

RESEARCH ARTICLE

Evaluation of volatile compounds in coffee (*Coffea arabica* L.) beans in response to biochar applications using an electronic nose

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ABSTRACT

The use of biochar (BC) seems to be a promising alternative for efficient and environmentally friendly waste management that could help to promote cleaner agricultural production. The objective of this research was to evaluate the aromatic profile of coffee (*Coffea arabica* L.) beans and cup quality parameters in response to the application of four different doses of biochar (0, 4, 8, and 16 t ha⁻¹) obtained from coffee pulp, and four levels of chemical fertilization (CF) (0%, 33%, 66% and 100% of nutritional requirements). An electronic nose was used to analyze volatile compounds and their relationship with coffee quality parameters: Soluble solids (TSS), pH, titratable acidity. Applications of 8 and 16 t ha⁻¹ BC and 66% and 100% CF registered greater sensitivity to the aromatic compounds of roasted coffee beans in sensors W1C, W3C, and W5C. The BC amendments between 8 and 16 t ha⁻¹ and CF 66% and 100% increased the TSS content (CF 66%: 1.32 °Brix and CF 100%: 1.38 °Brix), reduced the pH (CF 66%: 4.95 and CF 100%: 4.88) and increased titratable acidity (CF 66%: 697.88 mg CaCO₃ L⁻¹ and CF 100%: 662.56 mg CaCO₃ L⁻¹) in beverages of 'Castillo El Tambo' coffee bean in the year 2020. Finally, the co-application of BC as a complement to CF showed a positive effect on the aromatic profile. This methodology could be an original approach to characterize beans according to the coffee crop's nutritional status, helping in factors focused on quality and traceability.

Key words: Aromatic profile, cup quality, mineral nutrition, soluble solids.

INTRODUCTION

Coffee is one of the most popular beverages consumed by about a third of the world's population (Chinchilla-Soto et al., 2021). The coffee industry constitutes an important sector of the global economy and generates income for around 25 million small farmers (Garcia-Freites et al., 2020). Additionally, about 99% of coffee production is obtained mainly from two species, arabica coffee (*Coffea arabica* L.) and robusta coffee (*C. canephora* Pierre ex A. Froehner). However, arabica coffee is in relatively higher demand (over 70% of the world market) due to its high beverage quality (Chemura et al., 2021). In Colombia, coffee is one of the main crops with a harvest of 833 400 t green coffee (close to 8.4% of the world production) in an area of 853 700 ha in 2020 (Federación Nacional de Cafeteros de Colombia, 2022).

The coffee industry generates many by-products and waste throughout the stages of cultivation, harvesting, and processing that lead to environmental, health, and economic problems (Garcia-Freites et al., 2020). The pulp, shell, mucilage, and parchment are the main coffee by-products that represent around 45%-50% of the harvested fruits and pose a great environmental risk for producing countries (Gemetchu, 2020). Additionally, the coffee pulp has high levels of phenolic acids and caffeine that cause negative effects on the environment since they are toxic substances for mammals and aquatic organisms and cause negative effects on plants and the growth of bacteria and fungi (Hoseini et al., 2021). The future of coffee cultivation requires a more sustainable approach to the use of the by-products of the productive chain (Murthy and Naidu, 2012). Faced with this complex scenario, the management of by-products such as the coffee pulp through its transformation into biochar by the pyrolysis process and its subsequent incorporation into the soil can be an important alternative to complement the mineral nutrition of crops that can provide numerous benefits in terms of yield and quality.

Biochar (BC) seems to be a promising alternative for efficient and environmentally friendly waste management (Srivatsav et al., 2020). Generating value-added products such as BC through the pyrolysis of agricultural residues and their subsequent application to the soil may help the nutrient recycling cycle and guarantee cleaner agricultural production (Kizito et al., 2019). In this context, Zhang et al. (2020) reported that blueberry plants treated with 1.5% and 3.0% (w/w) BC (obtained from a mixture of wood waste collected from furniture factories) increased their yield and fruit nutritional quality, possibly due to higher nutrient availability in the soil. Almaroai and Eissa (2020) report that BC applications (between 5 and 10 t ha⁻¹) made from corn stalks improved the content of total soluble solids (TSS) (4.5 vs. 3.5 °Brix), total acidity (0.40% vs. 0.30%) and lycopene content (16.5 vs. 13.3 mg g⁻¹ FW) of tomato fruits compared to plants not treated with BC, respectively.

Coffee quality is a complex trait that involves bean characteristics, biochemical compound contents, and sensory attributes. In this aspect, the content of caffeine can be influenced by environmental aspects (geography, topography, soil, climate) and management factors (harvesting and processing of coffee cherries, shade) among others (Yadessa et al., 2020). The analysis of coffee quality attributes, such as caffeine content, is generally expensive, requires many procedures that are usually carried out through destructive chemical methods, and takes a long time to obtain results (Kyaw et al., 2020). Given this scenario, it is necessary to develop instrumental methods that support the determination of coffee aroma and allow producers to identify high-quality coffee (Knysak, 2017). In recent decades, the use of electronic nose devices has increased since they are a simple, non-invasive, and fast tool to evaluate the quality of biological products. Similarly, the use of techniques for the analysis of large data sets obtained from electrochemical transducers has facilitated a broader application of the electronic nose for the analysis of volatile substances (Rusinek et al., 2019).

Devices such as the electronic nose have been used in the analysis of volatile compounds in the identification of the presence of characteristic volatile compounds in coffee beans from different cultivation regions and their correlation with the place of origin (Marek et al., 2020). The study of the effects of BC application on plant physiology has gained importance in recent years; however, the information about the responses of coffee crops to the use of BC amendments in the soil and its effect in the coffee bean quality parameters remains scarce. Therefore, the objective of this research was to evaluate the aromatic profile of coffee (*Coffea arabica* L. 'Castillo El Tambo') beans in response to the application of four different doses of biochar (0, 4, 8, and 16 t ha⁻¹) obtained from coffee pulp and four levels of chemical fertilization (0%, 33%, 66% and 100% of the nutritional requirements) using an electronic nose and its relationship with parameters typically used to evaluate the quality of the coffee beverage such as total soluble solids, pH, and titratable acidity.

MATERIALS AND METHODS

Plant material and growth conditions

The experiment was carried out at the Luxemburgo farm, located in the municipality of Chaparral (3°49'39.2" N, 75°34'07.1" W; 1875 m a.s.l.), Tolima, Colombia, from August 2018 to August 2020. The growth conditions were 27.4/20.7 °C day/night temperature, 763 mm yr⁻¹ average rainfall (between 2017 and 2019), 55.4% to 84.8% relative humidity, and 12:12 h natural photoperiod with 2050.9/4619.6 W m⁻² active direct radiation depending on weather conditions (rainy periods). The experiment was carried out on 3-yr-old coffee (*Coffea arabica* L.) trees. All trees were spaced at 1.70 m × 1.30 m (4500 trees ha⁻¹). The characteristics of the soil were: pH 5.50; 11.51 meq 100 g⁻¹ effective cation exchange capacity (ECEC); 0.17 dS m⁻¹ electrical conductivity; chemical characteristics: Total N: 0.27%, Ca: 7.85%, K: 0.50%, Mg: 2.52%, Na: 0.15 meq 100 g⁻¹, P: 0.98 mg kg⁻¹; Cu: 1.40 mg kg⁻¹, Fe: 124 mg kg⁻¹, Mn: 65 mg kg⁻¹, B: 0.07 mg kg⁻¹, Zn: 2.90 mg kg⁻¹, and loam texture (46% clay, 30% silt, and 46% sand).

Biochar treatments and fertilization levels

Biochar (BC) treatments were established 4 mo after the last harvest of the coffee trees (August 2018) using four different doses of BC: 0, 4, 8 and 16 t ha⁻¹ (BC0 = 0.0 kg tree⁻¹; BC4 = 0.75 kg tree⁻¹; BC8 = 1.5 kg tree⁻¹, and BC16 = 3.0 kg tree⁻¹). The doses were established based on the agronomic responses observed in other species of cultivated plants (Sánchez-Reinoso et al., 2020). The BC was applied at a radius of 30 cm from the base of the coffee tree stem and was later covered with a layer of soil. The BC used was obtained from coffee pulp, which had medium pyrolysis at 500 °C using a rotary kiln (6 m long × 0.7 m internal diameter, Tecsol, Bogotá, Colombia). Finally, the BC had the following characteristics: Ashes 20.8%; cation exchange capacity (CEC) 103 meq 100 g⁻¹; pH 9.42; electrical conductivity 19.4 dS m⁻¹; organic C (OC) 46.4%; N 2.81%; P 1.11%; Ca 0.97%; K 4.37%; Mg 0.43%; Cu 53.5 mg kg⁻¹; Fe 2795 mg kg⁻¹; Zn 110 mg kg⁻¹; B 99.3 mg kg⁻¹; OC/N 16.5.

The fertilization treatments were applied in a fractional way (twice in the evaluation year), and carried out using a 17N-6P-18K-2Mg compound fertilizer (Nutrimon-Café Producción, Monómeros S.A., Barranquilla, Colombia) as a source of N, P, K, and Mg, and a simple 46N fertilizer (Urea, Yara, Colombia). The levels of used chemical fertilization (CF) were: i) 100% (114 kg ha⁻¹ N, 24 kg ha⁻¹ P₂O₅, 73 kg ha⁻¹ K₂O, 8 kg ha⁻¹ MgO-S-B, and 0.8 kg ha⁻¹ Zn); ii) 66% (75 kg ha⁻¹ N, 16 kg ha⁻¹ P₂O₅, 48 kg ha⁻¹ K₂O, 5 kg ha⁻¹ MgO-S-B, and 0.5 kg ha⁻¹ Zn); iii) 33% (38 kg ha⁻¹ N, 8 kg ha⁻¹ P₂O₅, 24 kg ha⁻¹ K₂O, 3 kg ha⁻¹ MgO-S-B, and 0.3 kg ha⁻¹ Zn); and iv) 0% (0 kg ha⁻¹ N, 0 kg ha⁻¹ P₂O₅, 0 kg ha⁻¹ K₂O, 0 kg ha⁻¹ MgO-S-B, and 0 kg ha⁻¹ Zn) of the nutritional requirements for coffee. The fertilization treatments were supplied with the following commercial fertilizers: F100 = 90 g tree⁻¹ 17N-6P-18K-2Mg and 22 g tree⁻¹ UREA; F66 = 60 g tree⁻¹ 17N-6P-18K-2Mg and 14 g tree⁻¹ UREA; F33 = 30 g tree⁻¹ 17N-6P-18K-2Mg and 7 g tree⁻¹ UREA; and F0 = 0 g tree⁻¹ 17N-6P-18K-2Mg and 0 g tree⁻¹ UREA, respectively. These doses were selected based on the physical and chemical analysis of the soil and the nutritional requirements reported by Salamanca-Jiménez (2017). Nutrients were applied every 6 mo (May and October). Additionally, the treatments were arranged in a design with plots divided into completely randomized blocks. The large plots were the four doses of biochar (0, 4, 8, and 16 t ha⁻¹) and the small plots corresponded to the four chemical fertilization levels (0%, 33%, 66%, and 100% of the nutritional requirements). The experimental unit was composed of five trees surrounded by guard trees (12 trees) and each treatment was repeated four times (four blocks). A total of 320 trees was used throughout the experiment.

Coffee roasting and preparation of the beverage

Coffee beans were roasted using two methods to evaluate the quality attributes of the coffee beverage: i) The first method was used only for the harvest carried out in 2019. A sample of 1 kg dry parchment coffee (DPC) from each experimental unit was threshed to remove

the outer layer of the grain (parchment) using a laboratory sheller (ING-C-200, Ingesecc, Bogotá, Colombia). After separating all defective grains, 200 g subsamples from each experimental unit were prepared for roasting. The coffee was roasted at 195 °C for 15 min and 45 s using a commercial drum roaster (KN-8828P-2K+ coffee roaster; Hottop, Branford, Connecticut, USA); ii) the second torrefaction method was carried out only on the harvest of the year 2020. Samples of 1 kg DPC from each experimental unit were threshed to remove the outer layer of the grain (parchment) using a laboratory sheller (ING-C-200, Ingesecc, Bogotá, Colombia). After separating all defective beans, beans were roasted at 195 °C for 10 min using a commercial drum roaster (GT12, Inmcaff, Bogotá, Colombia). The beverages were prepared by brewing 7 g roasted and ground coffee with 100 mL hot distilled water (90 °C) for 4 min. The solids were then removed, and the residues were allowed to settle at the bottom of the container.

Aromatic profile

An aromatic profile analysis was performed on the roasted coffee beans for the harvests carried out in the two evaluation periods using a portable electronic nose (PEN3, Airsense Analytics, Schwerin, Germany). The equipment consisted of three components: i) An automatic sampling unit; ii) a detector unit containing the sensors array, and iii) software for pattern recognition. The array was composed of 10 different non-specific metal-oxide-semiconductor (MOS) sensors: W1C (aromatic), W3C (aromatic), W5C (arom-aliph), W1S (broad-methane), W2S (broad-alcohol), W3S (methane-aliph), W5S (broadrange), W6S (hydrogen), W1W (sulphur-organic), and W2W (sulph-chlor), which were kept at 400-500 °C during all measurements. For each sample, 0.5 g were weighed and placed in a 20 mL vial with a silicone stopper. After an equilibration time of 20 min at room temperature, the measurement sequence was started with the following parameters: Analysis time 120 s, wash time 360 s, gas flow 150 mL min⁻¹, and an automatic dilution factor. The measurement sequence consisted of pumping reference air over the sensors (ambient air that was filtered through activated carbon), at a constant flow rate (1 mL s⁻¹) for 10 s to obtain a stable baseline. Then, the evaluated gas headspace over the sensor surfaces was pumped with a syringe for 120 s. Subsequently, the sensors were exposed to reference air to recover the baseline. The total cycle time for each measurement was 8 min. No sensor drift was experienced during the measurement period. Each sample was tested three times and the average of the results was used for analysis. Finally, the value of the mean-differential coefficient value (mdcv) was calculated to create a two-dimensional n × s matrix, defining the response curve of each sensor according to the methodology proposed by Yin and Tian (2007) using Equation 1:

$$\text{mdcv} = \frac{1}{N-1} \sum_{i=1}^{N-1} \frac{x_{i+1} - x_i}{\Delta t} \quad (1)$$

where mdcv is the characteristic value of the profile for each sensor and each sample; N is the number of time intervals analyzed; x_i and x_{i+1} correspond to the conductance result at times i and i+1; Δt is the time interval between conductance data, which is generally equal to 1. The results obtained allow determining the average speed of the responses of each sensor and represent its main features. The transformation of the electronic nose data allowed the reduction of the size of the matrix to two dimensions considered as n × s × t (where n is the number of rows, s the number of sensors, and t the number of times the system collected data).

Coffee bean quality attributes

One drop of the coffee beverage was used for the analysis of total soluble solids (TSS) through the refractometric method using a manual digital refractometer (PAL 1, Atago, Bellevue, Washington, USA) at 22 °C. The values were expressed as percentage of soluble solids or °Brix. The pH and titratable acidity were determined using a Hanna pH meter (HI 8424, Hanna Instruments, Woonsocket, Rhode Island, USA). The pH was quantified using 50 mL previously prepared beverage, considering the stabilized value after immersion of the electrode. The titratable acidity was determined according to the methodology described by Puerta-Quintero (2000), recording the number of milliliters of NaOH (0.1 M) necessary for the titration of 50 mL coffee beverage to pH = 8.3 and at 25 °C. The values were expressed in mg CaCO₃ L⁻¹ beverage.

Data analysis

In both experimental years, the different samples were analyzed using a split-plot design with random blocks; the large plots were the four doses of BC (0, 4, 8 and 16 t ha⁻¹), and the small plots corresponded to the four levels of chemical fertilization (0%, 33%, 66% and 100% of the nutritional requirements) for a total of 16 treatments with four replicates per treatment. Before ANOVA, the data normality was checked by the plotting of residuals. The data were analyzed using software Statistix v9.0 (Analytical Software, Tallahassee, Florida, USA). Additionally, a principal component analysis (PCA) was used to performed un cluster analysis using software InfoStat 2016 (Grupo InfoStat, FCA, Universidad Nacional de Córdoba, Córdoba, Argentina).

RESULTS

Aromatic profile and Pearson's correlation analysis (PCA)

The PCA showed that the different sensors of the electronic nose are represented by vectors while the BC and CF treatments are indicated by points (Figures 1 and 2). In general, PCA1 and PCA2 comprised 64.2% and 23.3% of the total explained variance of the different electronic nose sensors studied in 2019 (Figure 1), while in 2020, PCA1 and PCA2 indicated 78.1% and 14.7% of the variance (Figure 2), respectively. The vectors of the sensors W1C, W5C, and W3C have angles close to the origin, showing a greater correlation between the variables evaluated in the year 2019. Coffee beans from trees treated with 4.8 and 16 t ha⁻¹ BC + 0% CF, 0 and 16 t ha⁻¹ BC + 33% CF, 0 t ha⁻¹ BC + 66% CF, 4 and 8 t ha⁻¹ BC + 100% CF, and 4 and 8 t ha⁻¹ BC + 66% CF were located in the far-right sector of the biplot analysis (group III). However, the applications of 0 t ha⁻¹ BC + 100% CF; 4 t ha⁻¹ BC + 33% CF, and 8 t ha⁻¹ BC + 66% CF (group I) were located in the opposite side of group I, indicating a negative effect of these fertilization treatments of coffee trees on the parameters studied (group III). Finally, a third differential effect was observed regarding the doses of BC and CF in the responses of the electronic nose sensors of roasted coffee beans: 0 t ha⁻¹ BC + 0% CF; 4 t ha⁻¹ BC + 66% CF, and 16 t ha⁻¹ BC + 100% CF (group II) showed a lower negative effect on the behavior of the aromatic profile of roasted coffee beans.

Similar trends were recorded for the year 2020. The vectors of W1C, W5C, and W3C had angles close to the origin, indicating that these are the sensors that have the greatest sensitivity to aromatic compounds of coffee beans (Figure 2). Additionally, three differential effects were observed between the BC and CF doses in roasted coffee beans: i) Group III was made up of beans from trees treated with 4 t ha⁻¹ BC + 0% and 66% CF; 16 t ha⁻¹ BC + 0%, 33%, 66%, and 100% CF, which were located at the right end of the biplot analysis; ii) 0 t ha⁻¹ BC + 0%, 33%, 66% and 100% CF (group I) were located at the opposite end of group I; ii) 4 t ha⁻¹ BC + 33% and 66% CF; 8 t ha⁻¹ BC + 0%, 33%, 66% and 100% CF (group II) showed a lower negative effect on the studied variables. Finally, the electronic nose (especially the sensors W1C, W5C, and W3C) is a tool (or variables) of the aromatic profile useful to evaluate the response of coffee beans to fertilization treatments, amendments with BC, or their interaction.

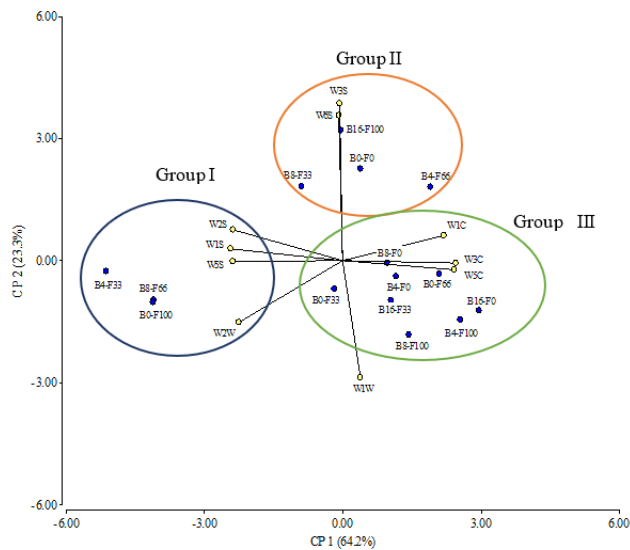


Figure 1. Biplot of the Principal Component Analysis (PCA) of electronic nose sensors in roasted coffee beans under different doses of biochar and chemical fertilization levels for the 2019 harvest: W1C (aromatic), W3C (aromatic), W5C (arom-aliph), W1S (broad-methane), W2S (broad-alcohol), W3S (methane-aliph), W5S (broadrange), W6S (hydrogen), W1W (sulphur-organic), W2W (sulph-chlor). B0: biochar dose of 0 t h⁻¹; B4: biochar dose of 4 t h⁻¹; B8: biochar dose of 8 t h⁻¹; B16: biochar dose of 16 t h⁻¹. F0: 0% of the nutritional requirements; F33: 33% of the nutritional requirements; F66: 66% of the nutritional requirements; F100: 100% of the nutritional requirements.

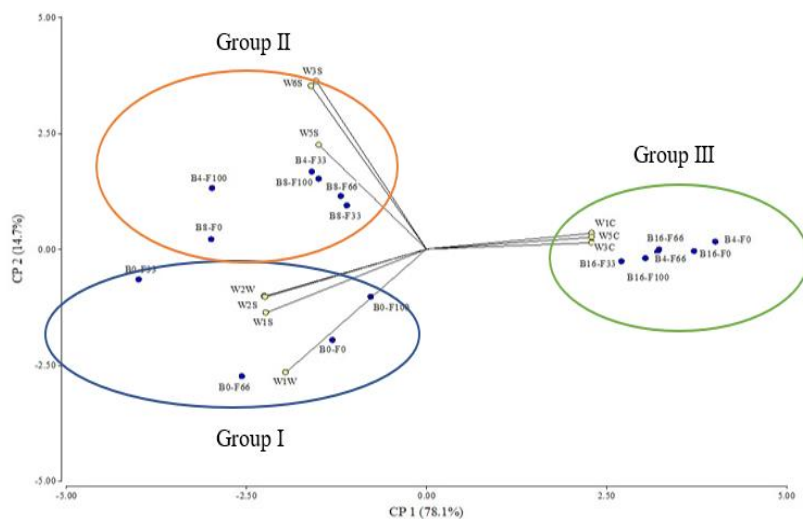


Figure 2. Biplot of the Principal Component Analysis (PCA) of electronic nose sensors in roasted coffee beans under different doses of biochar and chemical fertilization levels for the 2020 harvest: W1C (aromatic), W3C (aromatic), W5C (arom-aliph), W1S (broad-methane), W2S (broad-alcohol), W3S (methane-aliph), W5S (broadrange), W6S (hydrogen), W1W (sulphur-organic), W2W (sulph-chlor). B0: Biochar dose of 0 t h⁻¹; B4: biochar dose of 4 t h⁻¹; B8: biochar dose of 8 t h⁻¹; B16: biochar dose of 16 t h⁻¹. F0: 0% of the nutritional requirements; F33: 33% of the nutritional requirements; F66: 66% of the nutritional requirements; F100: 100% of the nutritional requirements.

The ANOVA indicates that differences were also found between the factors biochar, chemical fertilization level, and their interaction on the electronic nose sensors in 2019 and 2020 (Tables 1 and 2). In general, the trends evidenced in the PCA biplot were confirmed for the W1C, W5C, and W3C sensors in the 2 yr of evaluation. In this sense, treatments 0, 4 and 16 t ha⁻¹ BC + 0%, 33% and 100% CF showed the highest values for the aforementioned sensors (W1C: -3.80 and -1.48×10⁻⁴; W5C between 9.83×10⁻⁴ and 1.17×10⁻³; W3C between 4.55 and 8.37×10⁻⁴) in 2019 (Table 1), while for the year 2020 the treatments of 4 t ha⁻¹ BC + 0% and 66% CF and 16 t ha⁻¹ BC + 0%, 33%, 66% and 100% CF registered the highest values in W1C (between -7.68×10⁻⁵ and 1.69×10⁻⁴), W5C (between -7.29×10⁻⁵ and 1.79×10⁻⁴), and W3C (between -7.72×10⁻⁴ and 1.91×10⁻⁴) (Table 2). However, the sensors W5S, W6S, W1S, W1W, W2S, W2W, and W3S did not show a clear trend in the application of BC and CF levels for the year 2019. Additionally, an opposite trend was observed in W5S, W6S, W1S, W1W, W2S, and W2W, showing that applications of 16 t ha⁻¹ BC registered the lowest values compared to the other nutrition treatments of the coffee crop in 2020, whereas the highest values were found in roasted coffee beans harvested from trees that had 4 and 8 t ha⁻¹ BC at the different levels of chemical fertilization (Table 2), corroborating what was found in the PCA biplot.

Table 1. Summary of the ANOVA of the effect of the application of different doses of biochar (0, 4, 8, and 16 t ha⁻¹) on the electronic nose sensors in roasted coffee beans during the year 2019. Data represent the average of three samples per treatment (n = 3). *, **, ***Significantly different at 0.05, 0.01 and 0.001, respectively. The same letters within the column indicate that the means are not significantly different according to the Tukey's test at P ≤ 0.05. CV: Coefficient of variation.

Treatment	W1C	W5C	W3C	W5S	W6S	W1S	W1W	W2S	W2W	W3S
Biochar										
0 t ha ⁻¹	-3.50×10 ⁻⁴ a	7.61×10 ⁻⁴ ab	3.15×10 ⁻⁴ ab	3.44×10 ⁻⁴ ab	2.43×10 ⁻⁵ ab	-2.09×10 ⁻³ ab	1.46×10 ⁻⁴ b	-1.57×10 ⁻³ ab	1.23×10 ⁻⁴ bc	2.21×10 ⁻⁴ b
4 t ha ⁻¹	-3.41×10 ⁻⁴ a	8.75×10 ⁻⁴ a	3.92×10 ⁻⁴ a	2.17×10 ⁻⁴ b	3.15×10 ⁻⁶ b	-2.22×10 ⁻³ b	1.52×10 ⁻⁴ b	-1.67×10 ⁻³ b	9.99×10 ⁻⁵ c	2.32×10 ⁻⁴ ab
8 t ha ⁻¹	-3.73×10 ⁻⁴ ab	7.03×10 ⁻⁴ b	2.62×10 ⁻⁴ b	2.73×10 ⁻⁴ ab	1.06×10 ⁻⁵ b	-2.06×10 ⁻³ a	1.53×10 ⁻⁴ b	-1.56×10 ⁻³ ab	1.52×10 ⁻⁴ ab	2.06×10 ⁻⁴ b
16 t ha ⁻¹	-4.63×10 ⁻⁴ b	8.29×10 ⁻⁴ ab	3.25×10 ⁻⁴ b	3.84×10 ⁻⁴ a	-3.29×10 ⁻⁶ a	-2.15×10 ⁻³ a	2.13×10 ⁻⁴ a	-1.63×10 ⁻³ a	1.82×10 ⁻⁴ a	1.90×10 ⁻⁴ a
Significance	***	.	**	.
Chemical fertilization										
0%	-2.22×10 ⁻⁴ a	1.01×10 ⁻³ a	5.36×10 ⁻⁴ a	-7.63×10 ⁻⁵ c	2.09×10 ⁻⁵	-2.44×10 ⁻³ d	1.39×10 ⁻⁴ b	-1.85×10 ⁻³ d	4.66×10 ⁻⁵ c	2.06×10 ⁻⁴ b
33%	-4.80×10 ⁻⁴ b	6.65×10 ⁻⁴ b	2.02×10 ⁻⁴ b	4.97×10 ⁻⁴ a	3.36×10 ⁻⁵	-2.00×10 ⁻³ b	1.75×10 ⁻⁴ a	-1.48×10 ⁻³ b	1.64×10 ⁻⁴ ab	2.61×10 ⁻⁴ a
66%	-4.68×10 ⁻⁴ b	5.22×10 ⁻⁴ b	9.09×10 ⁻⁵ b	5.38×10 ⁻⁴ a	4.38×10 ⁻⁶	-1.76×10 ⁻³ a	1.52×10 ⁻⁴ b	-1.25×10 ⁻³ a	2.00×10 ⁻⁴ a	2.35×10 ⁻⁴ ab
100%	-3.69×10 ⁻⁴ b	9.09×10 ⁻⁴ a	4.16×10 ⁻⁴ a	3.19×10 ⁻⁴ b	3.92×10 ⁻⁵	-2.21×10 ⁻³ c	1.78×10 ⁻⁴ a	-1.70×10 ⁻³ c	1.33×10 ⁻⁴ b	2.18×10 ⁻⁴ b
Significance	***	***	***	***	NS	***	***	***	***	**
Interaction										
0 t ha ⁻¹ × 0%	-2.21×10 ⁻⁴ ab	7.89×10 ⁻⁴ bc	3.96×10 ⁻⁴ cd	2.04×10 ⁻⁴ def	1.03×10 ⁻⁴ b	-2.17×10 ⁻³ cd	9.55×10 ⁻⁵ gh	-1.55×10 ⁻³ cd	7.28×10 ⁻⁶ ef	3.28×10 ⁻⁴ bc
0 t ha ⁻¹ × 33%	-5.15×10 ⁻⁴ bcd	9.91×10 ⁻⁴ abc	4.38×10 ⁻⁴ bcd	4.83×10 ⁻⁴ cd	3.19×10 ⁻⁵ bcd	-2.36×10 ⁻³ def	2.09×10 ⁻⁴ abc	-1.88×10 ⁻³ defgh	1.56×10 ⁻⁴ cd	2.41×10 ⁻⁴ cde
0 t ha ⁻¹ × 66%	-1.45×10 ⁻⁴ a	1.17×10 ⁻³ ab	6.78×10 ⁻⁴ abc	-1.92×10 ⁻⁴ gh	-1.15×10 ⁻⁵ cd	-2.56×10 ⁻³ defg	1.41×10 ⁻⁴ efgh	-1.95×10 ⁻³ fgh	4.40×10 ⁻⁵ def	1.78×10 ⁻⁴ def
0 t ha ⁻¹ × 100%	-5.17×10 ⁻⁴ bcd	8.82×10 ⁻⁵ de	-2.51×10 ⁻⁴ e	8.80×10 ⁻⁴ b	-2.61×10 ⁻⁵ cd	-1.28×10 ⁻³ b	1.39×10 ⁻⁴ efgh	-8.79×10 ⁻⁴ b	2.85×10 ⁻⁴ bc	1.36×10 ⁻⁴ f
4 t ha ⁻¹ × 0%	-3.07×10 ⁻⁴ abc	1.01×10 ⁻³ abc	4.77×10 ⁻⁴ abcd	-6.02×10 ⁻⁵ fgh	1.65×10 ⁻⁵ bcd	-2.51×10 ⁻³ defg	1.66×10 ⁻⁴ cde	-1.91×10 ⁻³ efgh	6.97×10 ⁻⁵ def	1.91×10 ⁻⁴ def
4 t ha ⁻¹ × 33%	-6.81×10 ⁻⁴ de	1.34×10 ⁻³ de	-3.68×10 ⁻⁴ e	1.08×10 ⁻³ b	1.62×10 ⁻⁵ bcd	-1.16×10 ⁻³ b	1.61×10 ⁻⁴ cdef	-7.18×10 ⁻⁴ b	3.21×10 ⁻⁴ b	2.44×10 ⁻⁴ cde
4 t ha ⁻¹ × 66%	-1.57×10 ⁻⁴ a	1.12×10 ⁻³ ab	6.55×10 ⁻⁴ abc	-7.31×10 ⁻⁵ fgh	2.35×10 ⁻⁵ bcd	-2.46×10 ⁻³ defg	8.91×10 ⁻⁵ h	-1.83×10 ⁻³ defg	-3.47×10 ⁻⁵ f	3.41×10 ⁻⁴ ab
4 t ha ⁻¹ × 100%	-2.17×10 ⁻⁴ ab	1.36×10 ⁻³ a	8.04×10 ⁻⁴ ab	-8.15×10 ⁻⁵ fgh	-4.37×10 ⁻⁵ d	-2.74×10 ⁻³ f	1.94×10 ⁻⁴ abcd	-2.22×10 ⁻³ h	4.37×10 ⁻⁵ def	1.51×10 ⁻⁴ ef
8 t ha ⁻¹ × 0%	-2.42×10 ⁻⁴ abc	8.89×10 ⁻⁴ bc	4.33×10 ⁻⁴ bcd	-1.99×10 ⁻⁴ gh	1.20×10 ⁻⁵ bcd	-2.34×10 ⁻³ cde	1.25×10 ⁻⁴ efgh	-1.77×10 ⁻³ def	7.70×10 ⁻⁵ def	1.69×10 ⁻⁴ def
8 t ha ⁻¹ × 33%	-3.45×10 ⁻⁴ abc	5.95×10 ⁻⁴ c	2.09×10 ⁻⁴ d	3.26×10 ⁻⁴ de	7.96×10 ⁻⁵ bc	-1.96×10 ⁻³ c	1.12×10 ⁻⁴ fgh	-1.40×10 ⁻³ c	1.01×10 ⁻⁴ de	3.48×10 ⁻⁴ ab
8 t ha ⁻¹ × 66%	-5.59×10 ⁻⁴ cd	1.20×10 ⁻⁴ d	-2.48×10 ⁻⁴ e	8.45×10 ⁻⁴ bc	-3.57×10 ⁻⁵ d	-1.33×10 ⁻³ b	1.46×10 ⁻⁴ defg	-9.08×10 ⁻⁴ b	3.01×10 ⁻⁴ b	1.59×10 ⁻⁴ ef
8 t ha ⁻¹ × 100%	-3.47×10 ⁻⁴ abc	1.21×10 ⁻³ ab	6.54×10 ⁻⁴ abc	1.20×10 ⁻⁴ defg	-1.34×10 ⁻⁵ cd	-2.62×10 ⁻³ efg	2.29×10 ⁻⁴ a	-2.14×10 ⁻³ gh	1.30×10 ⁻⁴ de	1.48×10 ⁻⁴ ef
16 t ha ⁻¹ × 0%	-1.16×10 ⁻⁴ a	1.37×10 ⁻³ a	8.37×10 ⁻⁴ a	-2.51×10 ⁻⁴ h	-4.76×10 ⁻⁵ d	-2.75×10 ⁻³ g	1.71×10 ⁻⁴ bcd	-2.18×10 ⁻³ gh	3.22×10 ⁻⁵ def	1.37×10 ⁻⁴ f
16 t ha ⁻¹ × 33%	-3.80×10 ⁻⁴ abcd	1.06×10 ⁻³ ab	5.31×10 ⁻⁴ abcd	9.44×10 ⁻⁵ efgh	6.72×10 ⁻⁶ bcd	-2.52×10 ⁻³ defg	2.19×10 ⁻⁴ ab	-1.92×10 ⁻³ fgh	7.70×10 ⁻⁵ def	2.11×10 ⁻⁴ def
16 t ha ⁻¹ × 66%	-1.01×10 ⁻³ a	-3.30×10 ⁻⁴ e	-7.22×10 ⁻⁴ f	1.57×10 ⁻³ a	4.12×10 ⁻⁵ bcd	-7.07×10 ⁻⁴ a	2.33×10 ⁻⁴ a	-2.96×10 ⁻⁴ a	4.90×10 ⁻⁴ a	2.63×10 ⁻⁴ bcd
16 t ha ⁻¹ × 100%	-3.94×10 ⁻⁴ abcd	9.83×10 ⁻⁴ abc	4.55×10 ⁻⁴ abcd	3.56×10 ⁻⁴ de	2.40×10 ⁻⁴ a	-2.21×10 ⁻³ cd	1.49×10 ⁻⁴ def	-1.56×10 ⁻³ cde	7.14×10 ⁻⁵ def	4.36×10 ⁻⁴ a
Significance	***	***	***	***	***	***	***	***	***	***
CV, %	-28.15	18.23	25.04	37.43	142.59	-5.97	10.34	-7.33	32.33	13.26

Table 2. Summary of ANOVA of the effect of the application of different doses of biochar (0, 4, 8, and 16 t ha⁻¹) on the electronic nose sensors in roasted coffee beans during the year 2020. Data represent the average of three samples per treatment (n = 3). *, **, *** Significantly different at 0.05, 0.01 and 0.001, respectively. The same letters within the column indicate that the means are not significantly different according to the Tukey's test at P ≤ 0.05. CV: Coefficient of variation.

Treatment	W1C	W5C	W3C	W5S	W6S	W1S	W1W	W2S	W2W	W3S
Biochar										
0 t ha ⁻¹	-2.17×10 ⁻³ ^a	-2.21×10 ⁻³ ^c	-2.35×10 ⁻³ ^c	-2.07×10 ⁻³ ^b	-2.50×10 ⁻⁵ ^c	2.54×10 ⁻³ ^a	2.04×10 ⁻⁴ ^a	4.57×10 ⁻³ ^a	1.07×10 ⁻³ ^a	5.43×10 ⁻⁵ ^c
4 t ha ⁻¹	-1.03×10 ⁻³ ^b	-1.09×10 ⁻³ ^b	-1.18×10 ⁻³ ^b	-2.05×10 ⁻³ ^b	6.58×10 ⁻⁵ ^b	-1.98×10 ⁻⁴ ^c	7.44×10 ⁻⁵ ^c	1.88×10 ⁻³ ^c	5.51×10 ⁻⁴ ^c	2.92×10 ⁻⁴ ^b
8 t ha ⁻¹	-1.90×10 ⁻³ ^c	-1.95×10 ⁻³ ^c	-2.14×10 ⁻³ ^c	-9.42×10 ⁻⁴ ^a	1.52×10 ⁻⁴ ^a	1.50×10 ⁻³ ^b	1.13×10 ⁻⁴ ^b	3.54×10 ⁻³ ^b	7.57×10 ⁻⁴ ^b	4.72×10 ⁻⁴ ^a
16 t ha ⁻¹	-6.63×10 ⁻⁴ ^a	-7.62×10 ⁻⁴ ^a	-8.43×10 ⁻⁴ ^a	-2.11×10 ⁻³ ^b	-2.60×10 ⁻⁵ ^d	-7.34×10 ⁻⁴ ^d	3.82×10 ⁻⁵ ^d	8.64×10 ⁻⁴ ^d	2.85×10 ⁻⁴ ^d	-3.61×10 ⁻⁶ ^d
Significance	***	***	***	*	***	***	***	***	***	***
Chemical fertilization										
0%	-1.06×10 ⁻³ ^a	-1.10×10 ⁻³ ^a	-1.18×10 ⁻³ ^a	-2.53×10 ⁻³ ^c	-3.85×10 ⁻⁵ ^b	3.27×10 ⁻⁴ ^c	9.91×10 ⁻⁵	2.23×10 ⁻³ ^{bc}	5.16×10 ⁻⁴ ^b	4.13×10 ⁻⁵ ^b
33%	-1.70×10 ⁻³ ^b	-1.81×10 ⁻³ ^b	-1.96×10 ⁻³ ^b	-6.05×10 ⁻⁴ ^a	5.82×10 ⁻⁵ ^a	1.11×10 ⁻³ ^a	1.07×10 ⁻⁴	2.95×10 ⁻³ ^a	7.32×10 ⁻⁴ ^a	2.46×10 ⁻⁴ ^a
66%	-1.13×10 ⁻³ ^a	-1.14×10 ⁻³ ^a	-1.24×10 ⁻³ ^a	-2.60×10 ⁻³ ^c	-1.16×10 ⁻⁵ ^b	3.71×10 ⁻⁴ ^{bc}	1.04×10 ⁻⁴	2.19×10 ⁻³ ^c	5.68×10 ⁻⁴ ^{ab}	5.12×10 ⁻⁵ ^b
100%	-1.56×10 ⁻³ ^b	-1.63×10 ⁻³ ^b	-1.77×10 ⁻³ ^b	-1.75×10 ⁻³ ^b	7.66×10 ⁻⁵ ^a	7.33×10 ⁻⁴ ^{ab}	1.01×10 ⁻⁴	2.68×10 ⁻³ ^{ab}	7.20×10 ⁻⁴ ^a	2.75×10 ⁻⁴ ^a
Significance	***	***	***	***	***	***	NS	***	**	***
Interaction										
0 t ha ⁻¹ × 0%	-1.92×10 ⁻³ ^{abcd}	-1.92×10 ⁻³ ^{cdef}	-2.05×10 ⁻³ ^{cde}	-3.60×10 ⁻³ ^{de}	-3.47×10 ⁻⁵ ^{cd}	2.26×10 ⁻³ ^{abc}	1.98×10 ⁻⁴ ^{abc}	4.27×10 ⁻³ ^{abc}	9.32×10 ⁻⁴ ^{abcd}	-3.67×10 ⁻⁵ ^{fg}
0 t ha ⁻¹ × 33%	-2.73×10 ⁻³ ^e	-2.91×10 ⁻³ ^g	-3.06×10 ⁻³ ^f	1.74×10 ⁻³ ^a	-4.20×10 ⁻⁶ ^{abcd}	3.22×10 ⁻³ ^a	2.05×10 ⁻⁴ ^{ab}	5.17×10 ⁻³ ^a	1.28×10 ⁻³ ^{ab}	2.17×10 ⁻⁴ ^e
0 t ha ⁻¹ × 66%	-2.38×10 ⁻³ ^{cde}	-2.38×10 ⁻³ ^{defg}	-2.52×10 ⁻³ ^{def}	-2.80×10 ⁻³ ^{cde}	-5.69×10 ⁻⁵ ^d	3.23×10 ⁻³ ^a	2.40×10 ⁻⁴ ^a	5.07×10 ⁻³ ^a	1.31×10 ⁻³ ^a	-1.94×10 ⁻⁴ ^{hi}
0 t ha ⁻¹ × 100%	-1.64×10 ⁻³ ^b	-1.64×10 ⁻³ ^c	-1.78×10 ⁻³ ^c	-3.63×10 ⁻³ ^{de}	-4.20×10 ⁻⁶ ^{abcd}	1.47×10 ⁻³ ^{bc}	1.72×10 ⁻⁴ ^{abcd}	3.76×10 ⁻³ ^{bc}	7.60×10 ⁻⁴ ^{cd}	2.31×10 ⁻⁴ ^e
4 t ha ⁻¹ × 0%	1.69×10 ⁻⁴ ^a	1.79×10 ⁻⁴ ^a	1.91×10 ⁻⁴ ^a	-3.30×10 ⁻³ ^{de}	-8.80×10 ⁻⁵ ^d	-1.85×10 ⁻³ ^c	2.80×10 ⁻⁵ ^{gh}	-9.13×10 ⁻⁴ ^d	4.76×10 ⁻⁵ ^h	-8.21×10 ⁻⁵ ^{gh}
4 t ha ⁻¹ × 33%	-1.84×10 ⁻³ ^{bcd}	-1.90×10 ⁻³ ^{cdef}	-2.10×10 ⁻³ ^{cde}	-9.74×10 ⁻⁴ ^{bc}	2.06×10 ⁻⁴ ^a	9.03×10 ⁻⁴ ^d	9.19×10 ⁻⁵ ^{gh}	3.12×10 ⁻³ ^c	7.81×10 ⁻⁴ ^{bcd}	6.31×10 ⁻⁴ ^a
4 t ha ⁻¹ × 66%	-1.91×10 ⁻⁴ ^a	-1.59×10 ⁻⁴ ^{ab}	-1.89×10 ⁻⁴ ^{ab}	-3.54×10 ⁻³ ^{de}	-9.27×10 ⁻⁵ ^d	-1.39×10 ⁻³ ^c	5.27×10 ⁻⁵ ^{gh}	6.06×10 ⁻⁴ ^d	1.57×10 ⁻⁴ ^{gh}	2.91×10 ⁻⁵ ^f
4 t ha ⁻¹ × 100%	-2.26×10 ⁻³ ^{bcde}	-2.46×10 ⁻³ ^{cdef}	-2.61×10 ⁻³ ^{def}	-3.85×10 ⁻⁴ ^{ab}	2.38×10 ⁻⁴ ^a	1.54×10 ⁻³ ^{bc}	1.25×10 ⁻⁴ ^{cdef}	3.88×10 ⁻³ ^{bc}	1.22×10 ⁻³ ^{abc}	5.89×10 ⁻⁴ ^{ab}
8 t ha ⁻¹ × 0%	-2.39×10 ⁻³ ^{de}	-2.51×10 ⁻³ ^{ef}	-2.68×10 ⁻³ ^{ef}	-1.24×10 ⁻⁴ ^{ab}	9.80×10 ⁻⁵ ^{abc}	2.54×10 ⁻³ ^{ab}	1.53×10 ⁻⁴ ^{bcde}	4.71×10 ⁻³ ^{ab}	9.97×10 ⁻⁴ ^{abcd}	4.01×10 ⁻⁴ ^d
8 t ha ⁻¹ × 33%	-1.71×10 ⁻³ ^{bc}	-1.72×10 ⁻³ ^{cde}	-1.90×10 ⁻³ ^{cd}	-1.47×10 ⁻³ ^{bcde}	1.40×10 ⁻⁴ ^{ab}	1.25×10 ⁻³ ^{cd}	1.01×10 ⁻⁴ ^{efg}	3.29×10 ⁻³ ^c	6.30×10 ⁻⁴ ^{defg}	4.55×10 ⁻⁴ ^{cd}
8 t ha ⁻¹ × 66%	-1.70×10 ⁻³ ^{bc}	-1.69×10 ⁻³ ^{cd}	-1.90×10 ⁻³ ^{cd}	-1.31×10 ⁻³ ^{bcd}	1.69×10 ⁻⁴ ^a	1.10×10 ⁻³ ^{cd}	1.07×10 ⁻⁴ ^{def}	3.03×10 ⁻³ ^c	6.93×10 ⁻⁴ ^{def}	4.92×10 ⁻⁴ ^{bcd}
8 t ha ⁻¹ × 100%	-1.82×10 ⁻³ ^{bcd}	-1.87×10 ⁻³ ^{cdef}	-2.07×10 ⁻³ ^{cde}	-8.70×10 ⁻⁴ ^{ab}	2.01×10 ⁻⁴ ^a	1.10×10 ⁻³ ^d	9.24×10 ⁻⁵ ^{efgh}	3.14×10 ⁻³ ^c	7.08×10 ⁻⁴ ^{de}	5.42×10 ⁻⁴ ^{abc}
16 t ha ⁻¹ × 0%	-7.68×10 ⁻⁵ ^a	-1.36×10 ⁻⁴ ^{ab}	-1.58×10 ⁻⁴ ^{ab}	-3.08×10 ⁻³ ^{cde}	-1.29×10 ⁻⁴ ^d	-1.64×10 ⁻³ ^c	1.79×10 ⁻⁵ ^h	4.03×10 ⁻³ ^d	8.57×10 ⁻⁵ ^h	-1.17×10 ⁻⁴ ^{ij}
16 t ha ⁻¹ × 33%	-5.08×10 ⁻⁴ ^a	-7.29×10 ⁻⁴ ^b	-7.72×10 ⁻⁴ ^b	-1.72×10 ⁻³ ^{bcde}	-1.10×10 ⁻⁴ ^d	-9.39×10 ⁻⁴ ^e	2.80×10 ⁻⁵ ^{gh}	2.17×10 ⁻³ ^d	2.34×10 ⁻⁴ ^{efgh}	-3.18×10 ⁻⁴ ^j
16 t ha ⁻¹ × 66%	-2.50×10 ⁻⁴ ^a	-3.12×10 ⁻⁴ ^{ab}	-3.69×10 ⁻⁴ ^{ab}	-2.76×10 ⁻³ ^{cde}	-6.55×10 ⁻⁵ ^d	-1.46×10 ⁻³ ^c	1.43×10 ⁻⁵ ^h	6.39×10 ⁻⁵ ^d	1.14×10 ⁻⁴ ^h	-1.22×10 ⁻⁴ ^{gh}
16 t ha ⁻¹ × 100%	-5.11×10 ⁻⁴ ^a	-5.67×10 ⁻⁴ ^{ab}	-6.14×10 ⁻⁴ ^{ab}	-2.10×10 ⁻³ ^{bcde}	-1.27×10 ⁻⁴ ^d	-1.18×10 ⁻³ ^c	1.54×10 ⁻⁵ ^h	-3.87×10 ⁻⁵ ^d	1.92×10 ⁻⁴ ^{fgh}	-2.61×10 ⁻⁴ ^{ij}
Significance	***	***	***	***	***	***	***	***	***	***
CV, %	-15.26	-15.64	-14.19	-35.83	178.07	55.06	23.99	16.02	24.24	25.42

Coffee bean quality attributes

Figure 3 summarizes the differences in the interaction of the doses of BC and the levels of CF (P ≤ 0.05) on the content of total soluble solids (TSS) in the two evaluation periods (2019 and 2020). In summary, the trees treated with 0 t ha⁻¹ BC + 0% CF registered the lowest TSS contents (2019 = 0.85 °Brix and 2020 = 1.15 °Brix) (Figures 3A and 1B) compared to the other treatments in the 2 yr of evaluation. In general, the TSS was higher in coffee trees treated with 66% and 100% CF with the different doses of BC compared to trees without chemical fertilizers in both years, except for trees treated with 16 t ha⁻¹ BC during 2019 and 0% CF, which recorded the highest values of TSS (approx. 1.57 °Brix) (Figure 3A). An increase was observed in the TSS content of the different BC treatments compared to the gradual applications of CF in the year 2020 (0% CF: 1.19 °Brix; 33% CF: 1.22 °Brix; 66% CF: 1.32 °Brix and 100% CF: 1.38 °Brix, respectively), except for the beverages of the treatments with 16 t ha⁻¹ BC whose highest values were recorded with 0% CF (0% CF: 1.20 °Brix vs. 100% CF: 1.08 °Brix, respectively) (Figure 3B).

Differences were also found between BC dose treatments and CF levels on the pH of the coffee beverage (Figure 4). In general, the year 2019 showed higher pH values for the different treatments evaluated compared to the year 2020 (4.97 vs. 4.84). Applications of 8 t ha BC registered the highest pH values of coffee beverages; however, the pH showed a reduction for this treatment with the gradual application of the

different chemical fertilization levels (0% CF: 5.09; 33% CF: 5.04; 66% CF: 4.95, and 100% CF: 5.03, respectively) (Figure 4A). As for the year 2020, the pH of coffee beverages from treatments 0 and 8 t ha⁻¹ + 100% CF (4.95 and 4.88, respectively) and 16 t ha⁻¹ BC + 0% CF (approx. 4.88) recorded the highest values. Additionally, applications of 4 t ha⁻¹ BC showed similar pH values between the different CF levels (4.83), while the pH of the coffee beverages prepared with the grains of the treatments 16 t ha⁻¹ BC + 33%, 66%, and 100% CF was around 4.79 (Figure 4B).

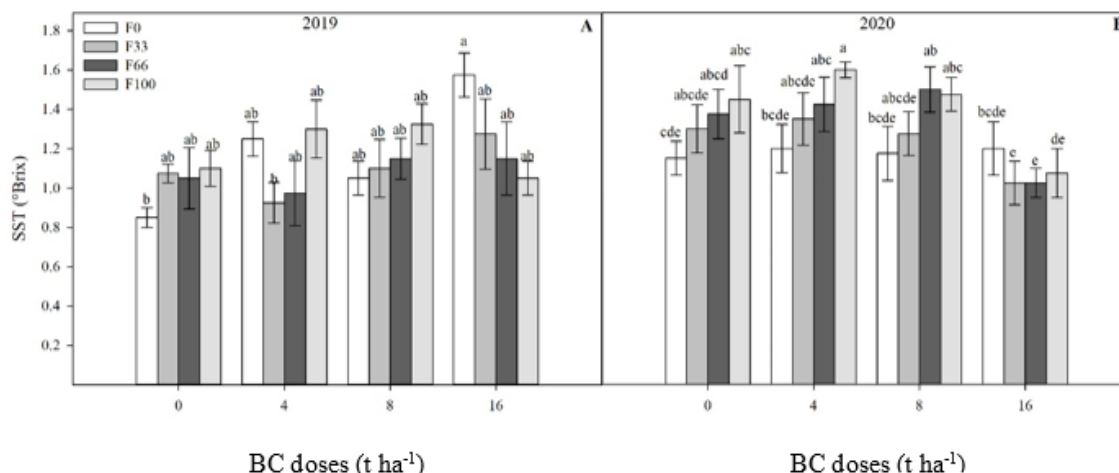


Figure 3. Effect of the application of different doses of biochar (BC; 0, 4, 8, and 16 t ha⁻¹) and chemical fertilization levels (0%, 33%, 66%, and 100% of the nutritional requirements) on total soluble solids (TSS) of the coffee beverage in the years 2019 (A) and 2020 (B). Points represent ± standard error (n = 4). Bars represent the mean of four blocks ± standard error. Same letters indicate that the means are not significantly different according to the Tukey's test at P ≤ 0.05.

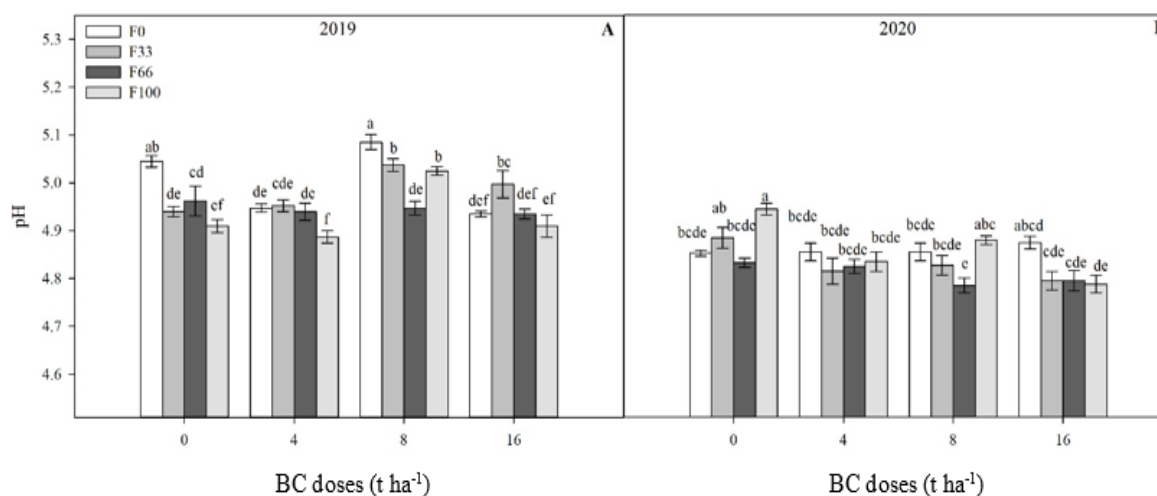


Figure 4. Effect of the application of different doses of biochar (BC; 0, 4, 8, and 16 t ha⁻¹) and chemical fertilization levels (0%, 33%, 66%, and 100% of the nutritional requirements) on the pH of the coffee beverage in the years 2019 (A) and 2020 (B). Points represent ± standard error (n = 4). Bars represent the mean of four blocks ± standard error. Same letters indicate that the means are not significantly different according to the Tukey's test at P ≤ 0.05.

The ANOVA shows that significant differences were found between BC treatments and CF levels on titratable acidity in the years 2019 and 2020 (Figure 5). In general, beverages prepared with roasted coffee beans from trees treated with 0 t ha⁻¹ BC showed an increase in titratable acidity with gradual applications of CF, especially with 100% CF (0% CF: 596.79 mg CaCO₃ L⁻¹ vs. 100% CF: 674.74 mg CaCO₃ L⁻¹, respectively). However, gradual applications of BC (4, 8, and 16 t ha⁻¹) showed high values of titratable acidity, especially with low levels of CF (0% CF: 699.91 CaCO₃ L⁻¹ and 33% CF: 678.80 mg CaCO₃ L⁻¹, respectively) (Figure 5A). Coffee beverages prepared with beans harvested from trees treated with 0 t ha⁻¹ BC showed high values of titratable acidity, especially when they had 0% CF in the year 2020 (Figure 5B). A reduction in titratable acidity was recorded with the gradual application between 33% and 100% CF, especially in the treatments that had 0, 8 and 16 t ha⁻¹ BC (33% CF: 718.58 mg CaCO₃ L⁻¹, 66% CF: 697.88 mg CaCO₃ L⁻¹, and 100% CF: 662.56 mg CaCO₃ L⁻¹, respectively).

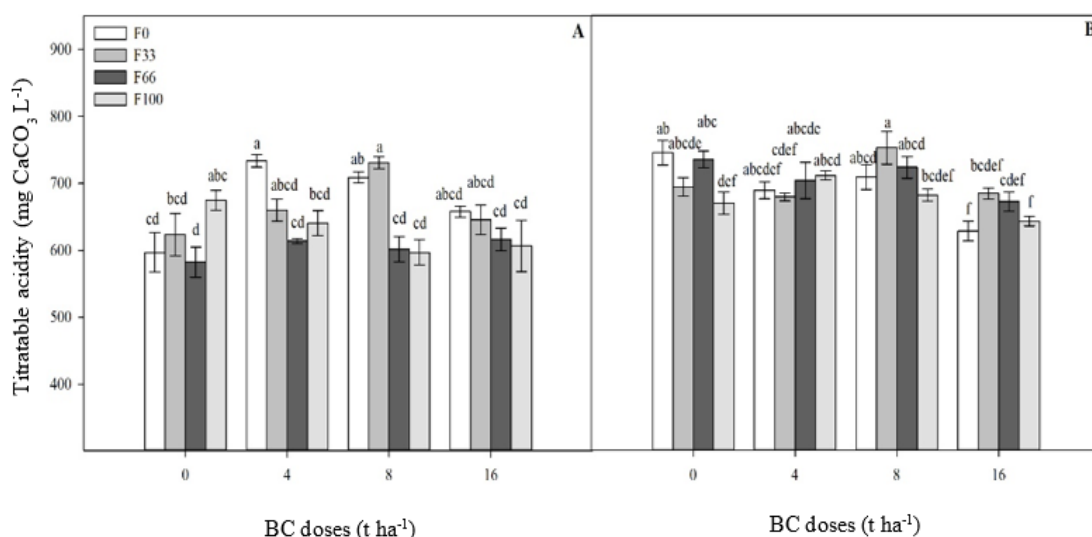


Figure 5. Effect of the application of different doses of biochar (BC; 0, 4, 8, and 16 t ha⁻¹) and chemical fertilization levels (0%, 33%, 66%, and 100% of the nutritional requirements) on titratable acidity of the coffee beverage in the years 2019 (A) and 2020 (B). Points represent \pm standard error (n = 4). Bars represent the mean of four blocks \pm standard error. Same letters indicate that the means are not significantly different according to the Tukey's test at $P \leq 0.05$.

Finally, Table 3 shows the coefficients (r) that describe the degree of correlation between the quality variables of the coffee beverage and the aromatic profile obtained by the sensors W1C, W5C, and W3C of the electronic nose for the years 2019 and 2020. In summary, the effects of the application of BC and CF were more significant in the second year of evaluation (2020). In response to the application of BC and CF, W1C showed strong positive and significant correlations with W5C and W3C. However, TSS content, pH, and titratable acidity had weak positive and nonsignificant correlations ($r < 0.3$, $P > 0.05$) regarding the response of the electronic nose sensors in coffee bean trees treated with BC from coffee pulp and different levels of chemical fertilization in the year 2019. Compared to the year 2020, similar trends were recorded for W1C in response to the application of BC and CF (strong positive and significant correlations with W5C and W3C). Additionally, the content of TSS and titratable acidity had negative and significant correlations with W1C, W5C, and W3C, indicating an inversely proportional correlation between these variables regarding the application of BC and CF.

Table 3. Pearson’s correlation coefficient (r) between different cup quality attributes and electronic nose sensors in response to biochar application and chemical fertilization levels in coffee trees. TSS: Total soluble solids. *, **, ***Significantly different at 0.05, 0.01 and 0.001, respectively. ^{ns}Not significantly different according to the Tukey’s test at P ≤ 0.05.

	W1C	W3C	W5C	°Brix	pH
2019					
W3C	0.881***				
W5C	0.841***	0.996***			
TSS	0.089 ^{ns}	0.169 ^{ns}	0.191 ^{ns}		
pH	0.110 ^{ns}	0.079 ^{ns}	0.053 ^{ns}	-0.264 ^{ns}	
Titratable acidity	0.159 ^{ns}	0.202 ^{ns}	0.204 ^{ns}	0.167 ^{ns}	0.149 ^{ns}
2020					
W3C	0.997***				
W5C	0.996***	0.999***			
TSS	-0.332*	-0.321*	-0.312*		
pH	-0.062 ^{ns}	-0.047 ^{ns}	-0.054 ^{ns}	0.055 ^{ns}	
Titratable acidity	-0.436**	-0.409**	-0.405*	0.111 ^{ns}	-0.176 ^{ns}

DISCUSSION

The nutrients present in the soil play a key role in the growth and development of plants and the quality of coffee (Yadessa et al., 2019). Numerous studies have reported that the combined application of BC and chemical fertilizers improves the yield and quality of crops such as green chiretta *Andrographis paniculata* (Saha et al., 2019), tomato (*Solanum lycopersicum*) (Ronga et al., 2020), blueberry (*Vaccinium myrtillus*) (Zhang et al., 2020) and soybean (*Glycine max*) (Zhu et al., 2019). In this study, the volatile compounds of roasted coffee beans and cup quality parameters such as the content of TSS, pH, titratable acidity were favored when coffee trees were amended with BC (mainly with doses of 8 and 16 t ha⁻¹), especially with levels of chemical fertilization between 66% and 100% of the nutritional requirements. These responses were more significant in the second year of the trial (2020). Recent studies have concluded that the increase in the yield and quality parameters of crops in response to the application of BC is mainly due to the general improvement of the soil properties, generating an increase in the availability of plant nutrients (Saha et al., 2019; Ronga et al., 2020; Zhang et al., 2020). A previous study showed that a better nutritional status of coffee plants treated with BC is associated a higher total concentration of N, available P₂O₅, effective cation exchange capacity and soil pH (Sanchez-Reinoso et al., 2022).

It has been reported that the volatile and semi-volatile organic compounds of the aroma accumulated in the headspace where the sensors of the electronic nose take the measurements contribute significantly to the flavor of the product (Zuluaga-Domínguez et al., 2018). The results of this study show that the sensors W1C (aromatic compounds), W3C (ammonia and aromatic ingredients), and W5C (alkanes, aromatic compounds, less polar compounds) showed a greater sensitivity to those compounds and ingredients of roasted coffee beans, which were associated with the treatments amended with between 8 and 16 t ha⁻¹ BC and between 66% and 100% CF in 2019 and 2020, respectively (Figures 1 and 2). Dong et al. (2019) observed similar trends in the classification of aromatic profiles of coffee treated with different drying methods, showing that three electronic nose sensors used in the analysis had a greater influence on the differentiation capacity of the coffee samples. Makimori and Bona (2019) also indicate that the electronic nose was able to discriminate different instant coffee products, suggesting that it may be a technique with potential application in the coffee industry as a fast and efficient tool for aromatic quality control.

Regarding TSS, the electronic nose has been reported as an important criterion for evaluating coffee quality influencing the sensory properties of a coffee brew such as “body”, “mouthfeel” or “texture”, while organic acids regulate the pH and affect coffee flavor (Dong et al., 2017). In this

sense, our results indicate that the lowest values of TSS were found in coffee beans from trees with low levels of BC amendments (0 t ha⁻¹) and CF (0%), while coffee trees with applications of 8 and 16 t ha⁻¹ and 33% and 100% CF registered higher values of this variable. Similar trends were found in tomato fruits (Ronga et al., 2020), which showed an increase in TSS and pH in plants treated with BC (dose not clarified by the authors) obtained from vineyard pruning residues. These authors suggest that the results are due to faster N assimilation during the crop growth cycle. Regarding the pH, Sivetz and Desrosier (1979) indicate that for coffee beans without attributes of bitterness or acidity, the pH values should be between 4.95 and 5.20. The results of this study indicate that the pH values were found in said range for the year 2019, especially for the treatments that had 8 t ha⁻¹ BC, while for 2020 they were slightly lower. However, our results agree with those reported by Puerta-Quintero (2000), who evaluated the cup quality attributes of different mixtures of roasted coffee (*C. arabica*) varieties and concluded that the pH of the best mixtures varied between 4.6 and 4.8, the titratable acidity was in the range from 820 to 1000 mg CaCO₃ L⁻¹ beverage and the TSS was approximately between 1.25 and 1.65 g 100 g⁻¹.

The information obtained from this research indicates a series of advantages for coffee cultivation from the perspective of crop nutrition management using BC as a complement to chemical fertilization and its effects on the quality variables of the coffee bean. It is important to point out that the co-application of BC with chemically synthesized fertilizers is an interesting alternative that has been implemented in other cultivated species to increase plant yield and improve the quality of the harvested organs (Zhu et al., 2019; Ronga et al., 2020), which is consistent with the trends recorded in roasted coffee beans. Another important contribution of this research is that the use of BC can improve the quality of coffee beans, which is evidenced by a higher TSS content and titratable acidity in coffee beverages. This is probably due to the nutritional management of coffee trees, especially when BC is applied along with chemical fertilization. Based on our results, it is possible to recommend obtaining BC from coffee pulp through the pyrolysis process and its subsequent use in soils in coffee-growing areas. The amendments with BC have shown to have a positive effect on the soil-plant interaction by favoring the recycling of nutrients, which could represent an improvement in crop sustainability (Moreira et al., 2017; Das et al., 2020; Razzaghi et al., 2020). Finally, a better plant nutritional status in coffee plants can be also associated with direct effects of BC soil application such as better water holding in the soil (higher water content at field capacity) or a higher nutrients uptake from the soil (Asri, 2022; Sanchez-Reinoso et al., 2022).

CONCLUSIONS

In conclusion, the co-application of biochar (BC) obtained from the pyrolysis of coffee pulp as a complement to chemical fertilization showed a positive effect on the aromatic profile of roasted coffee beans and cup quality attributes. The application of 8 and 16 t ha⁻¹ along with chemical fertilization levels of 66% and 100% of the nutritional requirements increased the total soluble solid (TSS) content, reduced the pH, and increased the titratable acidity in beverages made with coffee beans 'Castillo El Tambo'. Our results suggest that the use of BC produced with coffee pulp, especially between 8 and 16 t ha⁻¹, can be an alternative as a complement to the mineral nutrition of commercial coffee crops. It also helps to take advantage of waste from the same production chain and allows mitigating the use of chemical fertilizers in the medium term. Finally, the principal component analysis allowed identifying the electronic nose sensors more sensitive to the functional groups corresponding to volatile compounds of roasted coffee beans and helped to study the effects of the applications of different doses of BC and levels of chemical fertilization on coffee trees. The use of this methodology in coffee production could represent an original approach to characterize coffee according to the nutritional status of the crop since it helps factors focused on quality and traceability.

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Author contribution

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