

# HEAVY METALS AND MICRONUTRIENTS IN THE SOIL AND GRAPEVINE UNDER DIFFERENT IRRIGATION STRATEGIES

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## ABSTRACT

Soils under natural conditions have heavy metals in variable concentrations and there may be an increase in these elements as a result of the agricultural practices adopted. Transport of heavy metals in soil mainly occurs in forms dissolved in the soil solution or associated with solid particles, water being their main means of transport. In this context, the aim of this study was to evaluate the heavy metal and micronutrient content in the soil and in the grapevine plant and fruit under different irrigation strategies. The experiment was carried out in Petrolina, PE, Brazil. The treatments consisted of three irrigation strategies: full irrigation (FI), regulated deficit irrigation (RDI), and deficit irrigation (DI). During the period of grape maturation, soil samples were collected at the depths of 0-10, 10-20, 20-40, 40-60, and 60-80 cm. In addition, leaves were collected at the time of ripening of the bunches, and berries were collected at harvest. Thus, the heavy metal and micronutrient contents were determined in the soil, leaves, and berries. The heavy metal and micronutrient contents in the soil showed a stochastic pattern in relation to the different irrigation strategies. The different irrigation strategies did not affect the heavy metal and micronutrient contents in the vine leaves, and they were below the contents considered toxic to the plant. In contrast, the greater availability of water in the FI treatment favored a greater Cu content in the grape, which may be a risk to vines, causing instability and turbidity. Thus, adoption of deficit irrigation is recommended so as to avoid compromising the stability of tropical wines of the Brazilian Northeast.

**Keywords:** water availability, nutrients, grape.

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## RESUMO: METAIS PESADOS E MICRONUTRIENTES NO SOLO E NA VIDEIRA SOB DIFERENTES ESTRATÉGIAS DE IRRIGAÇÃO

Os solos naturalmente possuem metais pesados em teores variáveis, podendo ocorrer incremento desses elementos em razão de práticas agrícolas adotadas. O transporte de metais pesados no solo ocorre, principalmente, nas formas dissolvidas na solução desse ou associado às partículas sólidas, sendo a água sua principal via de transporte. Nesse contexto, este trabalho teve por objetivo avaliar o teor de metais pesados e micronutrientes no solo, na planta e nos frutos de videira, submetida a diferentes estratégias de irrigação. O experimento foi instalado em Petrolina, PE. Os tratamentos foram constituídos de três estratégias de irrigação: IP (irrigação plena); IDC (irrigação com déficit controlado); e ID (irrigação com déficit). Durante o período de maturação da uva, foram coletadas amostras de solo nas profundidades de 0-10; 10-20; 20-40; 40-60; e 60-80 cm. Também foram coletadas folhas, no momento da maturação dos cachos, e bagas, no instante da colheita. Determinaram-se no solo, na folha e baga os teores de metais pesados e micronutrientes. Os teores de metais pesados e micronutrientes no solo apresentaram padrão estocástico em relação às diversas estratégias de irrigação. As diferentes estratégias de irrigação não influenciaram os teores de metais pesados e micronutrientes na folha de videira, estando esses abaixo dos teores considerados tóxicos para a planta. Entretanto, a maior disponibilidade de água no tratamento com IP favoreceu maior teor de Cu na uva, podendo ser um risco para os vinhos, causando instabilidade e turbidez. Dessa forma, recomenda-se adotar irrigação com déficit, evitando-se assim comprometer a estabilidade de vinhos tropicais da região Nordeste do Brasil.

*Palavras-chave:* disponibilidade de água, nutrientes, uva.

## INTRODUCTION

Chemical elements with a density greater than  $6 \text{ kg dm}^{-3}$  are considered to be heavy metals (Hooda, 2010). Of these, more than 20, called micronutrients, are essential to the life cycle of plants, animals, and human beings. Among these are Cu, Fe, Mn, Ni, and Zn (Kabata-Pendias, 2011). Depending on the contents and the environmental physicochemical conditions, such elements may pass from the condition of micronutrients to that of toxic elements, acting as contaminating agents of the soil, water, and air (Larcher, 2004). However, some heavy metals, like Pb, Hg, As, and Cd, do not have any biological activity and, even at low concentrations, may have a harmful effect on plants (Lasat, 2002).

Soils in their natural state have heavy metals at varied concentrations, depending on the material of origin and the processes involved in their formation (Fadigas et al., 2006). There may also be deposition in the soil through industry or use of agricultural inputs such as fertilizers and pesticides (Xue et al., 2003), or diffuse contamination through deposit of aerosols on the soil surface.

The frequency and intensity of rains, temperature, and evaporation, as well as edaphic conditions, are among the factors that most affect the dynamic of heavy metals in the environment and their consequent solubility, mobility, and uptake by plants (Kabata-Pendias, 2011). The process of plant uptake of these elements will occur through their contact with plant roots, and this process is dependent on the mechanisms of mass flow transport and

diffusion. For this transport to occur, the elements must be in a soluble form or associated with mobile ligands in the soil (Cunha et al., 1996).

Soils under irrigated cropping normally undergo changes of a chemical, physical, and biological order in a relatively short time and at an intensity that varies in accordance with the quality and quantity of the water applied, management practices, use of fertilizers, and the chemical and physical characteristics of the soils (Silva and Araújo, 2005). The region of the Vale do Submédio São Francisco (Lower-Middle São Francisco River Valley) is characterized by climatic conditions that make the use of irrigation indispensable for satisfactory plant development. Excess water, in addition to decreasing oxygen concentration (Pires et al., 2002), contributes to nutrient loss through leaching, especially in sandy soils. In contrast, lack of water significantly reduces plant nutrient uptake by compromising the diffusion and flux of nutrient mass in the soil (Novais and Smyth, 1999).

The mineral element composition of grape is varied. These elements are taken up through the grapevine root system, and enrichment is observed during berry formation and maturation, affecting the final composition of the wine. Enrichment with some metals may lead to detrimental effects on quality, such as turbidity, precipitation, and oxidations (Catarino et al., 2008). In addition, according to the same researchers, depending on the concentration of the element present, problems of a toxicological and legal order may arise.

One of the main problems in vineyards irrigated for the purpose of obtaining quality grapes and

wines is the increase in vegetative vigor, causing an imbalance between leaf area and fruit production (Keller et al., 2008). The high vigor of shoots due to excessive irrigation increases competition for photoassimilates between fruits and shoots, changes the microclimate in the vicinity of the bunches (compromising synthesis of phenolic compounds), reduces the fertility of the buds, and creates difficulties in plant health treatments (Jackson and Lombard, 1993). Irrigation management has been one of the main resources for controlling vegetative vigor of the plant in recent years since composition of the grape berry is strongly affected by the moisture conditions of the grapevine (Dry and Loveys, 1998). Based on this principle, deficit irrigation strategies have been presented, seeking to establish balance between vegetative development and grape yield, without harming the qualitative aspects of the grapes (McCarthy, 1997). In addition, appropriate irrigation management constitutes an excellent opportunity for rational use of water resources.

In this context, the aim of this study was to evaluate the heavy metal and micronutrient contents in the soil, in the plant, and in the fruits of grapevines under different irrigation strategies in the region of the Vale do Submédio São Francisco, Brazil.

## MATERIAL AND METHODS

The experiment was carried out in the Bebedouro Experimental Field, belonging to Embrapa Semiárido in Petrolina, PE, Brazil, at latitude 9° 08' 08.9'' S, longitude 40° 18' 33.6'' W, and altitude of 373 m. According to the Geoviticulture Multicriteria Climatic Classification System, the region has a climate classification of IS<sub>1</sub> IH<sub>6</sub> IF<sub>1</sub>, with moderate dryness and very hot climate, and hot nights (Tonietto, 1999). Mean annual values of the climate variables are: air temperature: 26.5 °C, rainfall: 541.1 mm, relative air humidity: 65.9 %, class "A" evaporation pan: 2,500 mm yr<sup>-1</sup>, and wind speed: 2.3 m s<sup>-1</sup>. Rainfall is irregularly distributed in space and time, concentrated in December to April; annual solar radiation is greater than 3,000 h (Azevedo et al., 2003). Soil in the area was classified as an Ultisol (Silva, 2005), originating from alteration of the cobble covering schists from the Pre-Cambrian Eon (mica schists).

The Syrah grape cultivar (*Vitis vinifera* L.) on the 'Paulsen 1103' rootstock (*Vitis berlandieri* x *Vitis rupestris*) was chosen. The grapevines were planted on April 30, 2009 at a spacing of 3.0 × 1.0 (3.0 m between rows and 1.0 m between plants). At planting, fertilization for establishment of the vineyard was carried out with application of limestone (200 g per linear meter), goat manure (40 m<sup>3</sup> ha<sup>-1</sup>), and granulated

single superphosphate (18 % P<sub>2</sub>O<sub>5</sub>) (50 g/plant). In production fertilization, only goat manure was applied, at the rate of 0.02 m<sup>3</sup>/plant. The vineyard is trained in vertical shoot positioning and the pruning system is a bilateral spur pruned cordon de Royat.

The period of trellised vine formation (vegetative growth) was up to April 13, 2010, at which time the vines were pruned to begin the first production cycle. This study was carried out in the third production cycle, from May 10, 2011 to September 8, 2011. Drip irrigation was used at a flow rate of 2.5 L h<sup>-1</sup>, with nozzles spaced at 0.5 m in the plant row and service pressure of 100 kPa, calibrated in a field flow test. Calculation of irrigation was made using reference evapotranspiration (ET<sub>o</sub>) estimated by the Penman-Monteith FAO method through parameters measured by the automatic meteorological station set up approximately 60 m from the area of the experiment. In determination of the crop evapotranspiration values (ET<sub>c</sub>), the K<sub>c</sub> values recommended by Bassoi et al. (2007) were used. The agricultural chemicals used in pest and disease control in the area during the experiment were Equation® (mixture of cymoxanil and famoxadone) and Forum® (dimethomorph) in control of mildew, at the rate of 1,000 mg L<sup>-1</sup> (two applications); and Rumo® (indoxacarb) in control of citrus stem borer, at the rate of 80 mg L<sup>-1</sup> (one application). For control of rust, Rubigam® (fenarimol) was applied at the rate of 350 mg L<sup>-1</sup> (one application); and for powdery mildew, Amistar® (mixture of azoxystrobin and difenoconazole) and Cabrio top® (pyraclostrobin) were applied at the rate of 600 mg L<sup>-1</sup> (one application).

The experimental area was composed of 24 rows with 24 plants per row, for a total of 576 plants, and, of these, only the 12 central plants of each row were evaluated, for a total of 288 useful plants. The treatments consisted of three irrigation strategies: full irrigation (FI), where irrigation was carried out to restore the water depth corresponding to the quantity of water evapotranspired, without water restriction to the grapevines throughout the entire production cycle; regulated deficit irrigation (RDI), where water application was interrupted as of the bunch closure phenological phase (45 dapp - days after production pruning), but carried out at 70, 71, 87, 90, and 111 dapp, for the purpose of increasing soil moisture (θ, m<sup>3</sup> m<sup>-3</sup>) at the effective depth of the grapevine root system (0.6 cm), taking the soil moisture conditions into consideration, monitored weekly by the neutron moderation technique at 15, 30, 45, 60, 75, 90, 105, and 120 cm of depth; and deficit irrigation (DI), where water application was interrupted as of 45 dapp, bunch closure phenological phase, up to harvest at 115 dapp. The treatments were arranged in a randomized block design with four replications.

During the grape maturation period, soil samples were collected in the 0-10, 10-20, 20-40, 40-60, and 60-80 cm depth layers, removing six simple samples from each depth to obtain one combined sample per plot. The soil samples were air-dried, broken up, homogenized, and passed through a sieve with a 2.0 mm mesh to obtain air-dried soil samples. The physical soil analyses of bulk density, particle density, and texture were determined, according to the methods described by Claessen (1997). In chemical characterization, pH(H<sub>2</sub>O), electrical conductivity in the saturated paste extract (EC<sub>se</sub>), potential acidity (H+Al), soil organic matter content, and CEC and base saturation (V) were determined (Table 1), according to the methods proposed by Silva (2009). In addition, contents of Fe, Mn, Cu, Zn, Cr, Ni, Cd, and Pb were determined, after extraction with Mehlich-1 (0.05 mol L<sup>-1</sup> HCl + 0.0125 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>) at the ratio of 1:5 (soil:solution), with reading made by atomic absorption spectrophotometry (AAS) according to the methods proposed by Claessen (1997).

At the beginning of grape maturation (which occurred on August 3, 2011, at 85 dapp), samples of plant tissue were collected from whole leaves opposite the bunch, two leaves per plant (Albuquerque et al., 2009). Only leaves without damage and without any type of contamination were collected. For the grape samples (berries), collections were made at the time of harvest, taking three bunches per block for each treatment (randomly) as samples, collecting whole and healthy bunches. The plant material (leaves and berries) were dried in an air circulation laboratory oven at 70 °C for 72 h, weighed, and passed through a Willey mill. The plant

material (leaves and berries) was then mineralized by a nitric-perchloric acid mixture (3:1) for chemical analysis. Determination of micronutrients (Fe, Mn, Cu, and Zn) and heavy metals (Ni, Cd, Cr, and Pb) present in the extracts of leaves and berries was carried out by atomic absorption spectrophotometry (AAS), according to the methods proposed by Miyazawa et al. (2009). Crop yield (kg ha<sup>-1</sup>) in all the treatments was estimated from the data obtained from fruit production per plot (kg m<sup>-2</sup> of plot).

The effects of the different irrigation strategies on the contents of Fe, Mn, Cu, Zn, Cr, Ni, Cd, and Pb in the soil, leaves, and berries were subjected to analysis of variance, and were compared by the Tukey test (p<0.05). For analyses of the results of the micronutrient and heavy metal contents in the soil, variation at different depths in the treatments was not taken into consideration but rather variation among the treatments in each soil layer evaluated.

## RESULTS AND DISCUSSION

### Soil moisture

Soil moisture ( $\theta$ ) exhibited quite different behavior among the irrigation management treatments evaluated up to the 90 cm depth layer (Figure 1). As of interruption of irrigation (49 days after production pruning - dapp), there was a steady decline in  $\theta$  in the treatments with regulated deficit irrigation (RDI) and deficit irrigation (DI) where, after water application in the RDI treatment (71 and 92 dapp), an increase of  $\theta$  up to the 45 cm depth was

**Table 1. Physical and chemical characteristics of the Ultisol cultivated with grapevines under different irrigation strategies**

Depth	BD	PD	Sand	Silt	Clay	pH(H <sub>2</sub> O)	EC <sub>se</sub>	H+Al
cm	kg dm <sup>-3</sup>			g kg <sup>-1</sup>			dS m <sup>-1</sup>	cmol <sub>c</sub> dm <sup>-3</sup>
0-10	1.32	2.53	779	149	72	6.79	0.38	1.29
10-20	1.37	2.53	778	133	89	6.57	0.32	1.62
20-40	1.35	2.51	738	116	146	6.41	0.21	1.59
40-60	1.32	2.52	716	104	180	6.27	0.28	1.74
60-80	1.32	2.53	686	101	213	5.87	0.24	1.71
	SB	CEC	SOM	P	K	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>
	cmol <sub>c</sub> dm <sup>-3</sup>		g kg <sup>-1</sup>	mg dm <sup>-3</sup>		cmol <sub>c</sub> dm <sup>-3</sup>		
0-10	7.80	9.03	27.41	113.25	0.52	4.80	2.65	0.09
10-20	6.50	8.04	12.90	96.64	0.53	3.74	2.47	0.08
20-40	5.70	7.50	7.32	91.85	0.34	3.32	2.22	0.06
40-60	5.30	6.99	5.69	54.90	0.29	3.03	1.98	0.06
60-80	5.20	7.11	4.23	28.16	0.29	2.84	2.03	0.05

BD: soil bulk density; PD: particle density; pH in water, 1:2.5 v/v; EC<sub>se</sub>: electrical conductivity in the saturated paste extract; SB: sum of bases; CEC: cation exchange capacity; SOM: soil organic matter.

observed. In the deeper soil layers (105 and 120 cm), there was similar behavior in regard to variation of  $\theta$  in all the treatments.

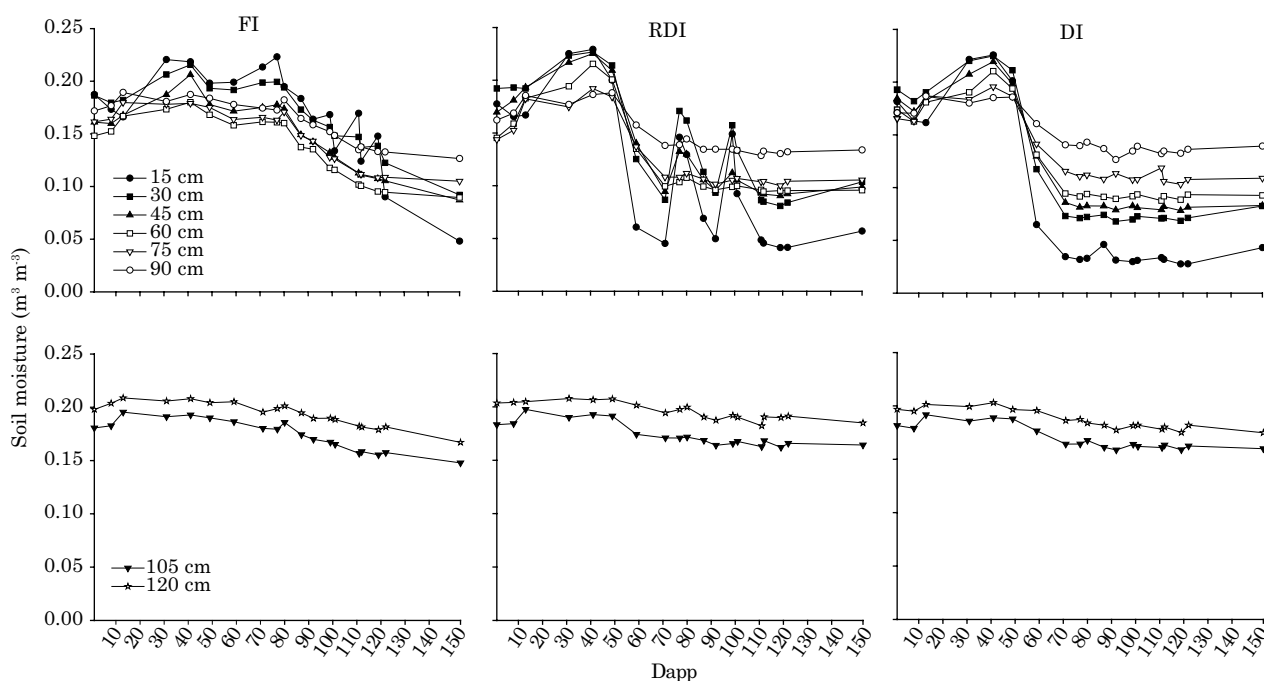
## Soil

In figure 2, the micronutrient contents in accordance with the different irrigation strategies are shown. The mean contents of available  $\text{Fe}^{2+}$  observed ranged from 3.9 to 37.3  $\text{mg dm}^{-3}$ , which was classified as very low to good, according to Alvarez et al. (1999). Among the irrigation strategies evaluated, no difference was observed in the contents of  $\text{Fe}^{2+}$  only at the depth of 0-10 cm (Figure 2a). At the depth of 10-20 cm under regulated deficit irrigation (RDI), the Fe content was higher when compared to the other irrigation strategies (FI and DI). Under conditions of greater water availability (full irrigation treatment - FI), reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  is favored, contributing to its movement in the soil profile beyond the layers evaluated, especially in sandy soils, as in this study (Table 1). Under conditions of greater water availability, dissolution and remobilization mechanisms of Fe come into action, which include reduction and complexation reactions (Schwertmann, 1991), favoring its greater concentration and leaching in soils with a low level of clay. In a study carried out by Hernández and Meurer (1998) in 10 soils of Uruguay, subject to temporal variations in oxidation-reduction conditions, it was observed that soil with low clay contents (cretaceous sandstones) exhibited lower Fe

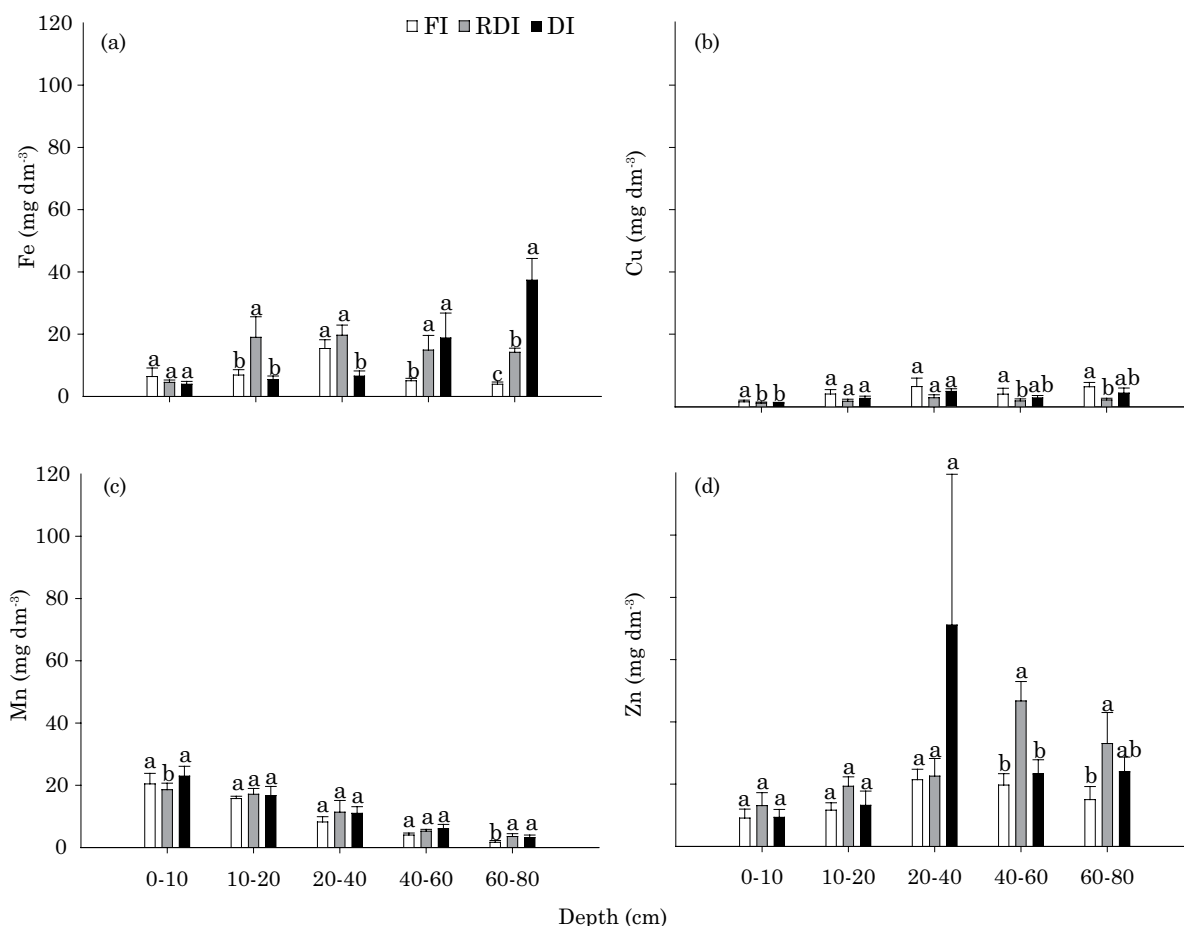
content, and a correlation was observed between Fe contents and clay contents of the soils. In a study evaluating eight soil samples from the provinces of Antwerp and West-Flanders in Belgium with known micronutrient and heavy metal values, and subjected to the treatments of dry soil, soil at field capacity, and saturated soil, Tack et al. (2006) observed that the events of wetting and drying of the soil changed the hydration, oxidation, and crystallinity status of the Fe and Mg oxides of the soil, favoring the release of these elements under wetter environments.

Soils under the FI and RDI treatments exhibited greater Fe content at the depth of 20-40 cm in relation to the soil under the DI treatment. For the 40-60 and 60-80 cm layers, soils under the DI and RDI treatments exhibited greater Fe contents in relation to the FI treatment. It may be observed that in the aerobic environment, the element Fe exhibits high thermodynamic stability and reduced solubility, persisting in the soil for a long period (Schwertmann and Taylor, 1989). This may have occurred under the condition of lower water availability in the more subsurface layers. In addition, in deeper soil layers, oxygen content becomes scarcer, making soil organisms use other elements as the terminal electron acceptor, resulting in its reduction.

According to Alvarez V et al. (1999), the available Cu contents observed are considered high ( $>1.8 \text{ mg dm}^{-3}$ ) and are above those observed by Pietrzak and McPhail (2004) and Komárek et al. (2008)



**Figure 1.** Soil moisture ( $\theta$ ) at the 15, 30, 45, 60, 75, 90, 105, and 120 cm depths in accordance with irrigation strategies, with full irrigation - FI, regulated deficit irrigation - RDI, and deficit irrigation - DI. Dapp: days after production pruning.



**Figure 2. Micronutrient contents in the soil cultivated with grapevine in accordance with different irrigation strategies - full irrigation (FI), regulated deficit irrigation (RDI), and deficit irrigation (DI). Columns followed by the same letter at the same depth do not differ among themselves by the Tukey test at 5 % of significance. The vertical deviation bars represent the standard deviation of the mean value (n = 12).**

studying the accumulation of Cu in vineyard soils in Australia and the Czech Republic, respectively. The FI treatment showed greater Cu content in the 0-10 cm soil layer in relation to the other treatments (RDI and DI) (Figure 2b). In the 10-20 and 20-40 cm soil layers, there was no difference in the Cu content among the treatments evaluated. The FI treatment exhibited a greater Cu content in relation to the RDI treatment in the 40-60 and 60-80 cm layers, not differing from the DI treatment. There was a tendency toward an increase in Cu contents at greater depths, in spite of this element showing low mobility due to its strong adsorption to organic and inorganic soil colloids (Pietrzak and McPhail, 2004; Nascimento and Fontes, 2004; Komárek et al., 2008). The increase in the Cu contents in the soil in the deeper layers indicates that the contents in the surface layers are above the soil adsorption capacity and, thus, its percolation in the soil profile may have been facilitated, especially through the treatment with greater water availability. Costa et

al. (2009), studying changes in the total contents of Cu in soils planted to grapes in the Vale do Submédio São Francisco, observed that there was an increase in the contents according to years of grape growing, attributed to human influence, with the greatest contents being found in the uppermost soil layer.

In addition, the slight increase in clay content with the increase in soil depth (Table 1) favored greater Cu contents in the FI treatment, which may be observed by their positive correlation value ( $r = 0.4058^{**}$ , data not shown). Pombo and Klamt (1986), evaluating Cu adsorption in two soils in the state of Rio Grande do Sul also found significant correlation between Cu adsorption and the clay content of the soil.

The contents of available Mn observed ranged from 1.3 to 25.5 mg dm<sup>-3</sup>, which was considered very low (<2 mg dm<sup>-3</sup>) to very good (>12 mg dm<sup>-3</sup>) (Alvarez et al., 1999). There were significant differences only in the 0-10 and 60-80 cm layers,

with the lowest content found in the RDI treatment in the 0-10 cm layer and in the FI treatment in the 60-80 cm layer (Figure 2c). Evaluating the mobility of six heavy metals ( $Mn^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Pb^{2+}$ , and  $Cr^{3+}$ ) during percolation of a multispecies contaminant solution in a compacted residual soil of the municipality of Visconde do Rio Branco, MG, Nascentes (2006) observed that the mobility of  $Mn^{2+}$  practically did not depend on soil hydraulic conductivity. In a study evaluating the forms of Mn in reference soils of the state of Pernambuco, Oliveira and Nascimento (2006) observed that organic matter was mainly responsible for the retention and availability of Mn in the soil. Thus, the greater content of soil organic matter (SOM) found in the 0-10 and 10-20 cm layers (Table 1) allowed greater Mn contents ( $r = 0.8783^{**}$ , data not shown). A strong correlation between the  $Mn^{2+}$  and the SOM contents was also observed in various studies (Bayer et al., 2002; Motta et al., 2002). This occurs due to the  $Mn^{2+}$  being adsorbed to the functional groups of the SOM, such as carboxylic and phenolic groups, in the form of outer and inner sphere complexes (Lakatos and Meisel, 1977). In the outer sphere complex, the Mn is adsorbed only through electrostatic attraction (attraction between opposite charges), while in the inner sphere complex, the Mn is adsorbed by covalent bonding (sharing electrons).

Just as for Cu, a tendency toward an increase in the Zn levels at greater depth was observed. The available Zn contents observed were much above the reference value considered very good for crops ( $>2.2 \text{ mg dm}^{-3}$ ), according to Alvarez et al. (1999). Silva et al. (2003), evaluating extractors for quantification of Zn and Cu in soils planted to soybean in the State of Parana, Brazil, observed available Zn contents ranging from 0 to  $10 \text{ mg dm}^{-3}$  after extraction by Mehlich-1. Just as Cu, Zn tends to accumulate in the surface layer of the soil, due to low mobility in the soil profile (Bertol et al., 2010). Therefore, in general, they exhibit low leaching potential. However, continued applications of these elements to the soil may lead to losses to the subsurface. There was no difference in the available Zn contents among the treatments evaluated in the 0-10, 10-20, and 20-40 cm soil layers (Figure 2d). For the 40-60 and 60-80 cm layers, the RDI treatment exhibited a greater Zn content than the FI treatment.

For Cr contents, a significant difference was observed among the treatments for all the soil layers evaluated (Figure 3a). Lower water availability in the RDI and DI treatments contributed to greater contents of this element in the 0-10 and 10-20 cm soil layers. Cr is concentrated in the soil surface layers in the form of  $Cr^{3+}$ , and  $Cr^{6+}$  is unstable and rapidly converted to  $Cr^{3+}$  by the action of organic matter (Bergmann, 1992). In the 20-40 cm layer, the RDI treatment was that which favored greater concentration of Cr in the soil. In the 40-60 cm soil

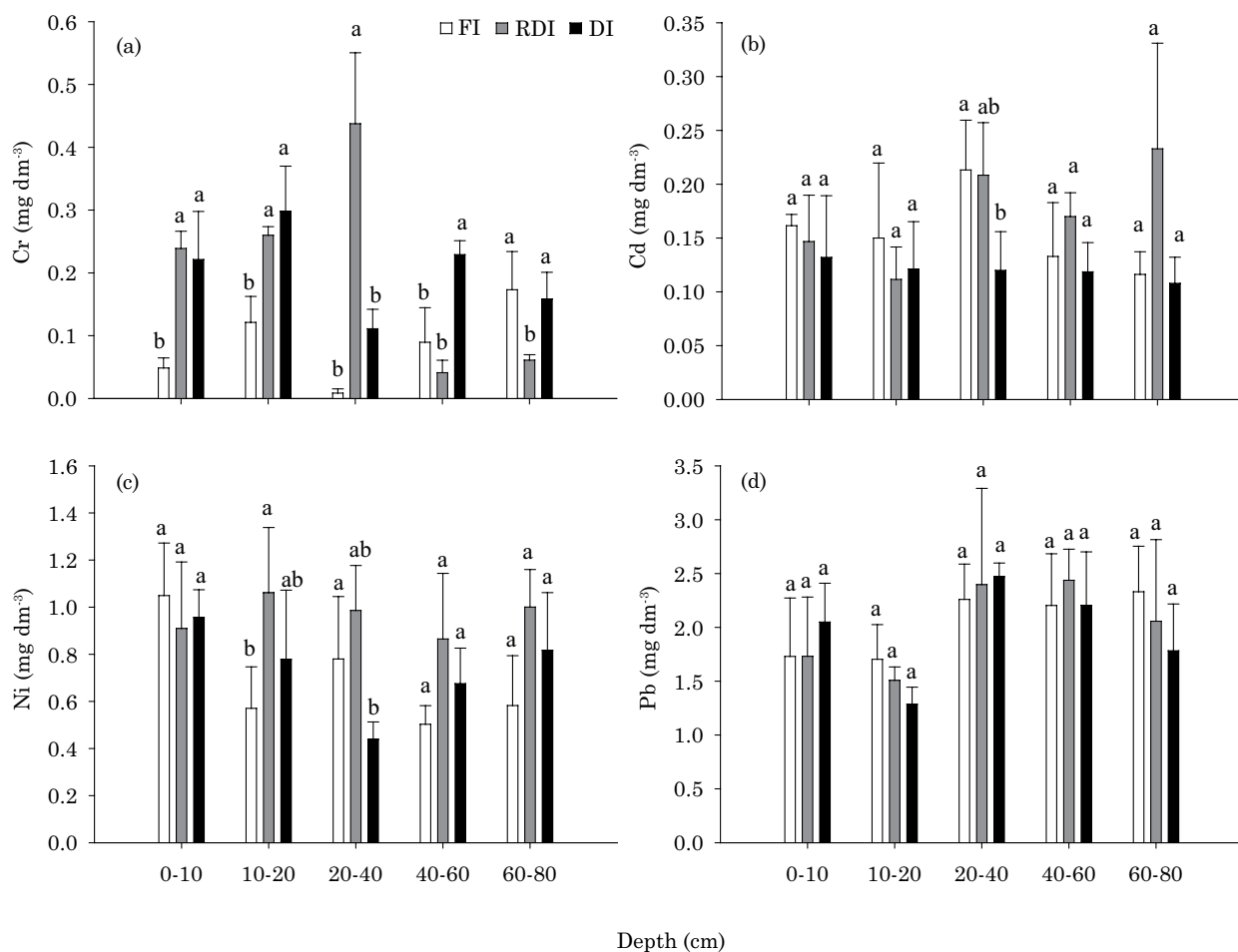
layer, the DI treatment exhibited greater Cr content when compared to the other treatments, while in the 60-80 cm layer, the FI and DI treatments exhibited greater Cr content in relation to the RDI treatment. Although the Cr element exists in diverse states of oxidation, only  $Cr^{3+}$  and  $Cr^{6+}$  are sufficiently stable to occur in the environment. The  $Cr^{6+}$  has more mobility than  $Cr^{3+}$  because its anions are easily transported through the soil (Shrivastava et al., 2002).

The Cd content was greater in the FI treatment in relation to the DI treatment only in the 20-40 cm soil layer (Figure 3b). For the other soil layers evaluated, no difference was observed in the Cd contents among the diverse treatments. Soils derived from igneous rocks contain from 0.1 to  $0.3 \text{ mg kg}^{-1}$  of Cd; those derived from metamorphic rocks, from 0.1 to  $1.0 \text{ mg kg}^{-1}$  of Cd; and in those derived from sedimentary rocks, the content may be up to  $10.0 \text{ mg kg}^{-1}$  of Cd (Kabata-Pendias, 2011). Campos et al. (2007) found mean values of  $0.66 \text{ mg kg}^{-1}$  of Cd in diverse Brazilian Oxisols. The Cd contents permitted for non-contaminated soils, according to Kabata-Pendias (2011), are less than  $1.0 \text{ mg kg}^{-1}$ , although in agricultural soils in China (SEPA, 1995) and the Czech Republic (Komárek et al., 2008), these limits are considered to be around 0.3 and  $0.4 \text{ mg kg}^{-1}$ , respectively. It should be noted that the reference values for quality are defined in accordance with the total contents and, for that reason, comparison with the contents observed in the study is not possible.

Differences were not observed in the Ni contents in the 0-10, 40-60, and 60-80 cm layers (Figure 3c). For the 10-20 cm layer, the RDI treatment had greater Ni content in the soil when compared to the FI treatment. As for the 20-40 cm layer, the FI treatment had greater Ni content in the soil in relation to the DI treatment, not differing from the RDI treatment. Ni is the most mobile heavy metal in the soil (Antoniadis and Tsadilas, 2007); however, the most important factor that determines the distribution of Ni between the solid and soluble phase of the soil is pH, and its availability is inversely related to this index (Uren, 1992). There was no difference in the Pb contents among the treatments evaluated in all the soil layers studied (Figure 3d), showing that the different irrigation strategies did not affect the Pb concentration in the soil.

## Leaf

The different irrigation strategies did not affect the micronutrient and heavy metal concentration in the grape leaves (Figure 4a,b). The soil volume utilized and the close contact between the surface of the roots and the soil are essential for effective uptake of water, micronutrients, and heavy metals by the roots. The growth of root hairs, with consequent increase in surface area, favors



**Figure 3. Heavy metal contents in the soil cultivated with grapevines in accordance with different irrigation strategies - full irrigation (FI), regulated deficit irrigation (RDI), and deficit irrigation (DI). Columns followed by the same letter at the same depth do not differ among themselves by the Tukey test at 5 % of significance. The vertical deviation bars represent the standard deviation of the mean value (n = 12).**

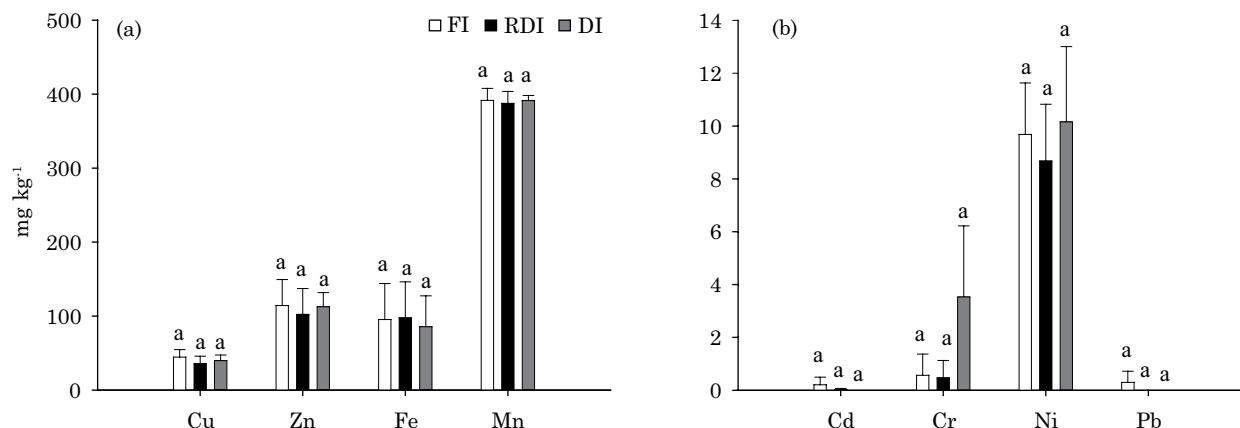
maximization of root-soil contact, increasing water, micronutrient, and heavy metal uptake capacity. Under water stress condition, plants dedicate more biomass to the root system, thus making it possible to increase nutrient uptake capacity and, consequently, nutrient accumulation in the plant shoots. Barbosa and Barbosa (1996) affirm that, in general, greater root growth in relation to the plant shoots is an adaptive trait, common to plants subjected to water stress. Thus, we believe that this morphological adaptation, increasing the volume of the root system under water deficit conditions, allowed similar micronutrient and heavy metal contents in the leaves among the treatments evaluated in the present study.

The Mn and Ni contents were greater than those of the other micronutrients and heavy metals evaluated. According to Marenco and Lopes (2005),

the Mn content in the leaf normally shows positive interaction with the Ni content.

The mean leaf contents of Cu (44.58 g kg<sup>-1</sup>), Zn (114.25 mg kg<sup>-1</sup>), and Mn (387.50 mg kg<sup>-1</sup>) are above the critical level (>20, >50, and >300 mg kg<sup>-1</sup>, respectively) (Faria and Soares, 2004). In contrast, these values are in agreement with those found by Giovannini (2008). In spite of these elements appearing in the excessive range of leaf concentration, no visual symptom of toxicity was observed in the field. High values of Cu, Zn, and Mn have been attributed to the genesis of the soils in the region, which under ideal conditions of redox reactions may favor the solubilization of these elements (Faria and Soares, 2004). Normally, leaf analyses of the grape crop in the Vale do Submédio São Francisco have shown very high Mn contents, without, however, affecting yield, in agreement with the results found in this study.





**Figure 4. Micronutrient and heavy metal contents in grapevine leaves in accordance with different irrigation strategies - full irrigation (FI), regulated deficit irrigation (RDI), and deficit irrigation (DI). Columns followed by the same letter do not differ among themselves by the Tukey test at 5 % of significance. The vertical deviation bars represent the standard deviation of the mean value (n = 12).**

In contrast, the leaf contents of Fe (85.60-95.28 mg kg<sup>-1</sup>) observed are within the range considered adequate for the grapevine (60-180 mg kg<sup>-1</sup>) (Faria and Soares, 2004). The contents of Cd (0.0-0.21 mg kg<sup>-1</sup>), Cr (0.47-3.53 mg kg<sup>-1</sup>), and Pb (0.0-0.30 mg kg<sup>-1</sup>) observed in the leaf tissue of the grape plants are considered adequate, which, according to Adriano (1986), should be in the range of 0.1-0.5 mg kg<sup>-1</sup> for Pb and 0.05-0.5 mg kg<sup>-1</sup> for Cr. Evaluating the concentration of Pb and Cd in different parts of the grapevine in the village of Brestnik, Bulgaria, Angelova et al. (1999) found values of 19 mg kg<sup>-1</sup> of Pb, and 0.5 mg kg<sup>-1</sup> of Cd in leaf samples in the grape maturation phase. These same authors affirm that there is a tendency for an increase in the concentrations of Pb and Cd as vegetation ages, up to grape maturity.

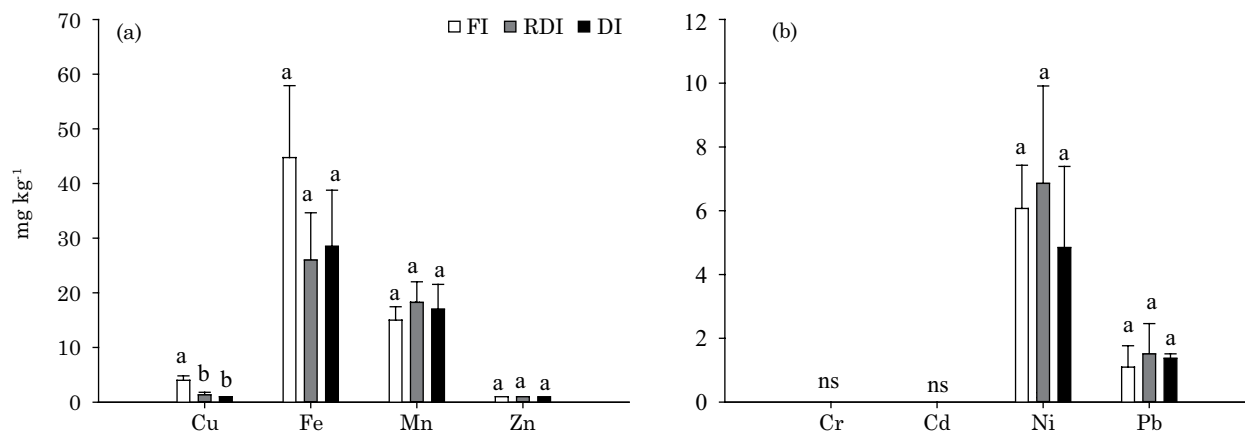
The Ni contents (8.68 to 10.16 mg kg<sup>-1</sup>) observed in the grape leaves are greater than the range considered adequate (0.1 to 5 mg kg<sup>-1</sup>), according to Adriano (1986). This author affirms that the Ni content in plant dry matter varies depending on the species, part of the plant, phenological stage, soil content, and soil acidity, among other factors. Possibly, the grape cultivar studied, and the Ni<sup>2+</sup> contents observed in the soil, associated with the fact of this element being very mobile in the soil (Antoniadis and Tsadilas, 2007), contributed to high contents of this nutrient in the leaves.

## Grape

The different irrigation strategies affected grape yield, with the FI treatment obtaining greater yield (6,600 kg ha<sup>-1</sup>) in relation to the other treatments (5,130 kg ha<sup>-1</sup> for RDI and 4,000 kg ha<sup>-1</sup> for DI). Several studies also report variation in grape yield

when grown under different irrigation strategies. In most situations, there were greater yields with full irrigation (Esteban et al., 2001; Nadal and Lampreave, 2007). Under water stress conditions, berry size and grape yield is normally less due to lower water availability for cell division and elongation (Esteban et al., 2002). In a study evaluating the effect of irrigation management practices on aspects of ecophysiology and production of the grapevine cv. Syrah/Paulsen 1103 in the Brazilian semi-arid region, Bassoi et al. (2011) also observed that water deficit generally results in lower grape yields. Water deficit between flower opening (anthesis) and the beginning of berry maturation (veraison) reduces the final berry size in an irreversible manner and, consequently, reduces yield, even if there is wetting after veraison. In the phase between veraison and harvest, the berries increase in volume, weight, and sugar content. Interruption of water application in this study occurred at 49 dapp, in the bunch closure phase (before veraison, which occurred at 85 dapp), and the water availability in the soil in the RDI and DI treatments steadily declined (Figure 1), resulting in lower yields in these treatments in relation to the treatment under full irrigation.

The inorganic components of the grapes significantly affect wine production and quality, and they are fundamental for human nutrition (Ribéreau-Gayon et al., 2006). The quality of the must and, consequently, of the wine depend, in part, on the metallic elements present (Puig-Deu et al., 1994). Elements such as Fe, Cu, Al, Zn, and Ni in excess contribute to the formation of precipitates and may cause an effect on color, aroma, or flavor of the wine (Galani-Nikolakaki et al., 2002). In addition, it is known that an excess of Fe and Cu determine



**Figure 5. Micronutrient and heavy metal contents in grapevine under different irrigation strategies - full irrigation (FI), regulated deficit irrigation (RDI), and deficit irrigation (DI). Columns followed by the same letter do not differ among themselves by the Tukey test at 5 % of significance. The vertical deviation bars represent the standard deviation of the mean value (n = 12).**

wine turbidity, may delay fermentation during winemaking, and are important causes of instability, as in the case of formation of unstable colloids resulting from a reaction between two unstable cations, proteins and phosphoric acids (iron and copper casse) (Sofa et al., 2012).

The micronutrient contents in the grape showed a significant difference only for Cu, among the treatments evaluated, and the FI treatment obtained a greater concentration in relation to the RDI and DI treatments (Figure 5a), which may be a risk for the wines, causing instability and turbidity. Therefore, adoption of deficit irrigation is recommended to avoid compromising the stability of tropical wines from the Northeast of Brazil. So that nutrients may be taken up by the plants, there must be transport in the soil by processes of mass flow and diffusion (Silva and Araujo, 2005). The element Fe moves in the soil through mass flow; whereas, for Zn, diffusive flow or diffusion is the most important form of transport, given its low concentration in the soil solution. According to Silva and Mendonça (2007), among the micronutrients, Cu is one of the least mobile in the soil due to its strong adsorption on the organic and inorganic colloids of the soil, and diffusion is one of the main means of transport of this element. Greater availability of water in the full irrigation treatment favored the transport and, consequently, uptake of Cu by the grape crop.

In a study evaluating the effect of water deficit on nutrient export in different grape varieties in the region of Parma, Idaho, USA, Shellie and Brown (2012) observed that the concentrations of Zn, Fe, and Mn in the grape were not affected by the irrigation regime, but differed among the nine cultivars. Also evaluating grape composition affected by water availability in five-year-old vineyards in

Italy, Sofa et al. (2012) observed that the contents of Cu, Fe, and Zn in the grape were greater in the irrigated treatment (0.23 mg kg<sup>-1</sup> of Cu, 0.24 mg kg<sup>-1</sup> of Fe, and 0.47 mg kg<sup>-1</sup> of Zn) in relation to the treatment without irrigation (0.11 mg kg<sup>-1</sup> of Cu, 0.064 mg kg<sup>-1</sup> of Fe, and 0.23 mg kg<sup>-1</sup> of Zn). For the present study, the FI treatment had 4.0 mg kg<sup>-1</sup> more Cu, in relation to the DI treatment.

There was no difference in the Cr, Cd, Ni, and Pb contents among the treatments evaluated (Figure 5b). Possibly, expansion of the root system in the soil profile in search of water, stimulated by water deficit (Santos and Carlesso, 1998), allowed for greater uptake of heavy metals and, consequently, their accumulation in the berries similar to the conditions under full irrigation. In general, greater root growth in relation to the shoots is an adaptive trait, common to plants subjected to water stress (Barbosa and Barbosa, 1996), resulting in an increase in nutrient uptake capacity. It should be noted that during wine production, there may be partial elimination of metals by the processes of precipitation under the form of organic salts and through uptake and adsorption by yeasts and bacteria used during grape fermentation (Catarino et al., 2008). Thus, the occurrence of metals at very high concentrations in wine indicates, in general, the occurrence of contaminations after fermentation (Jackson, 2000).

## CONCLUSIONS

The heavy metal and micronutrient contents in the soil exhibited a stochastic pattern in relation to the different irrigation strategies.

The different irrigation strategies did not have an effect on the micronutrient and heavy metal contents in the grape leaf, and are below the values considered toxic to the plant.

The greater availability of water in the full irrigation (FI) treatment favored greater Cu content in the grape (berries). Therefore, adoption of deficit irrigation is recommended to avoid compromising the stability of wines from the Northeast of Brazil by Cu. The different irrigation strategies did not affect the heavy metal contents in the grape.

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