Revista Brasileira de Ciência do Solo

Division - Soil Use and Management | Commission - Soil fertility and plant nutrition

Soil chemical properties and nutrition of conilon coffee fertilized with molybdenum and nitrogen

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Received: April 21, 2021

Approved: August 23, 2021

How to cite: Rosado TL, Freitas MSM, Carvalho AJC, Gontijo I, Pires AA, Vieira HD, Barcellos R. Soil chemical properties and nutrition of conilon coffee fertilized with molybdenum and nitrogen. Rev Bras Cienc Solo. 2021;45:e0210034.
https://doi.org/10.36783/18069657rbcs20210034

Editors: José Miguel Reichert and Adelson Paulo de Araújo.

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ABSTRACT: Molybdenum (Mo) availability is strongly affected by soil pH, which determines the dynamics of electrical charges and the adsorption of molybdate. This study evaluated the effects of nitrogen (N) and Mo application on the chemical properties of a *Latossolo Amarelo* (Oxisol) and in *Coffea canephora* nutrition and productivity throughout two productive cycles under field conditions. The experiment was conducted from June 2018 to May 2020. The experimental design used was in randomized blocks, in a 2 × 5 factorial scheme, the first factor being the absence and presence (4 kg ha^{-1} yr^{-1}) of molybdic fertilization and the second factor was the N dose (300, 500, 700, 900, and 1,100 kg ha^{-1} yr^{-1}). At the end of each production cycle, soil samples were collected to evaluate the pH(H_2O), pH(KCl), exchangeable aluminum, potential acidity, organic matter, and Mo, at layers of 0.00-0.20 and 0.20-0.40 m. Leaves were sampled from the coffee tree to determine Mo and N contents and the coffee beans were harvested to evaluate the yield of processed coffee. The results showed that urea has a high potential for soil acidification, influencing the values of exchangeable aluminum, potential acidity, and ΔpH, at layers of 0.00-0.20 and 0.20-0.40 m. The decrease in pH caused by increasing doses of N increased the density of positive electrical charges of the soil and reduced Mo content in the leaves of *C. canephora* by 67 %. The application of sodium molybdate via soil was efficient in providing Mo to Conilon coffee and provided a 3.7 % increase in the yield of processed coffee. Nevertheless, molybdic fertilization did not influence the Mo content in the soil in the evaluations carried out at the end of each production cycle.

Keywords: *Coffea canephora,* soil acidity, electrical charges, molybdic nutrition.

INTRODUCTION

In Conilon coffee crops (*Coffea canephora* Pierre ex A. Froehner), the use of fertilizers containing nitrogen (N) in ammoniac or amidic form is the main factor responsible for soil acidification (Theodoro et al., 2003). Nitrogen is the nutrient required in greater quantity by Conilon coffee (Colodetti et al., 2015), so much so that Prezotti et al. (2017) recommend doses of N greater than 500 kg ha^{-1} for crops with a high productive potential of more than 6,000 kg of processed coffee per hectare.

Economic factors related to the production process make urea the most used nitrogen fertilizer in world agriculture (Silva et al., 2011). Due to the easily acquisition, high concentration of N, lower cost per kilogram of N, low corrosivity, and high solubility, urea is the most used source of N in *C. canephora* crops (Oliosi et al., 2017).

After being applied to the soil, urea undergoes enzymatic hydrolysis, resulting in the formation of ammonium, the consumption of H^+ ions, and an increase in pH. However, NH_4^+ nitrification leads to the generation of protons, reducing pH to values lower than the original (Rochette et al., 2013). A decrease in soil pH because of the supply of N in the form of urea is reported in areas cultivated with coffee (Díaz et al., 2011; Partelli et al., 2012).

Molybdenum (Mo) is an essential mineral element for plants found in low contents in the soil. It integrates different enzymatic systems in the plants, being found in xanthine dehydrogenase, mitochondrial amidoxime reductase, oxidase aldehyde, sulfite oxidase, and nitrate reductase (McGrath et al., 2010). Molybdenum is found in low concentrations in the lithosphere, being more abundant in basic igneous rocks (Kaiser et al., 2005). In the soil solution, it remains in the form of H_2MoO_4, $HMoO_4^-$, or MoO_4^{2-}, depending on the acidity of the medium. However, molybdate (MoO_4^{2-}), the ionic form most absorbed by plants, predominates in soils with a pH higher than 5 (Nie et al., 2020).

Several factors affect the availability of Mo in the soil, including the soil texture, the presence of iron and aluminum hydroxides in the clay fraction, the organic carbon supply, the redox potential, the ionic interaction with phosphorus and sulfur, and the acidity (Rutkowska et al., 2017). The pH is the main factor that influences the Mo availability in the soil solution (Xu et al., 2013). In acidic soils, there is an increase in the density of positive electrical charges on the surface of mineral colloids, favoring specific adsorption and the formation of non-labile Mo.

Soils can be naturally acidic due to the parent material and the intensity of weathering agents. However, in cultivated soils, several factors can contribute to the acidification process, such as the absorption of cations by plants with subsequent extrusion of H^+ ions, the leaching of bases in the soil, the exudation of organic acids by the roots of plants, nitrification and the use of mineral fertilizers (Goulding, 2016).

This study aimed to evaluate the effects of the application of N doses and Mo fertilization on the chemical properties of a *Latossolo Amarelo* (Oxisol); molybdenum and nitrogen nutrition; and productivity of *Coffea canephora* throughout two production cycles.

MATERIALS AND METHODS

The experiment was carried out from June 2018 to May 2020 in the municipality of Santa Teresa, state of Espírito Santo, Brazil, located in the coordinates 19° 47’ 15” south latitude and 40° 38’ 52” west longitude of Greenwich, and an average altitude of 165 m. The region’s climate is tropical, with dry winter and rainy summer, Aw according to the Köppen classification system (Alvares et al., 2013).

The soil, from a smooth-wavy relief, was classified as Oxisol according to Soil Survey Staff (2014), which corresponds to *Latossolo Amarelo* according to the Brazilian Soil Classification System (Santos et al., 2018a), with 436, 243 and 321 g kg^{-1} of sand, silt, and clay, respectively, in the layer of 0.00-0.20 m; and 367, 265 and 368 g kg^{-1} of sand, silt and clay, respectively, in the layer of 0.20-0.40 m.

The Conilon coffee crop was planted in April 2016, with a 3.0 × 0.9 m spacing and 3,704 plants ha^{-1}, with three stems per plant. Plants of clone 108P, belonging to the variety Diamante ES8112, were evaluated. Since planting the coffee trees, soil fertility management has been carried out following the recommendations of Prezotti et al. (2017) for the coffee tree in formation, using calcium nitrate, monoammonium phosphate, potassium chloride, magnesium sulfate, zinc oxide, and boric acid fertilizers as sources of N+Ca, P+N, K, Mg+S, Zn and B, respectively.

After the first harvest, in June 2018, the soil was collected in the experimental area for chemical characterization, at layers of 0.00-0.20 and 0.20-0.40 m (Table 1). The results of the soil analysis did not indicate the need for the use of acidity correction.

The maintenance fertilization of *C. canephora*, except for N and Mo, during the experimental period followed the recommendations of Prezotti et al. (2017) for crops with estimated productivity between 7,860-10,200 kg ha^{-1}. On the other hand, the crop practices used in the coffee plantation concerning the growth, pruning, phytosanitary management, and control of weeds followed the technical recommendations of Ferrão et al. (2017).

During the experimental period, whenever rainfall was insufficient to raise soil moisture to field capacity, the coffee crop was irrigated, with the applied irrigation depth calculated based on the crop evapotranspiration. Evapotranspiration was calculated using the Penman-Monteith-FAO56 method, using meteorological data obtained from an automatic weather station belonging to IFES - *Campus* Santa Teresa, located 3.8 km from the experimental area. For the crop coefficients, values suggested by Bonomo et al. (2017) were adopted.

A drip irrigation system was used, with a 0.30 m spacing between drippers, resulting in a continuous irrigated line. The fixed irrigation intervals were adopted, with the irrigations carried out every three days, aiming to raise the soil moisture to the field capacity. Figure 1 shows the values of the meteorological data observed during the experimental period.

The experimental design used was in randomized blocks, in a 2 × 5 factorial scheme, the first factor being the absence and presence of molybdic fertilization and the second factor was the N dose (300, 500, 700, 900, and 1,100 kg ha^{-1} yr^{-1}), with four replications, totaling 40 experimental units. For the choice of N doses, the study adopted the dose of 560 kg ha^{-1} yr^{-1}, suggested by Prezotti et al. (2017) for Conilon crop with estimated

Table 1. Chemical soil characterization of the experimental area at layers of 0.00-0.20 and 0.20-0.40 m

Layer	pH(H_2O)	Ca^{2+}	Mg^{2+}	Al^{3+}	H+Al	CEC	SB	P	K	S	Cu	Fe	Zn	Mn	B	Mo	OM	V
m		cmol$_c$ dm^{-3}						mg dm^{-3}									%	
June 2018																		
0.00-0.20	6.3	5.0	1.0	0.0	2.9	9.9	7.0	123	350	16	3.0	137	14	139	0.6	0.7	2.4	70.8
0.20-0.40	6.1	4.0	0.6	0.0	2.5	7.9	5.4	55	280	8	2.0	175	12	120	0.4	0.5	1.7	68.5
June 2019																		
0.00-0.20	5.9	4.6	1.2	0.0	3.3	10.0	6.7	108	335	19	7.2	142	9.3	151	0.8	3.1	2.1	67.0
0.20-0.40	5.8	3.8	0.6	0.1	2.9	8.1	5.2	45	316	9	3.8	156	9.1	109	0.4	1.4	1.5	64.2

pH in H_2O 1:2.5; Ca^{2+}, Mg^{2+} and Al^{3+} extracted by KCl; H+Al: extracted by calcium acetate; P: extracted by anion exchange resins; K, Cu, Fe, Zn, Mn, and Mo: extracted by Mehlich-1; S-SO_4^{2-}: extracted by calcium phosphate; B: extracted by barium chloride; CEC: cation exchange capacity at pH 7.0; SB: sum of bases; OM: organic matter, Walkley-Black method; V: percentage saturation by bases.

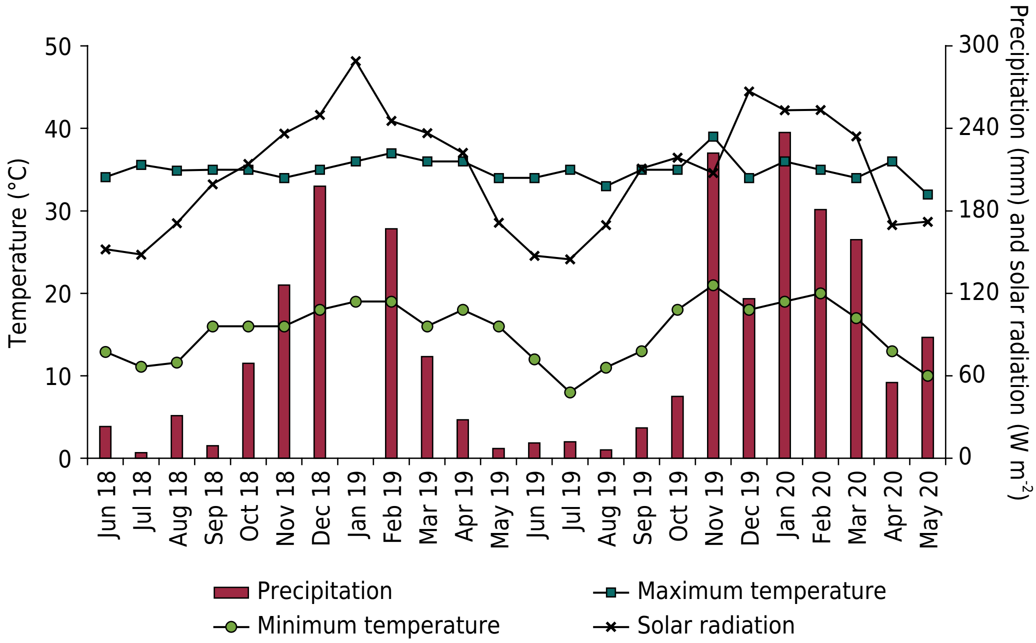

Figure 1. Values of climatic variables observed during the study period (June 2018 to May 2020).

productivity of 7,860 to 10,200 kg ha^{-1}. The lowest dose of N used in this study represents approximately half of the recommendation, while the highest one is almost twice the indicated dose. The experimental plot was composed of 21 plants, arranged in three rows, considering the five internal plants of the central line useful, while the others served as a border.

The N dose proposed for the different treatments was divided into five applications in each agricultural year and performed in October, November, December, January, and February. Urea was the N source, a fertilizer that has 46 % of N and high solubility. For the application of N, urea was dissolved in water, obtaining a homogeneous solution with 129.1 g L^{-1}. Subsequently, with the help of previously gauged polyethylene cups, the solution was applied over the soil, parallel to the irrigation hose, in the strip of soil wetted by the drippers. In each of the five applications, each plant received 0.272, 0.454, 0.636, 0.818, and 1.0 L of solution, referring to the treatments 300, 500, 700, 900 and 1,100 kg ha^{-1} of N, respectively. Immediately after the supply of N, irrigation was carried out, aiming to promote the rapid incorporation of urea into the soil.

We opted for the dose of 4 kg ha^{-1} yr^{-1} of Mo applied to the soil; this value was based on the intensity of the Mo adsorption process and non-labile Mo formation in tropical soils (Santos, 2012; Wurzburger et al., 2012; Nie et al., 2020); the high limit of Mo toxicity observed in different cultivated species (Gupta and Gupta, 1998; Singh et al., 2010); and the N doses used in this study. In each agricultural year, the Mo dose was divided into two applications, carried out in November and January, using the sodium molybdate fertilizer (39 % Mo) as a source of Mo. Initially, the fertilizer was dissolved in water, obtaining a homogeneous solution with 55.4 g L^{-1} of sodium molybdate. Then, each plant received 25 mL of the solution using a fixed-volume semi-automatic pipette. Subsequently, the irrigation system was started, aiming to incorporate the fertilizer into the soil.

In each agricultural year evaluated, at the end of November and January, after the first application of Mo and the second application of N and after the second application of Mo and the fourth application of N, respectively, the Conilon coffee leaves were collected to determine the Mo and N contents. The third and fourth pairs of leaves were collected from the end of the plagiotropic branches located in the middle third of the plant, in two plagiotropic branches facing opposite sides, between the lines of the crop, totaling eight leaves per plant, following the methodology proposed by Malavolta (2006), for dense coffee crops. The collection was carried out in all five useful plants of each experimental unit. The leaves were packed in paper bags, and dried in an oven with air circulation by 96 h at 65 °C. Leaf samples were ground in a Willey mill and packed for later nutrient analysis. The levels of Mo were determined after open digestion with HNO_3 and H_2O_2 and quantified in an atomic emission spectrometry device (ICPE-9000) (Peters, 2005). The total N was obtained using the methodology described by Silva (2009).

At the end of May 2019 and 2020, soil samples were taken with the aid of a Dutch auger at layers of 0.00-0.20 and 0.20-0.40 m. In the irrigated area of each plot, five simple samples were collected for each evaluated layer and were homogenized to obtain a composite sample. Then, it was analyzed as to the pH(H_2O) (1:2.5 soil:solution ratio), pH(KCl) (KCl 1.0 mol L^{-1}; 1:2.5 soil:solution ratio), ΔpH [pH(KCl) – pH(H_2O)], exchangeable Al (KCl extractor 1.0 mol L^{-1}), potential acidity (calcium acetate extractor 0.5 mol L^{-1}), organic matter (Walkley-Black method, wet oxidation with $Na_2Cr_2O_7$ + H_2SO_4) and Mo (Mehlich-1 extractor, HCl 0.05 mol L^{-1} + H_2SO_4 0.0125 mol L^{-1}), following the methodologies described by Silva (2009).

The harvest of Conilon coffee for the 2019 and 2020 harvests was carried out in May when the crop presented approximately 80 % of cherry fruits. The harvest of all five useful plants that make up each experimental unit was carried out using manual stripping on cloth. The production of processed coffee was obtained after drying and processing the fruits.

Experimental data were submitted to analysis of variance and F-test at 5 % probability. When there was a significant effect, polynomial regression analysis was applied to the "N doses", selecting the model with the highest significance in the F-test, while the interaction nitrogen × molybdenum was explored only when were significant with a 5 % probability using the R Development Core Team (2014).

RESULTS

There was no significant interaction between Mo and N factors for soil properties during the agricultural years of 2018/2019 and 2019/2020. However, there was an isolated effect of nitrogen fertilization for the variables evaluated. The increase in the doses of N applied to the soil promoted a decrease in the pH values for the analyzed layers (Figure 2a). Compared to the treatment that received the lowest dose of N, the application of 1,100 kg ha^{-1} of N reduced the soil pH by 1.38 and 1.28 unit, for the layers of 0.00-0.20 and 0.20-0.40 m, respectively, in the results observed in 2019. In the second year evaluated, there were decreases of 1.23 and 1.58 unit, for layers of 0.00-0.20 and 0.20-0.40 m, respectively.

Nitrogen fertilization caused a significant change in the profile of electrical charges on the soil (Figure 2b). Higher doses of nitrogen resulted in an elevation of soil ΔpH, at the different years and layers sampled. The less negative values of ΔpH point to an increase in the density of positive electrical charges due to the increase in soil acidity.

The nitrogen fertilization promoted a linear increase of exchangeable Al (Figure 3a), demonstrating a very close inverse relationship between soil pH, which was reduced by the application of N urea, and exchangeable Al levels.

The application of N doses increased potential acidity for the different layers evaluated (Figure 3b). In the analysis carried out in 2020, for the layer of 0.20-0.40 m, the quadratic adjustment model was the one that best represented the behavior of the obtained data. In the other evaluations, there was a linear increase in the values of H+Al.

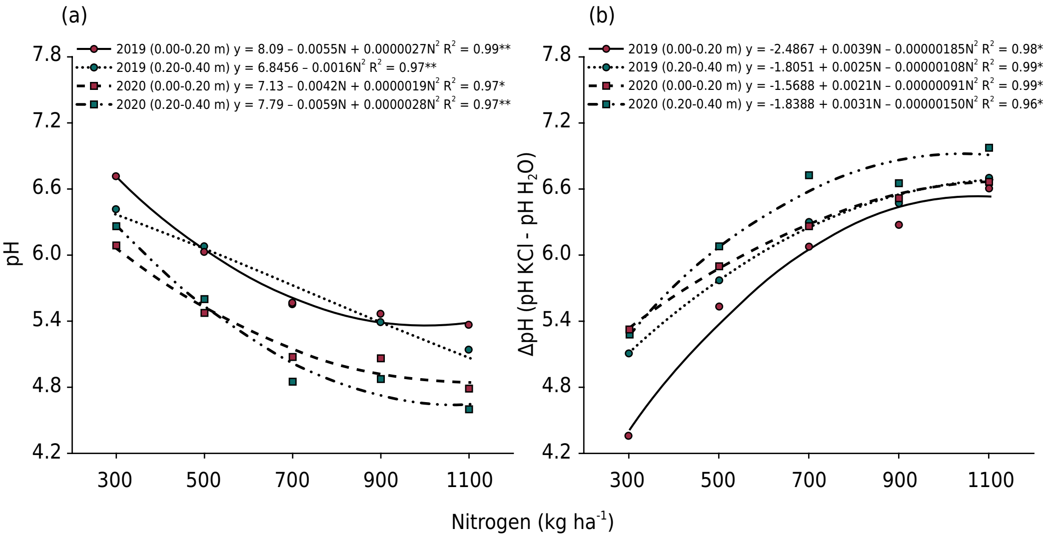

Figure 2. pH(H_2O) (a) and ΔpH [pH(KCl) – pH(H_2O)] (b) at layers of 0.00-0.20 and 0.20-0.40 m in the soil cultivated with Conilon coffee, in response to the application of nitrogen doses. * and **: significant at 5 and 1 % probability, respectively.

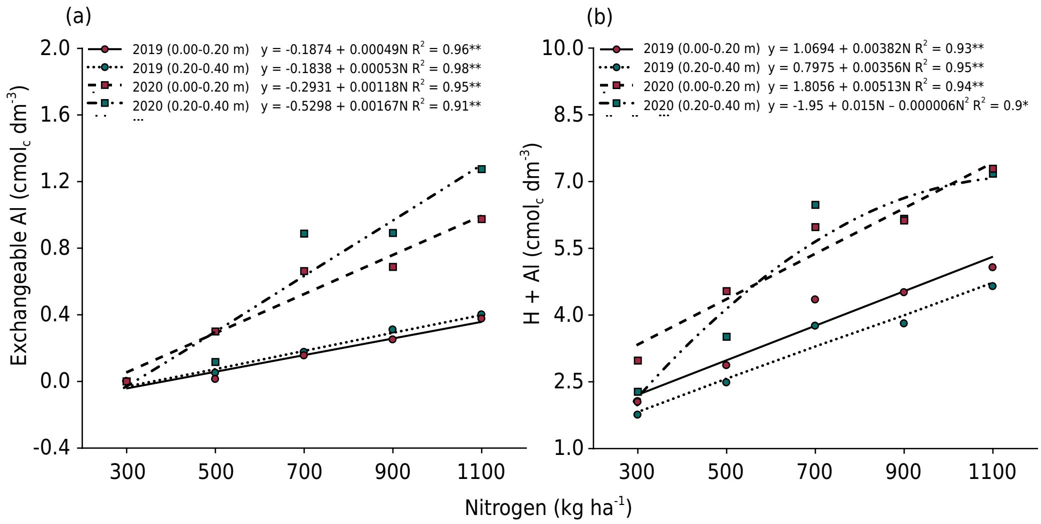

Figure 3. Exchangeable Al values (a) and H+Al (b) at layers of 0.00-0.20 and 0.20-0.40 m in the soil cultivated with Conilon coffee, in response to the application of nitrogen doses. * and **: significant at 5 and 1 % probability, respectively.

It was observed during the period evaluated that, for the different layers, no variation in organic matter was obtained with increasing urea dose (Figure 4). It was also noted that the Mo content in the soil was neither influenced by molybdic fertilization, nor by the doses of N (Figure 5a). It is seen that the average Mo contents in the soil reached 1.7 mg dm^{-3} in the first year evaluated, for the layers of 0.00-0.20 and 0.20-0.40 m. In the analysis carried out in 2020, the values were reduced to 1.0 mg dm^{-3}, in both sampled layers.

Despite the results presented for the Mo content in the soil, it can be seen in figure 5b that an increase in nitrogen fertilization resulted in a decrease in the Mo contents in coffee leaves. In the evaluations carried out in November 2018, January and November 2019, there was no significant interaction between Mo and N. However, the increase in nitrogen fertilization decreased leaf Mo contents. In the evaluation carried out in January 2020, there was a significant interaction between doses of N and molybdic fertilization. The increase in nitrogen fertilization resulted in a decrease in the Mo contents, while in the absence of the supply of Mo, the means did not differ statistically.

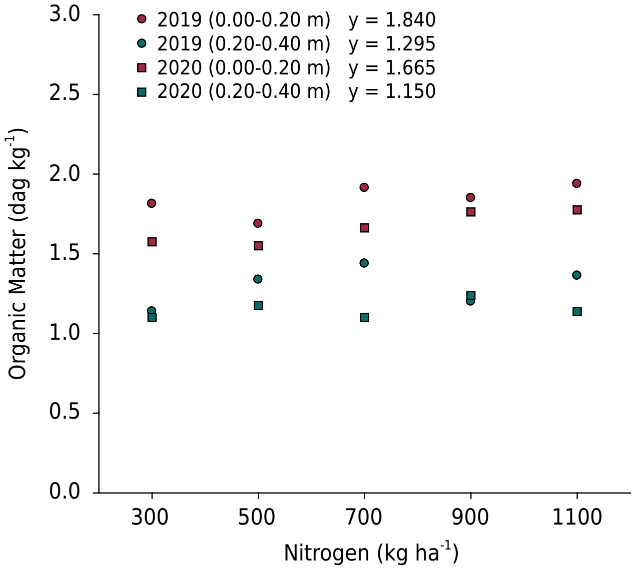

Figure 4. Organic matter contents at layers of 0.00-0.20 and 0.20-0.40 m in the soil cultivated with Conilon coffee, in response to the application of nitrogen doses.

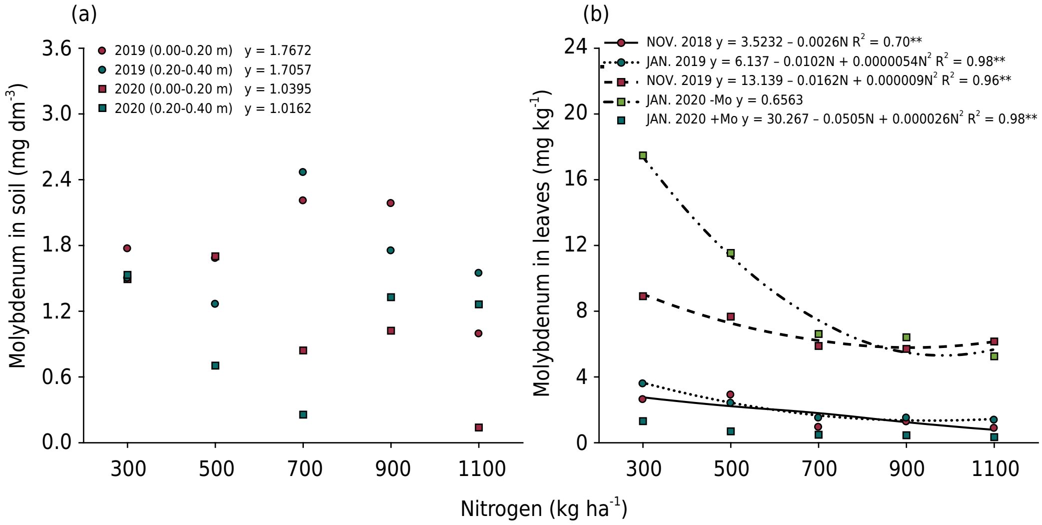

Figure 5. Contents of molybdenum at layers of 0.00-0.20 and 0.20-0.40 m in the soil (a) and leaves of Conilon coffee (b), for the harvests 2018/2019 and 2019/2020, in response to the application of molybdenum and nitrogen doses. ** significant at 1 % probability.

In the assessment carried out in January 2020, the average Mo concentration for treatments that did not receive molybdic fertilization was 0.65 mg kg^{-1}, while the Mo levels varied between 5.75 and 17.46 mg kg^{-1} in plants fertilized with sodium molybdate. These results demonstrate that soil fertilization was efficient in providing Mo to Conilon coffee since the application of 4 kg ha^{-1} of Mo raised the average micronutrient content in the leaves of the coffee tree. Even so, for the two years evaluated, molybdic fertilization in November and January did not increase the Mo content in the soil, in the observations made in May 2019 and 2020.

The increase in the supply of N resulted in increments of N in the leaves for the two agricultural years evaluated (Figure 6a). In the different observation periods, higher levels of N can be seen in the sampled carried out in November. In this period, the highest concentration of N in the leaves was verified when Conilon coffee was submitted to doses of 755 and 950 kg ha^{-1} of N for the years 2018 and 2019, respectively.

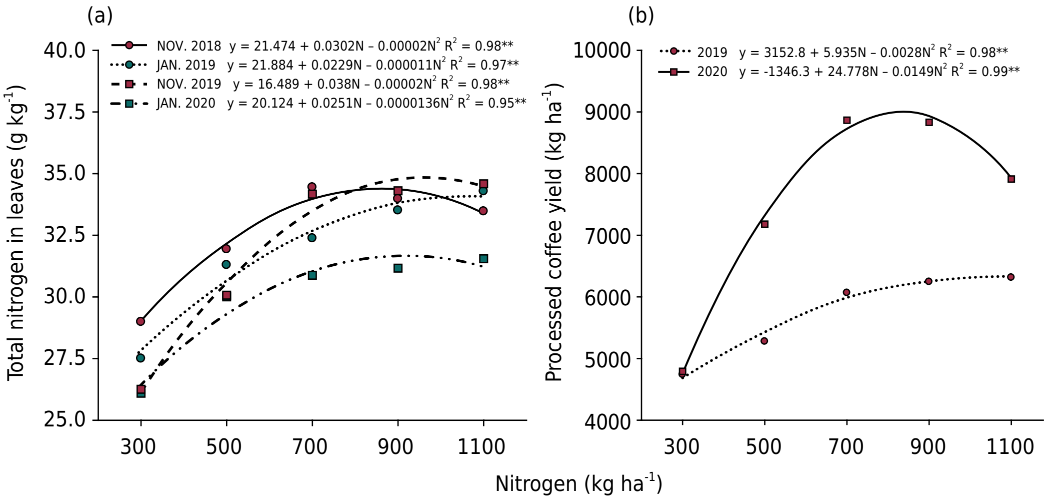

Figure 6. Concentration of total nitrogen in leaves of Conilon coffee (a) and processed coffee yield (b), for the harvests 2018/2019 and 2019/2020, in response to the application of nitrogen doses. ** significant at 1 % probability.

Table 2. Conilon coffee productivity in response to molybdenum fertilization

Variable	Harvest 2018/2019			Harvest 2019/2020		
	+ Mo(1)	- Mo	Mean	+ Mo(1)	- Mo	Mean
Productivity (kg ha^{-1})	5,704 a	5,755 a	5,730	7,651 a	7,381 b	7,516

(1) Dose of 4 kg ha^{-1}. Means followed by the same letter (for each harvest) do not differ by the F-test at 5 % of probability.

The supply of N resulted in increased coffee productivity in both years evaluated (Figure 6b). For the harvest carried out in 2019, the maximum yield of 6,343 kg ha^{-1} was obtained with the application of 1,075 kg ha^{-1} of N. In the second year evaluated, yield increases were registered up to the dose of 832 kg ha^{-1} of N, reaching 8,954 kg ha^{-1}. In 2019, the application of 1,075 kg of N resulted in an increase in yield of 35.3 % compared to the lowest dose of N. In 2020, yield increases of 88.9 % were observed when the plants were fertilized with 832 kg ha^{-1} of N. The supply of 4 kg ha^{-1} of Mo resulted in a significant increase in the yield of *C. canephora* in 2020 (Table 2). Molybdic fertilization provided a 3.7 % increase in the yield of processed coffee.

DISCUSSION

Intense acidification of the soil after applying N in the form of urea is reported in the literature. In an Oxisol cultivated with Conilon coffee, Guarçoni (2011) recorded an increase in soil acidity at the layer of 0.00-0.20 m, with an average pH reduction of 0.9 unit after the addition of 450 kg ha^{-1} yr^{-1} of N. When assessing the effect of nitrogen fertilization on *C. canephora* crop in two Cuban Inceptisols, Díaz et al. (2011) found that the supply of 400 kg ha^{-1} of N promoted a decrease in pH values of 0.72 and 0.67 unit, for the layer of 0.00-0.30 m. The increase in acidity can be caused by several events that occur in the soil (Goulding, 2016). Mineral fertilization, with emphasis on the application of N in amidic and ammoniacal forms, represents the main agent of acidification of soils (Tian and Niu, 2015).

How mineral fertilizers were applied to the soil may have contributed to the marked reduction in pH. During the two coffee production cycles, the recommended fertilizers, as well as the proposed treatments, were dissolved in water and applied to the soil strip wetted by the drippers. This management, which aimed to simulate the practice of fertigation, certainly favored the maintenance of fertilizers in the wet bulb. As a result, the volume of soil in contact with urea was lower, intensifying the acidification. When assessing spatial pH variability in coffee tree fertigated with urea, Rezende et al. (2012) found that the concentration of fertilizers in the strip of fertigated soil resulted in greater acidification, due to the maintenance of nutrients in a reduced soil volume.

The ΔpH is an important property to determine the net electrical charge of the soil (Dinali et al., 2019). Reducing the pH increases the density of positive electrical charges in the soil (Sun and Selim, 2019). The addition of positive electrical charges in the sorption complex increases the maximum anion adsorption capacity, such as phosphate and molybdate, which makes the soil a strong drain of P and Mo, competing with the plants for the anions in solution (Nie et al., 2020).

The ΔpH obtained in 2020 for the different layers was closer to the ZPC when compared to the values achieved in 2019. The results indicate that the increase in acidity observed in the evaluated period made the soil less electronegative. Figure 2b also shows more negative ΔpH values for the layer of 0.00-0.20 m, in the assessments made in 2019 and 2020. It is possible to assume that the highest levels of organic carbon in the 0.00-0.20 m layer are responsible for the obtained results, due to the high density of electrical charges and low ZPC, mainly of carboxylic groups of the organic matter, as in the results found by Ramos et al. (2018). The increase in the density of negative electrical charges in the superficial layer of the soil was observed by Baldotto and Velloso (2014) in a study of soil electrochemistry in tropical environments. The authors attributed the results to the organic matter present in great concentration in the first centimeters of the soil.

The relationship between exchangeable Al levels and soil pH due to acidification caused by the application of urea is shown in figure 3a. After extensive research and based on the results of 106 scientific articles that evaluated the effects of the application of mineral N on the chemical properties of different soils, cultivated with different plant species, Tian and Niu (2015) observed that nitrogen fertilization with ammonia and amidic sources contributed to acidifying the soil and increasing the levels of exchangeable Al.

Figures 3a and 3b show the close relationship between exchangeable Al and H+Al, described by Almeida Junior et al. (2015). The increase in potential acidity in soils cultivated with *C. canephora*, due to acidification caused by the application of urea, was also observed by Guarçoni (2011) and Partelli et al. (2012). The supply of N in the form of urea showed great potential for soil acidification and an increase in the values of exchangeable Al and H+Al (Figure 3), and this behavior extended to the layer of 0.20-0.40 m from the soil. Maintaining adequate pH and low exchangeable Al values in the 0.20-0.40 m layer of soil are of great importance for Conilon coffee. In a drip-irrigated *C. canephora* crop, Covre et al. (2015) found 32 % of the root surface area in this layer of soil.

The lack of changes in the organic matter contents for the soil layers of 0.00-0.20 and 0.20-0.40 m (Figure 4) is similar to the results reported by Guarçoni (2011) for the soil layer of 0.00-0.20 m, cultivated with Conilon coffee. Despite higher content for the layer of 0.00-0.20 m (Figure 4), the levels of organic matter are below that recommended for *C. canephora* (Prezotti et al., 2017).

During the evaluated period, the available Mo contents in the soil, extracted by Mehlich-1 (Figure 5a), followed the same trend described by Santos (2012), who found values close to 1.0 mg dm^{-3} in different Ultisols in Brazil, employing the same extractor. On the European continent, McGrath et al. (2010) found Mo contents extracted by Ammonium Oxalate between 0.50 and 2.91 mg dm^{-3} when evaluating ten different soils, while Rutkowska et al. (2017) observed that 96 % of the 62 soils sampled had Mo contents extracted by HCl below 1.5 mg dm^{-3}.

The lack of variation in the Mo content in the soil (Figure 5a) can be explained by the high affinity of the molybdate anion for the positive charges of the mineral colloids that make up the clay fraction. When assessing the availability of Mo in acidic soil, Nie et al. (2020) observed intense specific adsorption of molybdate to positive charges of the assortment complex, especially in iron oxides. Aging of these covalent bonds of high stability, with the exchange of ligands, prevents the return of Mo to the soil solution.

The availability of Mo in the solution of acid oxidid soils can be reduced by the formation of precipitates with iron and aluminum (Rutkowska et al., 2017). The stability of iron-molybdate and aluminum-molybdates compounds, as well as the reversibility of these reactions, will depend on the solubility of the compounds formed and the pH of the medium (Dechen et al., 2018).

Several studies evaluating the adsorption kinetics of Mo demonstrated the speed with which the molybdate anion is removed from the soil solution, especially in acidic and oxidic soils, rich in Fe and Al, with high ZPC. When investigating the adsorption of Mo in Chilean soils, Vistoso Gacitua et al. (2009) found that after adding Mo to the soil samples, more than 89 % of the molybdate had been adsorbed at the end of 72 h. More striking results were presented by Wurzburger et al. (2012), in a study on adsorption and desorption of Mo in tropical soils in Panama. After applying molybdate to the soil followed by 25 h of incubation, the authors observed that the levels of labile Mo, extracted with anion exchange resin, represented less than 2 % of total Mo.

From the above, it appears that the soil can act as a Mo sink, resulting in the depletion of molybdate in solution, thus compromising the plants' molybdic nutrition. Considering the results obtained in the January 2020 assessment (Figure 5b), it is postulated that the Mo contents in coffee were influenced by molybdic fertilization, due to the high absorption capacity of Mo by the roots, favoring the removal of molybdate of the soil solution, especially in the first hours after fertilization. Over time, however, it is assumed that the soil acted as a strong Mo sink, removing the molybdate from the solution and transforming it into non-labile Mo, which justifies the low levels of Mo in the soil (Figure 5a) in the analyses carried out months after molybdic fertilization.

The fact that the Mo content in the soil has not been influenced by molybdic fertilization may be related to the low sensitivity of the extractors currently used to determine Mo. Analytical results are often inconsistent due to the low levels of Mo in the soil, close to the detection limit of different extraction solutions (Popov et al., 2014). This argument was made by Duval et al. (2015) to justify the absence of correlation between Mo in the soil and leaves of *Quercus myrtifolia*, for all the extractors evaluated.

It can also be seen, when looking at figure 5b, that the application of doses of N reduced the levels of Mo in *C. canephora* leaves. These results can be attributed to the acidification of the soil caused by the supply of N (Figure 2a), resulting in a higher density of positive charges in the soil complex (Figure 2b). In a study on kinetic modeling, adsorption, and desorption of Mo, Sun and Selim (2019) concluded that pH is the main factor that governs the availability of molybdate in the soil solution. When researching the influence of soil physicochemical properties on the Mo content in solution, Rutkowska et al. (2017) reported a significant reduction in labile Mo with increasing soil acidity. The authors recorded an increase of 164 % in the concentration of Mo with an increase in pH in one unit. They also mentioned that the molybdic nutrition of the crops was affected by changes in the soil pH.

It was verified during the evaluated period that the Mo values in the soil were not related to the levels obtained in Conilon coffee leaves. Similar results were presented by Santos (2012) when comparing methods of extracting Mo in three Ultisols of northeastern Brazil. The author did not observe, for the different extractors used, the correlation between the Mo content in the soil, and the molybdic nutrition of sugarcane.

In the January 2020 evaluation, average Mo values of 0.65 mg kg^{-1} can be observed in leaves of coffee unfertilized with sodium molybdate (Figure 5b). In a pioneering study on the mineral nutrition of *Coffea arabica*, Malavolta et al. (1961) observed symptoms of Mo deficiency in plants with leaf contents of 0.9 mg kg^{-1}. Information about the sufficiency range for Mo in agricultural crops is scarce. In general, Sun and Selim (2019) report that the demand for Mo is met with leaf contents between 0.1 to 1.0 mg kg^{-1}. For Kaiser et al. (2005), the critical level for Mo is very variable between cultures and dependent on the management of nitrogen nutrition due to the close relationship of this nutrient with N metabolism.

The increase in the supply of N resulted in quadratic increments of N in the leaves (Figure 6a), similar to observed by Vilela et al. (2017) while testing increasing doses of N in plants of *C. canephora* in the formation phase. The reduction of N levels in the evaluations of January 2019 and 2020 compared to the values obtained in November can be attributed to the mobilization of nitrogen compounds from the leaves to the fruits. This statement can be supported by assessing the N levels in January 2019 and 2020 and the productivity of Conilon coffee in the agricultural years 2018/2019 and 2019/2020 (Figure 6b), where lower N levels are found in the second year due to the higher productivity of the coffee crop. These results corroborate those obtained by Abranches et al. (2019) when studying levels of nutrients in leaves of Arabica coffee, submitted to nitrogen fertilization. The authors observed in the first year a reduction in the levels of total N in coffee leaves during grain formation, with lower levels of N in March compared to values obtained in October.

Partelli et al. (2016) established a sufficiency range for N between 25.2 and 30.6 g kg^{-1}. During the two agricultural years evaluated, the concentrations of N varied between 26.1 and 34.5 g kg^{-1}. It appears that the upper limit of the proposed sufficiency range was outdone with the provision of low doses of N. In the first three evaluations, levels of N above 30.6 g kg^{-1} were obtained with the application of higher doses of N at 507 kg ha^{-1}. These results, supported by productivity data (Figure 6b), point to the need of reviewing the sufficiency ranges for Conilon coffee of high productivity.

The synergistic relationship between N and Mo reported by Marschner (2011) and verified by Imran et al. (2019) for wheat, and by Santos et al. (2019) for sugar cane, was not observed in this study. The results suggest that the content of Mo in Conilon coffee was influenced by the acidity of the soil resulting from the doses of N, indicating that the effect of pH on the specific adsorption and lability of Mo, elucidated by Rutkowska et al. (2017), has a greater influence on the absorption of Mo by coffee, outdoing the effects from ionic interactions.

The increase in the supply of N resulted in quadratic increments in coffee productivity. The results described, especially in 2020, corroborate those presented by Busato (2015), studying the biometric characteristics of irrigated Conilon coffee, submitted to doses of N. The author verified in the first year of evaluations that the highest yield, of 8,670 kg ha^{-1}, was obtained when the coffee tree received 829 kg ha^{-1} of N.

It is important to highlight the yield of Conilon coffee in 2020, which is higher than that obtained in 2019 for all doses of N. When comparing the maximum yield achieved in the two years evaluated, it appears that the value recorded in 2020 is 41.4 % higher than that observed in 2019. The phenological phase of the crop, the favorable climatic conditions, with an adequate distribution of rainfall during the period of growth and fruit filling, as well as nutritional management, can explain the results obtained.

The yields greater than 8,700 kg ha^{-1} in 2020 were achieved with N doses between 698 and 967 kg ha^{-1}. In the same period, it appears that the highest concentrations of N in the leaves in the Conilon coffee are included in the mentioned range, demonstrating the close relationship between nitrogen nutrition and coffee yield. It is noteworthy that the supply of Mo resulted in a significant increase in the yield of *C. canephora* (Table 2). Despite the paucity of studies on coffee, recent studies show that Mo's application increased the yield in crops such as sugarcane (Santos et al., 2018b) and corn (Caioni et al., 2016).

CONCLUSIONS

Urea showed a high potential for soil acidification, influencing the values of exchangeable Al, potential acidity, and ΔpH at the 0.00-0.20 and 0.20-0.40 m soil layers.

The reduction in pH caused by the doses of N affected the profile of electrical charges in the soil, making it less electronegative and impacting Mo levels in *C. canephora*.

The application of sodium molybdate via soil was efficient in providing Mo to coffee trees. Nevertheless, molybdic fertilization did not influence the Mo content in the soil in the evaluations carried out at the end of each production cycle.

ACKNOWLEDGMENTS

The authors are thankful to Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ), State University of Northern Rio de Janeiro (UENF), and the Federal Institute of Espirito Santo (IFES) for technical and financial support.

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REFERENCES

Abranches JL, Soratto RP, Perdoná MJ, Parecido RJ. *Arabica coffee* response to rates of coated and conventional urea in sandy soil. Pesq Agropec Bras. 2019;54:e00767. https://doi.org/10.1590/s1678-3921.pab2019.v54.00767

Almeida Junior AB, Nascimento CWA, Barros FMR. Acidez potencial estimada pelo método do pH SMP em solos do estado da Paraíba. Rev Bras Cienc Solo. 2015;39:767-73. https://doi.org/10.1590/01000683rbcs20140307

Alvares CA, Stape JL, Sentelhas PC, Moraes JLM, Sparovek G. Köppen's climate classification map for Brazil. Meteorol Zeitschrift. 2013;22:711-28. https://doi.org/10.1127/0941-2948/2013/0507

Baldotto MA, Velloso ACX. Eletroquímica de solos modais e de sua matéria orgânica em ambientes tropicais. Rev Ceres. 2014;61:1012-21. https://doi.org/10.1590/0034-737X201461060018

Bonomo DZ, Bonomo R, Partelli FL, Souza JM. Genótipos de café conilon sob ajuste de diferentes coeficientes de cultura ajustados. Irriga. 2017;22:236-48. https://doi.org/10.15809/irriga.2017v22n1p236-248

Busato C. Características biométricas do cafeeiro conilon irrigado associadas a índices fisiológicos e nutricionais de nitrogênio [tese]. Alegre: Universidade Federal do Espírito Santo; 2015.

Caioni S, Lazarini E, Parente TL, Pivetta RS, Souza LGM. Nitrogênio e molibdênio para milho irrigado em região de cerrado de baixa altitude. Rev Bras Milho Sorgo. 2016;15:419-28. https://doi.org/10.18512/1980-6477/rbms.v15n3p418-427

Colodetti TV, Rodrigues WN, Martins LD, Brinate SVB, Tomaz MA, Amaral JFT, Verdin Filho AC. Nitrogen availability modulating the growth of improved genotypes of *Coffea canephora.* Afr J Agr Res. 2015;10:3150-6. https://doi.org/10.5897/AJAR2015.9692

Covre AM, Partelli FL, Gontijo I, Zucoloto M. Distribuição do sistema radicular de cafeeiro conilon irrigado e não irrigado. Pesq Agropec Bras. 2015;50:1006-16. https://doi.org/10.1590/S0100-204X2015001100003

Dechen AR, Nachtigall GR, Carmello QAC, Santos LA, Sperandio MVL. Micronutrientes. In: Fernandes MS, Souza SR, Santos LA, editors. Nutrição mineral de plantas. Viçosa, MG: Sociedade Brasileira de Ciência do Solo; 2018. p. 491-562.

Díaz AP, González CAB, Alonso GMM, Espinosa RAR, Núñez RV, Castro MIR. Fertilización nitrogenada después de la poda del cafeto robusta en Cambisoles. Pesq Agropec Bras. 2011;46:935-43. https://doi.org/10.1590/S0100-204X2011000800021

Dinali GS, Root RA, Amistadi MK, Chorover J, Lopes G, Guilherme LRG. Rare earth elements (REY) sorption on soils of contrasting mineralogy and texture. Environ Int. 2019;128:279-91. https://doi.org/10.1016/j.envint.2019.04.022

Duval BD, Natali SM, Hungate BA. What constitutes plant-available molybdenum in sandy acidic soils? Commun Soil Sci Plan. 2015;46:318-26. https://doi.org/10.1080/00103624.2014.969405

Ferrão RG, Fonseca AFA, Ferrão MAG, De Muner LH. Café conilon. 2. ed. Vitória: Incaper; 2017.

Goulding KWT. Soil acidification and the importance of liming agricultural soils with particular reference to the United Kingdom. Soil Use Manage. 2016;32:390-9. https://doi.org/10.1111/sum.12270

Guarçoni AM. Características da fertilidade do solo influenciadas pelo plantio adensado de café conilon. Semin-Cienc Agrar. 2011;32:949-58. https://doi.org/10.5433/1679-0359.2011v32n3p949

Gupta UC, Gupta SC. Trace element toxicity relationships to crop production and livestock and human health: implications for management. Commun Soil Sci Plan. 1998;29:1491-522. https://doi.org/10.1080/00103629809370045

Imran M, Sun X, Hussain S, Ali U, Rana MS, Rasul F, Saleem MH, Moussa MG, Bhantana P, Afzal J, Elyamine AM, Hu CX. Molybdenum-induced effects on nitrogen metabolism enzymes and elemental profile of winter wheat (*Triticum aestivum* L.) under different nitrogen sources. Int J Mol Sci. 2019;20:3009. https://doi.org/10.3390/ijms20123009

Kaiser BN, Gridley KL, Brady JN, Phillips T, Tyerman SD. The role of molybdenum in agricultural plant production. Ann Bot-London. 2005;96:745-54. https://doi.org/10.1093/aob/mci226

Malavolta E. Manual de nutrição mineral de plantas. São Paulo: Agronômica Ceres; 2006.

Malavolta E, Haag HP, Johnson CM. Estudos sobre a alimentação mineral do cafeeiro: VI efeitos das deficiências de micronutrientes em *Coffea arabica* L. var. Mundo Novo cultivado em solução nutritiva. An Esalq. 1961;18:147-67.

Marschner P. Mineral nutrition of higher plants. 3rd ed. London: Academic Press; 2011.

McGrath SP, Micó C, Curdy R, Zhao FJ. Predicting molybdenum toxicity to higher plants: influence of soil properties. Environ Pollut. 2010;158:3095-102. https://doi.org/10.1016/j.envpol.2010.06.027

Nie Z, Li J, Liu H, Liu S, Wang D, Zhao P, Liu H. Adsorption kinetic characteristics of molybdenum in yellow-brown soil in response to pH and phosphate. Open Chem. 2020;18:663-8. https://doi.org/10.1515/chem-2020-0501

Oliosi G, Rodrigues JO, Falqueto AR, Pires FP, Monte JA, Partelli FL. Fluorescência transiente da clorofila *a* e crescimento vegetativo em cafeeiro conilon sob diferentes fontes nitrogenadas. Coffee Sci. 2017;12:248-59. https://doi.org/10.25186/cs.v12i2.1268

Partelli FL, Gomes WR, Oliveira MG, Dias JRM, Espindula MC. Normas foliares e diagnóstico nutricional do cafeeiro conilon na pré-florada e granação, no Espírito Santo. Coffee Sci. 2016;11:544-54.

Partelli FL, Vieira HD, Ferreira EPB, Viana AP, Martins MA, Urquiaga S. Chemical and microbiological soil characteristics under conventional and organic coffee production systems. Commun Soil Sci Plant. 2012;43:847-64. https://doi.org/10.1080/00103624.2012.648470

Peters JB. Wisconsin procedures for soil testing, plant analysis and feed & forage analysis. Madison: University of Wisconsin; 2005. Available from: https://uwlab.soils.wisc.edu/about-us/lab-procedures-and-methods/

Popov AM, Labutin TA, Zaytsev SM, Seliverstova IV, Zorov NB, Kalko IA, Sidorina YN, Bugaev IA, Nikolaev YN. Determination of Ag, Cu, Mo and Pb in soils and ores by laser-induced breakdown spectrometry. J Anal Atom Spectrom. 2014;29:1925-33. https://doi.org/10.1039/C4JA00199K

Prezotti LC, Guarçoni MA, Bragança SM, Lani JA. Calagem e adubação do café conilon. In: Ferrão RG, Fonseca AFA, Ferrão MAG, De Muner LH, editors. Café conilon. 2. ed. Vitória: Incaper; 2017. p. 347-57.

R Development Core Team. R: A language and environment for statistical computing. R Foundation for Statistical Computing. Vienna, Austria; 2014. Available from: http://www.R-project.org/.

Ramos FT, Dores EFC, Weber OLS, Beber DC, Campelo Jr JH, Maia JCS. Soil organic matter doubles the cation exchange capacity of tropical soil under no-till farming in Brazil. J Sci Food Agr. 2018;98:3595-602. https://doi.org/10.1002/jsfa.8881

Rezende FC, Ribeiro VB, Ávila LF, Faria MA, Silva EL. Variabilidade espacial do pH em área com cafeeiro fertirrigado e sistema tradicional. Coffee Sci. 2012;7:198-207. https://doi.org/10.25186/cs.v7i3.522

Rochette P, Angers DA, Chantini MH, Gasser M, Macdonald JD, Pelster DE, Bertrand N. NH_3 volatilization, soil NH_4 concentration and soil pH following subsurface banding of urea at increasing rates. Can J Soil Sci. 2013;93:261-8. https://doi.org/10.4141/cjss2012-095

Rutkowska B, Szulc W, Spychaj-Fabisiak E, Pior N. Prediction of molybdenum availability to plants in differentiated soil conditions. Plant Soil Environ. 2017;63:491-7. https://doi.org/10.17221/616/2017-PSE

Santos HG, Jacomine PKT, Anjos LHC, Oliveira VA, Lumbreras JF, Coelho MR, Almeida JA, Araújo Filho JC, Oliveira JB, Cunha TJF. Sistema brasileiro de classificação de solos. 5. ed. rev. ampl. Brasília, DF: Embrapa; 2018a.

Santos MJ. Extração e determinação de Mo em três Argissolos do nordeste cultivados com cana-de-açúcar [dissertação]. Recife: Universidade Federal Rural de Pernambuco; 2012.

Santos RL, Freire FJ, Oliveira ECA, Freire MBGS, West JB, Barbosa JA, Bezerra PC. Nitrate reductase activity and nitrogen and biomass accumulation in sugarcane under molybdenum and nitrogen fertilization. Rev Bras Cienc Solo. 2019;43:e0180171. https://doi.org/10.1590/18069657rbcs20180171

Santos RL, Freire FJ, Oliveira ECA, Simões Neto DE, Medeiros MRFA, Bezerra PC, Moura MJA, Barbosa JA, Lopes NRC, Santos NL. Productivity and technological quality of sugarcane under fertilization of nitrogen and molybdenum. J Soil Sci Plant Nut. 2018b;18:1002-20. https://doi.org/10.4067/S0718-95162018005002901

Silva FC. Manual de análises químicas de solos, plantas e fertilizantes. 2. ed rev ampl. Brasília, DF: Embrapa Informação Tecnológica; 2009.

Silva NS, Guido ML, Luqueño FF, Marsch R, Dendooven L. Emission of greenhouse gases from an agricultural soil amended with urea: a laboratory study. Appl Soil Ecol. 2011;47:92-7. https://doi.org/10.1016/j.apsoil.2010.11.012

Singh AL, Jat RS, Chaudhari V, Bariya H, Sharma SJ. Toxicities and tolerance of mineral elements boron, cobalt, molybdenum and nickel in crop plants. P Stress. 2010;4:31-56.

Soil Survey Staff. Keys to soil taxonomy. 12th ed. Washington, DC: United States Department of Agriculture, Natural Resources Conservation Service; 2014.

Sun W, Selim HM. Kinetic modeling of pH-dependent molybdenum (VI) adsorption and desorption on iron oxide-coated sand. Soil Sci Soc Am J. 2019;83:357-65. https://doi.org/10.2136/sssaj2018.11.0449

Theodoro VCA, Alvarenga MIN, Guimarães RJ, Souza CAS. Alterações químicas em solo submetido a diferentes formas de manejo do cafeeiro. Rev Bras Cienc Solo. 2003;27:1039-47. https://doi.org/10.1590/S0100-06832003000600008

Tian D, Niu S. A global analysis of soil acidification caused by nitrogen addition. Environ Res Lett. 2015;10:024019. https://doi.org/10.1088/1748-9326/10/2/024019

Vilela DJM, Carvalho GR, Botelho CE, Carvalho AM, Praxedes MA, Santos MC, Fernandes FC. Crescimento inicial de cultivares de cafeeiro com diferentes doses de nitrogênio, fósforo e potássio. Coffee Sci. 2017;12:552-61. https://doi.org/10.25186/cs.v12i4.1370

Vistoso Gacitua EM, Bolan NS, Theng BKG, Mora ML. Kinetics of molybdate and phosphate sorption by some Chilean Andisols. Rev Cienc Suelo Nutr. 2009;9:55-68. https://doi.org/10.4067/S0718-27912009000100005

Wurzburger N, Bellenger JP, Kraepiel AML, Hedin LO. Molybdenum and phosphorus interact to constrain asymbiotic nitrogen fixation in tropical forests. PLoS ONE. 2012;7:e33710. https://doi.org/10.1371/journal.pone.0033710

Xu N, Braida W, Christodoulatos C, Chen J. A review of molybdenum adsorption in soils/bed sediments: speciation, mechanism, and model applications. Soil Sediment Contam. 2013;22:912-29. https://doi.org/10.1080/15320383.2013.770438