highlands subjected to successive corrections of soil acidity, as well as phosphate fertilization, because calcium, besides being a component in soil acidity correctives, is also present in the composition of phosphate fertilizers.

Soil pH values varied from 4.20 to 6.43 (Table 2). The values in the area under longest period of grapevine cultivation (16 years) were below the recommendation for grapevine, which is pH 6.0 (CQFS - RS/SC, 2004), compared with the younger areas (4 and 9 years), regardless of depth. These results can be attributed to the successive applications, in the oldest vineyard, of ammoniacal nitrogen fertilizers and urea, which are often carried out indiscriminately, considering only plant development, corroborating the results found by Teixeira, Panosso, Cerri, Pereira, & La Scala (2011) in a vineyard in the São Francisco Valley. The nitrification process leads to the formation of two (H⁺) protons for every NH₃ ion nitrified (Campos, 2004; Batista, 2006), which, associated with the loss of cations to deeper layers accompanying the NO₃⁻ anion, acidifies the soil (Tisdale, Nelson, Beaton, & Havlin, 1993).

Soil potential acidity (H⁺-Al) ranged from 2.23 to 19.40 cmolc dm⁻³, as depth increased, regardless of the time of grapevine cultivation (Table 2). In surface, the lowest values are similar to those found by Tecchio, Teixeira, Moura, Pires, and Terra (2012), in vineyards with the cv. ‘Niagara Rosada’ in the São Paulo state. These authors attributed the values of soil potential acidity to the practice of liming and to the action of soil organic matter (OM).

OM contents varied between 13 and 29 g kg⁻¹, with highest values in the superficial soil layers (Table 3). The area with 16 years of cultivation after grapevine planting showed lower OM values, compared with the younger areas, which is attributed to successive managements of rows and interrows, with chemical and mechanical control of cover plants.

Sulfur contents (S-SO₄) increased in subsurface for the three times of management after grapevine planting, and the highest values were observed from the 30 cm depth (Table 3). Among the factors related to S accumulation in subsurface, pH becomes one of the main controllers of SO₄²⁻ availability and movement. Thus, more SO₄²⁻ remains free in the soil solution and the surplus can be easily leached to subsurface horizons, which may mean loss if high rainfalls occur (Alvarez, 2004).

Similar results were observed in a vineyard with the cv.
Phosphorus accumulation in a commercial vineyard with 14 and 20 months of application and observed greater S accumulation in the second period of evaluation, especially in the first 60 cm depth.

Table 2. Contents of exchangeable calcium (Ca$^{2+}\text{exc}$), contents of exchangeable magnesium (Mg$^{2+}\text{exc}$), active acidity (pH$_H^2O$) and potential acidity (H+Al) of the areas with different years cultivation after grapevine planting and different depth (cm).

| Depth (cm) | 4 | 9 | 16 | 4 | 9 | 16 |
|-----------|---|---|----|---|---|----|
|           | Ca$^{2+}\text{exc}$, cmol dm$^{-3}$ | Mg$^{2+}\text{exc}$, cmol dm$^{-3}$ | pH$H^2O$ | H+Al, cmol dm$^{-3}$ |
| 0-10      | 5.40±1.27$^b$ | 5.97±0.78$^a$ | 4.70±1.40$^b$ | 2.40±0.40$^a$ | 2.20±0.20$^a$ | 1.63±0.36$^b$ |
| 10-20     | 3.97±1.24$^b$ | 6.50±0.93$^a$ | 3.87±1.09$^b$ | 2.27±0.29$^a$ | 2.67±0.38$^a$ | 1.83±0.42$^b$ |
| 20-30     | 2.50±1.27$^b$ | 4.00±0.80$^a$ | 2.33±0.71$^b$ | 2.13±0.42$^a$ | 2.03±0.62$^a$ | 1.37±0.10$^b$ |
| 30-40     | 1.47±0.76$^b$ | 4.00±0.53$^a$ | 1.43±0.44$^b$ | 1.77±0.84$^b$ | 2.03±0.62$^a$ | 1.00±0.27$^c$ |
| 40-50     | 0.77±0.18$^b$ | 1.23±0.38$^a$ | 1.20±0.47$^a$ | 1.23±0.62$^a$ | 0.93±0.16$^b$ | 0.83±0.31$^b$ |
| 50-60     | 5.17±1.89$^a$ | 2.10±0.73$^b$ | 0.90±0.20$^c$ | 0.80±0.27$^a$ | 1.27±0.24$^a$ | 0.67±0.16$^b$ |

Mean values followed by the same capital letters (between cultivation times for the same variable) and lowercase letters (between depths for the same variable) showed no significant difference by Tukey test ($p$ < 0.05).

Table 3. Contents of organic matter (OM), sulfur (S-SO$_4^-$), available phosphorus (H$_3$PO$_4$$_{ava}$) and available potassium (K$_{ava}$) of the areas with different years cultivation after grapevine planting and different depth (cm).

| Depth (cm) | 4 | 9 | 16 | 4 | 9 | 16 |
|-----------|---|---|----|---|---|----|
|           | OM, g kg$^{-1}$ | S-SO$_4^-$, mg cm$^{-3}$ | H$_3$PO$_4$$_{ava}$, mg cm$^{-3}$ | K$_{ava}$, mg cm$^{-3}$ |
| 0-10      | 27.33±6.22$^b$ | 29.00±6.00$^a$ | 23.67±4.44$^c$ | 1.10±0.67$^a$ | 12.33±1.12$^a$ | 10.15±0.85$^a$ |
| 10-20     | 20.00±2.67$^b$ | 23.00±3.33$^a$ | 17.67±0.44$^c$ | 12.33±1.78$^a$ | 14.00±3.33$^a$ | 13.13±4.58$^a$ |
| 20-30     | 17.67±2.22$^b$ | 20.67±3.56$^a$ | 17.67±1.56$^c$ | 17.00±4.00$^b$ | 21.33±4.44$^a$ | 18.67±7.56$^a$ |
| 30-40     | 17.00±2.67$^b$ | 20.67±3.11$^a$ | 16.67±0.89$^b$ | 30.00±6.67$^b$ | 21.33±11.56$^b$ | 35.67±10.89$^b$ |
| 40-50     | 14.67±3.11$^a$ | 16.67±3.56$^a$ | 15.00±2.00$^a$ | 49.67±8.89$^a$ | 75.33±5.56$^a$ | 49.00±12.00$^b$ |
| 50-60     | 13.00±2.67$^b$ | 17.00±5.33$^a$ | 13.33±1.56$^b$ | 56.00±8.67$^b$ | 69.33±7.78$^a$ | 74.00±17.33$^a$ |

Mean values followed by the same capital letters (between cultivation times for the same variable) and lowercase letters (between depths for the same variable) showed no significant difference by Tukey test ($p$ < 0.05).

Available phosphorus (H$_3$PO$_4$$_{ava}$) contents in the soil varied from 1.17 to 38.33 mg dm$^{-3}$, with highest values in the first 10 cm depth, particularly in the areas with 9 and 16 years, in which 72% and 68% of the total phosphorus contents were available, whereas in the area with 4 years of cultivation 37% of the total phosphorus content was available at this same depth (Table 3). Similar results were found by Mello et al. (2012), evaluating phosphorus accumulation in a commercial vineyard with 14 and 30 years of cultivation. These authors found higher phosphorus contents in the first 5 cm depth and attributed these results to the application of phosphate fertilizers in the maintenance fertilization, applied on surface and without incorporation, during the cycle of the grapevines.

Available potassium (K$_{ava}$) contents varied from intermediate to high (CQFS - RS/SC, 2004), and the highest values occurred in the areas with 9 and 16 years of...
cultivation (Table 3). The behavior was similar to that observed for phosphorus contents, in which potassium fertilization along the years of grapevine cultivation, without incorporation, led to accumulation of this nutrient in the first 10 cm depth, corroborating the results found by Dalla Rosa et al. (2009), in a vineyard with 28 years of planting at the Rio Grande do Sul Highlands, and by Luciano (2012), evaluating the variability of nutrients in soil cultivated with grapevine at the Santa Catarina Highlands.

According to Oliveira, Trivelin, Boaretto, Muraoka, and Mortatti (2002), liming favors the maintenance of the K-ava content in the superficial soil layer, because it increases the effective CEC and reduces losses by leaching. However, depending on the potassium content in the soil and rainfall intensity, this element may move to subsurface layers by mass flow, due to water percolation following the gravitational force, which is greater than the horizontal movement of this nutrient in the soil (Ernani, Almeida, & Santos, 2002; Ernani, Dias, & Flore, 2007).

Exchangeable acidity (Al\textsuperscript{3+}\textsubscript{exc}) ranged from 0 to 4.30 cmolc dm\textsuperscript{-3}, with lowest values in the first 30 cm depth. Younger areas, 4 and 9 years of cultivation after planting, showed lower values compared to the area with 16 years (Table 4). These results can be attributed to both liming and the higher OM contents found in the younger areas and are similar to those found by Blum (2008), who analyzed the effect of soil correction after 8 and 20 months of agricultural gypsum application, and by Stöcker (2015), who evaluated the effect of liming in vineyards with different periods of cultivation after planting.

| Depth (cm) | 4 | 9 | 16 |
|-----------|---|---|----|
| 0-10      | 0.00±0.00\textsuperscript{A} | 0.07±0.09\textsuperscript{A} | 0.00±0.00\textsuperscript{B} |
| 10-20     | 0.03±0.04\textsuperscript{B} | 0.30±0.33\textsuperscript{A} | 0.00±0.00\textsuperscript{B} |
| 20-30     | 0.17±0.20\textsuperscript{B} | 1.27±0.96\textsuperscript{B} | 0.30±0.33\textsuperscript{B} |
| 30-40     | 1.07±1.09\textsuperscript{C} | 3.00±0.80\textsuperscript{A} | 2.30±0.62\textsuperscript{BC} |
| 40-50     | 2.43±0.89\textsuperscript{A} | 3.50±0.47\textsuperscript{A} | 5.37±18.5\textsuperscript{A} |
| 50-60     | 3.20±0.47\textsuperscript{A} | 4.30±0.33\textsuperscript{A} | 35.67±6.29\textsuperscript{A} |

Mean values followed by the same capital letters (between cultivation times for the same variable) showed no significant difference by Tukey test (p < 0.05).

As a consequence of the reduction in Al\textsuperscript{3+}\textsubscript{exc} contents, aluminum saturation (m\%) varied from 0 to 72% in the studied areas, with the lowest values in the first 30 cm depth, especially in the younger areas, 4 and 9 years of cultivation after planting, compared with the area with 16 years (Table 4). With the practice of liming, cation exchange sites were occupied by exchangeable bases, simultaneously increasing soil pH and base saturation, and at the same time reducing the values of aluminum saturation (Nicolodi, Anghinoni, & Gianello, 2008).

For the results of base saturation (V%), the areas showed values ranging from 8 to 79%, with highest values in the first 30 cm depth, especially in the younger areas, 4 and 9 years of cultivation after planting, in comparison to the area with 16 years (Table 4). These results can be attributed to the application of calcium and magnesium carbonates, besides fertilizers containing these nutrients in their composition, which besides contributing to the correction of the superficial acidity of the soil, was also responsible for the supply of Ca\textsuperscript{2+}\textsubscript{exc} and Mg\textsuperscript{2+}\textsubscript{exc} in the first 30 cm, especially in the younger areas (4 and 9 years), leading to increase in sum of bases and consequently in base saturation.

Similar results were found in vineyards of Vitis labrusca with the cv. ‘Niagara Rosada’, in the municipality of Ponta Grossa-PR (Blum, 2008) and with the cv. ‘Bordô’ in the municipality of Pelotas-RS (Stöcker, 2015), both studies analyzing soil fertility in different periods of grapevine cultivation.

The values of cation exchange capacity (CEC\textsubscript{pH7.0}), in general, were within the range recommended for the grape crop (3 to 15 cmolc dm\textsuperscript{-3}), and the highest values were observed in the first 30 cm depth (Table 4), especially in the areas with 4 and 9 years of cultivation after planting. Higher CEC values in surface, especially in younger areas (4 and 9 years), are related to the higher OM contents found in these sites. Ronquim et al. (2010) highlights that, according to the nature of the clay mineral (1:1 or 2:1), CEC may vary from 30 to 2,000 cmolc kg\textsuperscript{-1}, whereas the OM, normally present in lower amount, has CEC about five times higher than that of clays and can also exhibit large variation depending on the

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Table 4. Content of exchangeable aluminum (Al\textsuperscript{3+}\textsubscript{exc}), aluminum saturation (m), base saturation (V) and cation exchange capacity (CEC) of the areas with different years cultivation after grapevine planting and different depth (cm).

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Acta Brasiliensis 3(3): 116-123, 2019
molecular weight of the COOH groups.

The contents of copper (Cu\(^{2+}\)) found in the soil are considered as intermediate to high (Comissão de Química e Fertilidade do Solo - RS/SC [CQFS - RS/SC], 2004) in all areas studied (Table 5), with highest values in the first 10 cm, especially in the area with 16 years of planting, followed by the areas with 9 and 4 years. These results can be attributed to the successive application of copper fungicides for phytosanitary treatment of the vineyard. Extremely high contents of Cu, exceeding 3000 mg kg\(^{-1}\) have been reported by Mirlean, Roisenberg and Chies (2007) in clay soils of vineyards in Southern Brazil.

The behavior of zinc (Zn\(^{2+}\)) was similar to that of Cu, with accumulation in surface (Table 5), especially in the older area (16 years), compared with the younger areas (4 and 9 years), due to the successive applications of fungicides, which, besides Cu, also contain Zn in their formulation. Similar results have been found in other vineyards grown for long periods (Weingerl & Kerin, 2000; Chaignon, Sanchez-Neira, Herrmann, Jaille, & Hinsinger, 2003; Gaw, Wilkins, Kim, Palmer, & Robinson, 2006; Ramos, Nolla, Korndorfer, Pereira, & Camargo, 2006; Costa, 2009; Stöcker, 2015). In general, boron (B) contents ranged from 0.50 to 1.50 mg dm\(^{-3}\) and are considered as high for the grape crop according to CQFS - RS/SC (2004). The highest values were found in the area with 9 years of cultivation after planting (Table 5), which may be associated with the higher OM content in this site (Abreu, Lopes, & Santos, 2007; Dechen & Nachtigall, 2007).

### Table 5. Contents of copper (Cu\(^{2+}\)), zinc (Zn\(^{2+}\)), boron (B) and manganese (Mn) of the areas with different years cultivation after grapevine planting and different depth (cm).

| Depth (cm) | Cu\(^{2+}\), mg dm\(^{-3}\) | Cultivation time, years | Zn\(^{2+}\), mg dm\(^{-3}\) | B, mg dm\(^{-3}\) | Mn, mg dm\(^{-3}\) |
|-----------|------------------|----------------|-----------------|--------------|---------|
| 0-10      | 1.00±0.13\(^{aA}\) | 6.30±4.47\(^{aA}\) | 8.55±5.45\(^{aA}\) | 0.90±0.33\(^{aCD}\) | 3.40±1.67\(^{aB}\) |
| 10-20     | 0.53±0.04\(^{aA}\) | 0.80±0.27\(^{aA}\) | 1.20±0.27\(^{aB}\) | 0.63±0.18\(^{aA}\) | 1.10±0.47\(^{aA}\) |
| 20-30     | 0.53±0.04\(^{aA}\) | 0.40±0.07\(^{aA}\) | 0.67±0.18\(^{aB}\) | 0.53±0.24\(^{aA}\) | 0.50±0.07\(^{aB}\) |
| 30-40     | 0.57±0.11\(^{aA}\) | 0.40±0.07\(^{aA}\) | 0.63±0.22\(^{aB}\) | 0.53±0.18\(^{aA}\) | 0.50±0.07\(^{aB}\) |
| 40-50     | 0.53±0.16\(^{aA}\) | 0.23±0.04\(^{aA}\) | 0.63±0.22\(^{aB}\) | 0.50±0.13\(^{aA}\) | 0.30±0.07\(^{aB}\) |
| 50-60     | 0.43±0.16\(^{aA}\) | 0.97±0.96\(^{aA}\) | 0.40±0.20\(^{aB}\) | 0.43±0.18\(^{aA}\) | 1.03±0.91\(^{aA}\) |

Organic matter, besides containing B in its composition, contributes to the adsorption of its mineral form applied to the soil, through its positive charges (Valladares, Pereira, Souza, Pérez, & Anjos, 1999). In subsurface, the B contents found in all sites evaluated are due to the easy leaching of this element in the soil.

Manganese (Mn) contents, in general, were considered as high (CQFS - RS/SC, 2004) and varied from 1.0 to 11.0 mg dm\(^{-3}\). The highest values were found in the areas with 4 and 9 years of cultivation after grapevine planting, regardless of depth. Mn availability in the soil is related to oxido-reduction potential, OM content, balance with other cations, especially iron, calcium and magnesium, and mainly to soil pH (Bartlett, 1988).

### Conclusions

Areas with 9 and 16 years had higher macronutrient and micronutrient contents, mainly in the first 10 cm depth, due to the successive uses during the vineyard management years after the vines were planted.

Liming and fertilization of the soil should carefully follow the recommendations that are based on soil chemical analysis reports, to avoid the indiscriminate use of agrochemicals that can promote nutritional imbalance of plants and soil contamination.

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