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Honeys from the Argentine Phytogeographic Provinces Chaqueña and Monte in Catamarca and La Rioja

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Abstract

The characterization of Argentinean honeys from the vegetation units (VUs) of the phytogeographical provinces located in Catamarca and La Rioja was performed with the analysis used for honey quality control: sugar profile, free acidity, pH, electrical conductivity (EC), color and contents of moisture, ash, total soluble solids, and hydroxymethylfurfural (HMF). Honeys were authentic and traceable, and complied with the specifications of national and/or international standards, verifying their blossom origin, high quality, good maturity, and freshness. Honeys from VU-9 and VU-23 presented significantly distinctive physicochemical parameters, evidencing the influence of the flora and pedoclimatic conditions of these VUs. Honeys from VU-23 presented significantly higher contents of glucose and total reducing sugars (F + G), and lower EC, ash contents, fructose/glucose ratio, and concentrations of turanose and maltose than those from VU-9. Honeys from VU-23 in La Rioja also exhibited characteristic lighter colors and lower pH and ºBrix values and turanose amounts; and honeys from VU-9 in La Rioja exhibited highest pH values. Catamarca honeys were characterized by high free acidity and high amounts of turanose, regardless of the VUs. The contents of sugars and total soluble solids, moisture, pH, EC, and color of honeys from Catamarca and La Rioja are published here for the first time. This study contributes to the typification of honeys from these provinces, which will provide them an added value and allow them to access newer markets.

Keywords: *Argentinean honeys, carbohydrate, physicochemical parameter, vegetation unit, geographical origin, traceability*

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1. Introduction

Honey is a sweet food naturally produced by bees (*Apis mellifera*) from flower nectar and/or exudates of plants or plant-sucking insects (honeydew) [1]. Honey is an important economic resource in many poorly developed areas worldwide. The Argentinian territory is suitable for the development of beekeeping activity and presents productive potential for honey and other beehive products. Argentina is the third major global honey producer after China and the United States, and the main one in the American southern hemisphere with 70% of the honey produced [2]. Argentinean honey production is mainly located in the center of the country, with 80% of beehives located in the provinces of Buenos Aires, Entre Ríos, Santa Fe, and Córdoba. The expansion of beekeeping areas to the northwest of Argentina (NOA) would have a great impact on national honey production. These regions, not used at a large scale for beekeeping until now, present an adequate climate and characteristic vegetation that is not found in other Argentinean regions and that would contribute to producing different types of honeys with added value. Catamarca (25–30°S, 65–69°W) and La Rioja (27–31°S, 65–69°W), being provinces located in the NOA region, offer a unique opportunity for apiculture, since it is an area of reduced anthropogenic activity with native flora of different vegetation units (VUs) [3, 4]. Catamarca and La Rioja represent 0.5% and 0.3% of the Argentinian apiaries and 1.1% and 0.5% of the Argentinian honey producers, respectively [2].

Nowadays, the quality of honey is assessed with the analysis of several physicochemical parameters, such as free acidity, color, pH, electrical conductivity (EC), moisture, ashes, the contents of sugars, hydroxymethylfurfural (HMF), proline and minerals, and diastase and invertase activities. International

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regulatory bodies such as the International Honey Commission (IHC), the Codex Alimentarius Commission, the European Council, and the Mercosur enact specific regulations related to the quality and safety of honey for their commercialization and establish the physical and chemical parameters to be determined by harmonized methods for the quality and safety control of honeys [5]. The physicochemical properties of honey depend on the type of nectar, pedoclimatic conditions (climate and soil composition), beekeeper handling, processing, storage, and transportation conditions during commercialization [6]. Some physicochemical parameters have been used as markers to define the geographical or botanical origin of honey [7, 8] and to detect honey adulteration [9, 10]. Pedoclimatic conditions influence the growth of the plant species in a certain region and hence its flora, making each region unique. Bees feed on the nectar of plants near the hive (about 13.5 km around); therefore, the composition of honey reflects the characteristics of the nectar of the plants around the hive [11]. Consequently, there is a relationship between the composition of honey and the region where it is produced, which adds value that allows economic exploration and preserves the uniqueness of the product [7, 8, 12]. The main honey production regions in Catamarca and La Rioja include two Phytogeographic Provinces (PP) and two VUs, i.e., VU-9 in the PP Chaqueña and VU-23 in the PP Monte (**Figure 1**) [4], under arid and semiarid climates with different precipitation regimes (**Table 1**) [13, 14]. Taking into account that honey quality is a multifactorial parameter linked to the botanical and geographical origins and beekeeping practices, the characterization of honeys according to their area of production would allow to assure the quality and traceability of these honeys, their correct labeling, and even produce certified honeys with designation of origin, which will increase its commercial value. These issues are of great interest for producers, consumers, and food industry and regulatory authorities. In this context, the objective of this study was to characterize the Argentinian honeys produced in the different phytogeographical regions of Catamarca and La Rioja by their sugar profile and their physicochemical quality parameters.

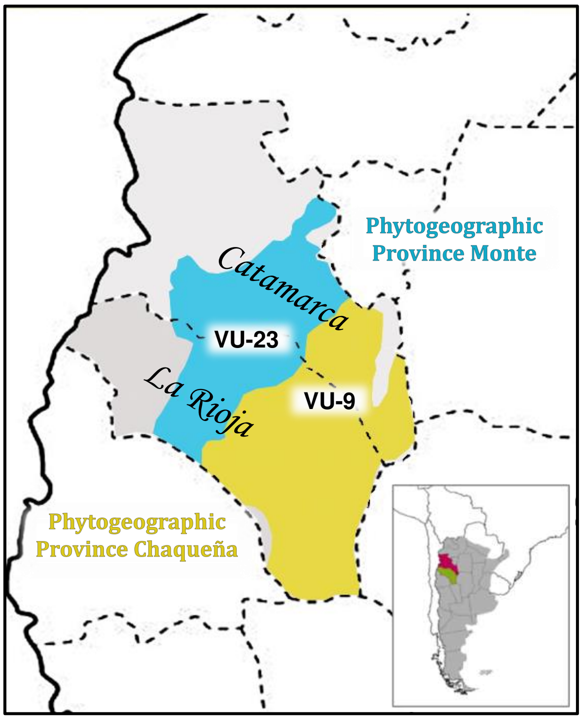


Figure 1 • Honey samples collected from the vegetation units (VUs) of the Phytogeographic Provinces (PP) Chaqueña (VU-9) and Monte (VU-23) in Catamarca and La Rioja (Argentina).

Table 1 • Honey Samples Collected from the Regions and Subregions of the Vegetation Units (VUs) of the Phytogeographic Provinces (PP) Chaqueña and PP Monte Located in Catamarca and La Rioja (Argentina)

PP/VU	*N*	Regions	*N*	Subregions	*N*	Climate	Average Annual Rainfall (mm)	Province
PP Chaqueña/VU-9	95	A	21	A-Catamarca	21	Cold semiarid	800–1,200	Catamarca
		B	74	B-Catamarca	35	Hot semiarid	400–500	Catamarca
				B-La Rioja	39		<400	La Rioja
PP Monte/VU-23	19	C	19	C-Catamarca	14	Cold arid	200–400	Catamarca
				C-La Rioja	5	Hot arid	200	La Rioja

2. Materials and methods

2.1. Honey samples

A total of 114 authentic and traceable honey samples of *Apis mellifera* were collected along four harvests (2014–2017) from apiaries of the main honey-producing areas of Catamarca and La Rioja (Argentina). The apiaries were located within the areas that corresponded to the vegetation units (VUs) (**Figure 1, Table 1**): (*i*) VU-9 of the PP Chaqueña, where the dominant vegetation is the open xerophytic forest with *Aspidosperma quebracho-blanco* in transition to bushy steppes (gradual transition between the PP Chaqueña to the PP Monte along vast plains among mountains) and (*ii*) VU-23 of the PP Monte, where the dominant vegetation type is the steppe of xerophytic shrubs with perennial and resinous foliage, mainly belonging to the family Zygophyllaceae (genus *Larrea*), with columnar Cactaceae and high grasslands [4]. The samples (about 1 kg of raw honey each) were provided directly by beekeepers and/or honey producer cooperatives along with farming information: harvest date and conditions, declared botanical origin, apiary location (GPS), agricultural system, colony treatments, etc. The honeys were harvested between November and May. All honey samples were stored in screw-capped plastic containers at 4°C in the dark until analysis.

2.2. Reagents and solvents

The analytical standards 5-hydroxymethyl-2-furaldehyde (HMF), fructose, glucose, sucrose, erlose, maltose, trehalose, and maltotriose were provided by Sigma–Aldrich (Darmstadt, Germany), as well as the HPLC-grade solvents methanol and acetonitrile. Sodium hydroxide, potassium acid phthalate, phenolphthalein, absolute ethanol, and the sugar standards of turanose, melezitose, and raffinose were supplied by Supelco (Bellefonte, PA, USA). All chemicals and reagents used were of analytical-quality grade. Water of HPLC-grade was used in all solutions and dilutions.

2.3. Determination of physicochemical parameters in honey

The physicochemical parameters, namely moisture, free acidity, pH, EC, and color, were measured in honey using the official methods of Instituto Argentino de Normalización y Certificación (IRAM) adopted from IHC. Three replicates were analyzed for each sample. Honey moisture and the total soluble solid content in degree Brix (°Brix) were determined according to IRAM standard 15931 (1994), using an Abbé refractometer 5 (Bellingham & Stanley Ltd, Longfield Road, Tunbridge Wells, UK). The EC was determined in a solution of honey at 20% (w/v) at 20 ± 2°C, according to IRAM standard 15945 (1997) using an Adwa AD31 conductometer (Adwa Instruments, Inc., Szeged, Hungary). The ash content in honey was calculated from the EC measurements, as described previously [5]. Free acidity of honey was determined by titration according to IRAM standard 15933 (1994). The pH was determined in a solution of honey at 10% (w/v), according to IRAM standard 15938 (1995) using a HI 2020-02 HANNA pH-meter (Hanna Instruments Inc., Woonsocket, RI, USA). Honey color measurements were performed according to IRAM standard 15941-2 (1997) using HI 96785C HANNA colorimeter (Hanna Instruments Inc., Woonsocket, RI, USA). In the case of crystallized honeys, honey was melted at 55 ± 2°C in thermostatic bath until complete dissolution of the crystals and elimination of air bubbles, as indicated in the IRAM standard protocol. Color was expressed in the Pfund scale.

2.4. Determination of sugars in honey

The contents of sugars in honey were determined according to IHC [15] on a Agilent Series 1100 HPLC system equipped with a binary pump, a thermostatted autosampler, a thermostatted column compartment, and a refractive index detector (RID) connected to an Agilent ChemStation software. A reversed-phase Zorbax NH_2 (250 mm × 4.6 mm i.d, 5 µm) column was used. The injection volume was 5 µL. The mobile phase was acetonitrile–water (83:17, v/v). Chromatographic separation was carried out in isocratic conditions at a flow rate of 0.65 mL/min and 35°C. The identification of saccharides in the HPLC chromatograms of the samples was achieved by comparison with the retention times of the available standards. Saccharides quantitation was performed by reporting the measured integration areas in the calibration equation of the corresponding standards.

2.5. Determination of HMF in honey

The HMF content in honey was determined according to IRAM standard 15937-3 (2008) on an Agilent Series 1100 HPLC system equipped with a binary pump, a thermostatted autosampler, a thermostatted column compartment, and a UV detector connected to an Agilent ChemStation software. A reversed-phase Waters Symmetry C18 (250 mm × 4.6 mm i.d, 5 µm) column was used. The injection volume was 20 µL. The mobile phase was water–methanol (95:5, v/v). The chromatographic separation was carried out in isocratic conditions at a flow rate of 0.7 mL/min and 25°C. HMF chromatographic peak was monitored and quantified at 280 nm. HMF identification was performed by comparison with the retention time of the standard; and its quantitation was performed by reporting the measured integration areas in the calibration equation of the standard.

2.6. Data analysis

For each honey sample, the mean and the standard deviation of the three replicates were calculated for the concentration of the individual sugar compounds and the quality parameters, which indicated that the relative standard deviation (n = 3) were at 5% or below, confirming a good repeatability of the analytical methodologies performed. Samples were grouped according to the VUs (VU-9 and VU-23) and climates (cold and hot, semiarid and arid) (**Table 1**). The dataset consisting of the mean values of the physical and chemical parameters measured on the honey samples were analyzed by statistical univariate procedures, such as analysis of variance (ANOVA), Fisher test, least significant difference test (LSD), and box and whisker plots. Regarding the box and whisker plots, the symmetry of data distribution, mean, median, minimum, maximum, outliers, and extreme values were evaluated according to the VUs and climates. Outliers or extremes values that strayed too far from data set were not considered in the final data analysis results for honey characterization. Bivariate correlations were studied by Pearson's correlation and linear regression. The significance was calculated for $p < 0.05$. Data analysis was performed by means of the statistical software packages SPSS Statistic 17

(SPSS Inc., Chicago, IL, USA, 1993–2007) and Statistica 7.0 (StatSoft Inc., Tulsa, OK, USA, 1984–2004)

3. Results

Honeys from VU-9 (PP Chaqueña) and VU-23 (PP Monte) in Catamarca and La Rioja were characterized by their individual sugar composition and physicochemical quality parameters, namely moisture, free acidity, pH, EC, color, and the contents of ash, total soluble solids, and HMF (**Tables 2–7**, **Figures 2–4**). These honeys analyzed along several seasons displayed characteristic sugar profiles and physicochemical parameters, which are described in the next sections. The different VUs and climates explained the honey composition and quality parameter values, which exhibited a great variability, likely due to the different botanical species flowering along the honey production season. However, significant differences were only found among certain seasons for particular physicochemical parameters (data not shown), as had been already observed [8].

3.1. Sugar profiles of honeys

3.1.1. Major sugars

Fructose and glucose, known as reducing sugars, are the major constituents of honey. According to the Codex Alimentarius standard, blossom honey should present a total content of fructose and glucose (F + G) higher than 60 g/100 g honey (%, w/w), and honeydew honey and its blends with blossom honey should contain F + G higher than 45 g/100 g honey [1]. This statement was fulfilled by all the honeys studied along all harvests, indicating that samples were genuine and blossom honeys (**Tables 2** and **4, Figure 2**). All samples contained higher amounts of fructose than glucose, supporting that almost all types of honey present greater contents of fructose than glucose [16, 17]. The amount of reducing sugars varied in the range of 33%–46% fructose, 26%–37% glucose, and 61%–78% F + G, presenting significant differences among phytogeographical origins and, in the case of glucose, also among climates.

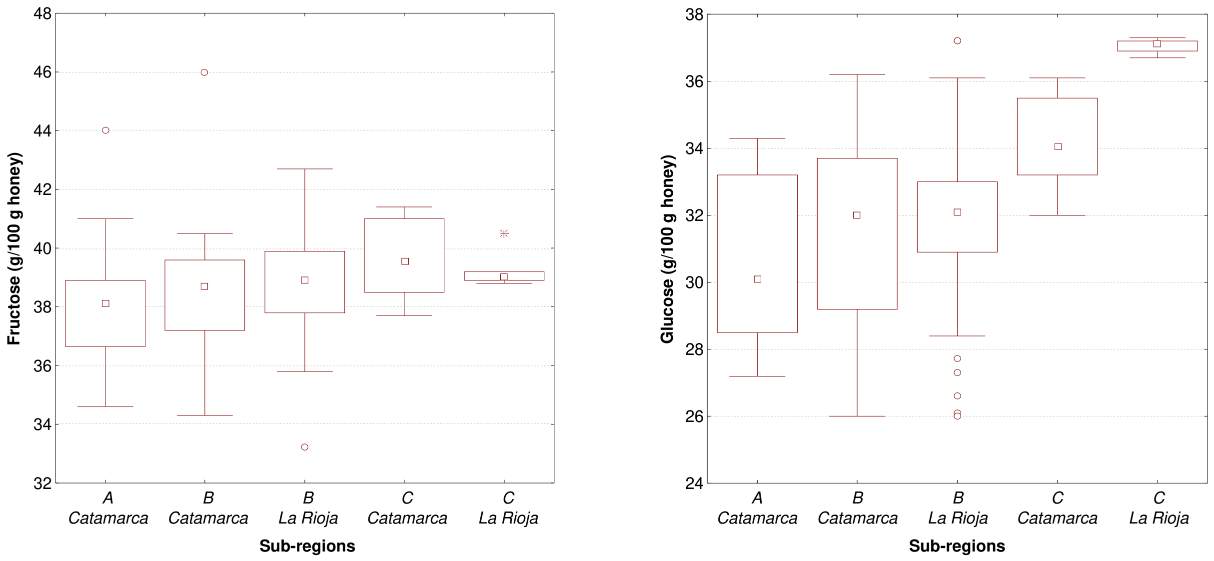
Table 2 • Sugar Composition of Honeys from the Vegetation Units (VUs) of the Phytogeographic Provinces (PP) Chaqueña and the PP Monte Located in Catamarca and La Rioja (Argentina)

		Phytogeographic Province		
		PP Chaqueña		**PP Monte**
Physicochemical		**VU-9**		**VU-23**
Parameter		**Region A**	**Region B**	**Region C**
Fructose	***N***	20	71	19
(g/100 g honey)	**Mean**	38.1^{a}	38.6^{a}	39.5^{b}
	SD	2.2	1.9	1.1
	Min	34.6	33.2	37.7
	Max	44.0	46.0	41.4
	Median	38.1	38.8	39.3
Glucose	***N***	20	71	19
(g/100 g honey)	**Mean**	30.7^{a}	31.7^{a}	34.9^{b}
	SD	2.4	2.7	1.8
	Min	27.2	26.0	32.0
	Max	34.3	37.2	37.3
	Median	30.1	32.1	35.0
F + G	***n***	20	71	19
(g/100 g honey)	**Mean**	68.8^{a}	70.3^{a}	74.3^{b}
	SD	3.2	4.0	2.5
	Min	64.4	60.9	69.7
	Max	75.3	78.2	77.6
	Median	67.6	70.9	75.3
F/G ratio	***n***	20	71	19
	Mean	1.25^{a}	1.22^{a}	1.135^{b}
	SD	0.12	0.10	0.058
	Min	1.03	1.04	1.043
	Max	1.55	1.64	1.220
	Median	1.21	1.21	1.142

		Phytogeographic Province		
		PP Chaqueña		PP Monte
Physicochemical		**VU-9**		**VU-23**
Parameter		**Region A**	**Region B**	**Region C**
Sucrose	***n***	20	73	19
(g/100 g honey)	**Mean**	0.30[a]	0.18[a]	0.28[a]
	SD	0.14	0.26	0.44
	Min	n.d.	n.d.	n.d.
	Max	0.40	1.20	1.80
	Median	0.35	n.d.	0.10
Maltose	***n***	12	16	10
(g/100 g honey)	**Mean**	2.8[a]	2.6[a]	2.04[a]
	SD	1.6	1.3	0.72
	Min	n.d.	n.d.	0.80
	Max	4.9	4.7	3.50
	Median	3.1	2.9	2.10
Turanose	***n***	12	16	10
(g/100 g honey)	**Mean**	2.27[a]	2.03[ab]	1.63[b]
	SD	0.82	0.48	0.51
	Min	0.50	1.50	1.10
	Max	3.20	3.10	2.80
	Median	2.30	1.90	1.60
Erlose	***N***	12	16	10
(g/100 g honey)	**Mean**	0.12[a]	0.23[a]	0.22[a]
	SD	0.18	0.18	0.34
	Min	n.d.	n.d.	n.d.
	Max	0.50	0.50	0.90
	Median	n.d.	0.30	n.d.

Abbreviations: *n*, number of samples; SD, standard deviation; Min, minimum; Max, maximum; nd, not detected; F + G, total content of fructose and glucose; and F/G ratio, fructose/glucose ratio.

Different letters within each row indicate significant differences according to Fisher's test ($p < 0.05$).



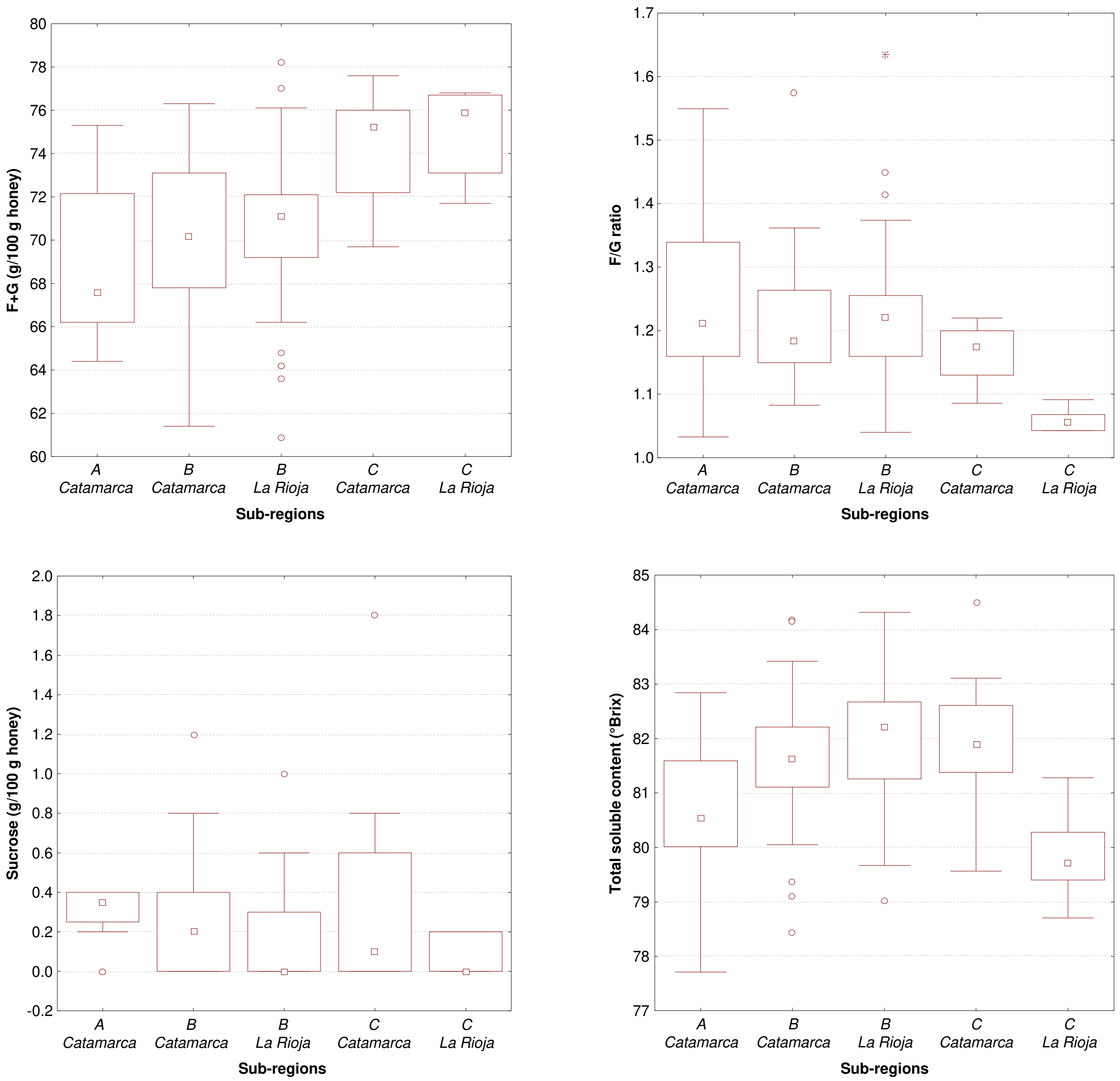


Figure 2 • Box and whisker plots for the content of fructose (F), glucose (G), sucrose and total soluble solids, and F + G and F/G ratio of honeys according to subregions of the vegetation units (VUs) of the Phytogeographic Provinces (PP), i.e., VU-9 of PP Chaqueña and VU-23 of PP Monte, located in Catamarca and La Rioja (Argentina).

The sucrose content in honey varies as a result of the invertase activity during the ripening process [18]. The presence of sucrose in honey can provide information about its adulteration and its botanical origin [19]. Unadulterated honey should contain less than 5% sucrose (w/w), according to the Codex Alimentarius standard [1]. Higher contents of sucrose can be due to the addition of exogenous sugars or the early harvesting of honey [9]. The sucrose contents measured (≤ 1.8%) confirmed that all the honeys studied were authentic mature honeys harvested at the proper time and not subjected to fraudulent practices (**Tables 2** and **4, Figure 2**).

The ability of honey to crystallize has been related to the fructose/glucose ratio (F/G); thus, honey with high F/G seemed to remain liquid and vice versa. Moreover, honey crystallization seemed to be slower when F/G ratio exceeded 1.3 and faster when the ratio was below 1.0. However, F/G-based crystallization remained not clearly demonstrated, since other sugars and insoluble substances in honey can influence the crystallization process [20]. Indeed, F/G of all honeys studied varied in the range from 1.03 to 1.64 (**Table 2, Figure 2**), and were found to be either crystallized or uncrystallized at room temperature. before analysis. An average F/G of 1.20 was reported for blossom honey and 1.30 for honeydew honey [21]. In this regard, even though honeys from VU-9 showed significantly higher average F/G (1.25 for region A and 1.22 for region B) than those from VU-23 (1.14), these F/G values confirmed the blossom origin of all honeys studied.

3.1.2. Minor sugars

Minor sugars were determined in honeys harvested during 2014 and 2015 (**Tables 2** and **4**). Trehalose, melezitose, raffinose, and maltotriose were not detected in most of the honey samples. The contents of maltose and erlose in honeys did not show significant differences among the regions and subregions studied. However, maltose was not detected in 8% (region A) and 6% (region B) of the honeys from VU-9, whereas it was presented in all the samples from VU-23, which showed less variability. Only significant differences were observed between the average turanose contents in honeys from region A of VU-9 (2.3%) and subregion C-La Rioja of VU-23 (1.3%).

3.2. Physicochemical parameters of honeys

3.2.1. Moisture

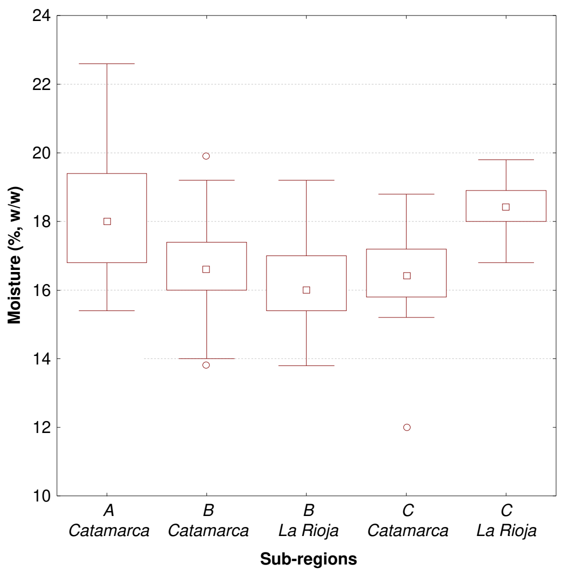
Honey moisture generally depends on its botanical and geographical origins, pedoclimatic conditions, harvest season, maturity and agricultural practices during extraction, and processing and storage [22–24]. High water content can cause the growth of yeasts and molds responsible for the fermentation of sugar in honey, causing bad flavors and a short shelf life [19]. According to the Codex Alimentarius standard for honey, the moisture of good-quality honey cannot be higher than 20 g/100 g of honey (%, w/w) [1]. Thus, honey moisture content lower than 20% (w/w) is important for the stability of the product during its storage. The humidity of all the honey samples studied was within the limits established by the international standards (**Tables 3** and **5, Figure 3**), except for two samples from subregion A, which also exceeded the Codex limits for free acidity. Moisture contents confirmed the good sanitary conditions of the honeys analyzed and were consistent with mature honeys; moreover, their average values corresponded to honeys extracted in summer [22–25]. Significant differences were found between the mean moisture contents of honeys from region A under cold semiarid climate (18%) and those from both region B under hot semiarid climate (16%) and region C under arid climate (17%). Honey is hygroscopic, i.e., it is capable of absorbing or losing water depending on environmental conditions (wet or dry, respectively) [20]. Therefore, honey moisture content is influenced by the climate and the precipitations of the geographical origin to which it belongs [7, 26]. In this sense, the average humidity of honeys from the different subregions agreed with their rainfall regimes (**Table 1**). Thus, with the average annual rainfall being 800–1,200 mm in region A, honeys presented an average humidity of 18%; 400–500 mm in subregion B-Catamarca, honeys contained 17% of moisture on average; and 200–400 mm in subregions B-La Rioja and C-Catamarca, honeys mean humidity was 16%. In contrast, honeys from subregion C-La Rioja exhibited considerably higher average moisture contents (18%) than expected during the hot arid climate with annual rainfall close to 200 mm in this subregion [13, 14].

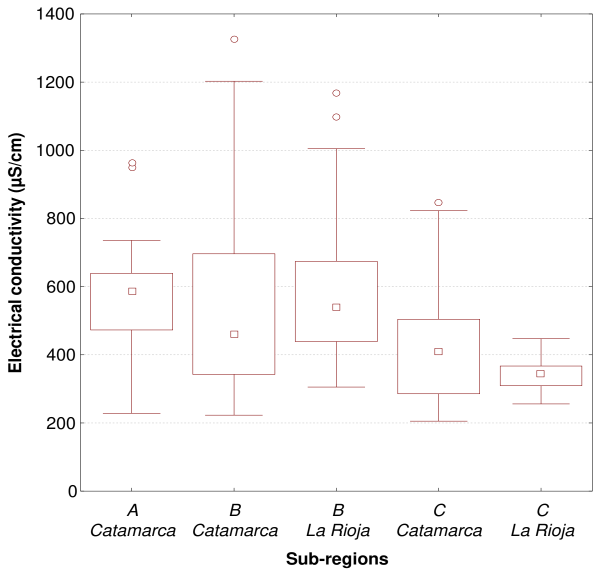
Table 3 • Physicochemical Parameters of Honeys from the Vegetation Units (VUs) of the Phytogeographic Provinces (PP) Chaqueña and the PP Monte Located in Catamarca and La Rioja (Argentina)

		Phytogeographic Province		
		PP Chaqueña		PP Monte
Physicochemical		VU-9		VU-23
Parameter		Region A	Region B	Region C
Moisture	*n*	21	70	18
(%)	Mean	18.1^{a}	16.4^{b}	16.9^{b}
	SD	1.8	1.3	1.8
	Min	15.4	13.8	12.0
	Max	22.6	19.9	19.8
	Median	18.0	16.2	16.9
EC	*n*	21	73	19
(µS/cm)	Mean	575^{a}	570^{a}	425^{b}
	SD	179	248	190
	Min	228	223	206
	Max	963	1,325	847
	Median	584	491	385
Ash content	*n*	21	73	19
(mg/100 g honey)	Mean	331^{a}	328^{a}	244^{b}
	SD	103	142	109
	Min	131	128	118
	Max	553	761	487
	Median	336	282	221
Free acidity	*n*	21	74	19
(meq/kg honey)	Mean	39^{a}	30^{b}	31^{ab}
	SD	14	16	9
	Min	12	11	19
	Max	78	93	52
	Median	39	26	31

		Phytogeographic Province		
		PP Chaqueña		PP Monte
Physicochemical		**VU-9**		**VU-23**
Parameter		**Region A**	**Region B**	**Region C**
pH	***n***	19	69	16
	Mean	4.22[a]	4.67[b]	3.81[a]
	SD	0.32	0.98	0.33
	Min	3.79	3.45	3.48
	Max	4.91	7.94	4.46
	Median	4.27	4.47	3.69
Color	***n***	21	74.00	19.00
(mm Pfund)	**Mean**	85[a]	73[a]	71[a]
	SD	21	28	40
	Min	45	32	27
	Max	120	150	150
	Median	89	70	54
Total soluble	***n***	20	70	18
content (°Brix)	**Mean**	80.6[a]	81.8[b]	81.4[ab]
	SD	1.3	1.2	1.5
	Min	77.7	78.4	78.7
	Max	82.8	84.3	84.5
	Median	80.5	81.9	81.5
HMF	***n***	9	36	5
(mg/kg honey)	**Mean**	7.7[a]	11.9[a]	12.0[a]
	SD	2.1	7.6	5.0
	Min	6.0	1.0	6.0
	Max	13.0	36.0	18.0
	Median	7.0	11.0	13.0

Abbreviations: See Table 2; EC, electrical conductivity; and HMF, 5-hydroxymethyl-2-furaldehyde.
Different letters within each row indicate significant differences according to Fisher's test ($p < 0.05$).





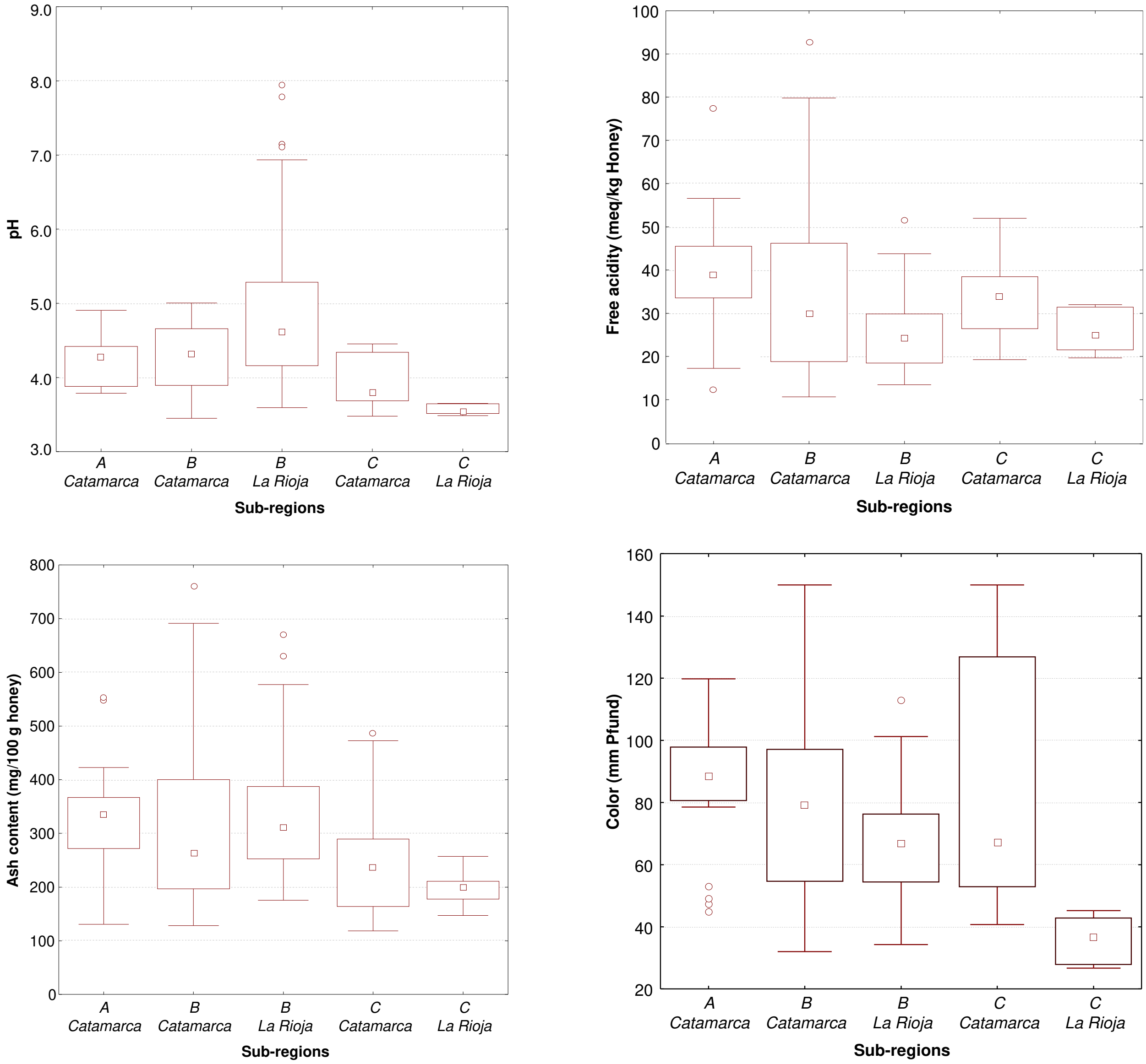


Figure 3 • Box and whisker plots for moisture, free acidity, electrical conductivity (EC), ash content, pH and color of honeys according to subregions of the vegetation units (VUs) of the Phytogeographic Provinces (PP), i.e. VU-9 of PP Chaqueña and VU-23 of PP Monte, located in Catamarca and La Rioja (Argentina).

Table 4 • Sugar Composition of Honeys from the Subregions of the Vegetation Units (VUs) of the Phytogeographic Provinces (PP) Chaqueña and the PP Monte Located in Catamarca and La Rioja (Argentina)

		Phytogeographic Province				
		PP Chaqueña			**PP Monte**	
Physicochemical		**VU-9**			**VU-23**	
Parameter		**A-Catamarca**	**B-Catamarca**	**B-La Rioja**	**C-Catamarca**	**C-La Rioja**
Fructose	***n***	20	33	38	14	5
(g/100 g honey)	**Mean**	38.1^{a}	38.3^{a}	38.8^{ab}	39.7^{b}	39.28^{ab}
	SD	2.2	2.2	1.7	1.3	0.70
	Min	34.6	34.3	33.2	37.7	38.80
	Max	44.0	46.0	42.7	41.4	40.50
	Median	38.1	38.7	38.9	39.6	39.00
Glucose	***n***	20	33	38	14	5
(g/100 g honey)	**Mean**	30.7^{a}	31.7^{a}	31.7^{a}	34.2^{b}	37.04^{c}
	SD	2.4	2.8	2.8	1.4	0.24

		Phytogeographic Province				
		PP Chaqueña			PP Monte	
Physicochemical		VU-9			VU-23	
Parameter		A-Catamarca	B-Catamarca	B-La Rioja	C-Catamarca	C-La Rioja
	Min	27.2	26.0	26.0	32.0	36.70
	Max	34.3	36.2	37.2	36.1	37.30
	Median	30.1	32.0	32.1	34.1	37.10
F + G	*n*	20	33	38	14	5
(g/100 g honey)	Mean	68.8^{a}	70.0^{a}	70.5^{a}	74.3^{b}	74.8^{b}
	SD	3.2	4.2	3.8	2.5	2.3
	Min	64.4	61.4	60.9	69.7	71.7
	Max	75.3	76.3	78.2	77.6	76.8
	Median	67.6	70.2	71.1	75.3	75.9
F/G ratio	*n*	20	33	38	14	5
	Mean	1.25^{a}	1.21^{ac}	1.23^{a}	1.162^{bc}	1.061^{b}
	SD	0.12	0.10	0.11	0.040	0.020
	Min	1.03	1.08	1.04	1.086	1.043
	Max	1.55	1.58	1.64	1.220	1.092
	Median	1.21	1.18	1.22	1.175	1.057
Sucrose	*n*	20	34	39	14	5
(g/100 g honey)	Mean	0.30^{a}	0.24^{ab}	0.13^{b}	0.34^{a}	0.08^{ab}
	SD	0.14	0.29	0.23	0.50	0.11
	Min	n.d.	n.d.	n.d.	n.d.	n.d.
	Max	0.40	1.20	1.00	1.80	0.20
	Median	0.35	0.20	n.d.	0.10	n.d.
Maltose	*n*	12	15	1	8	2
(g/100 g honey)	Mean	2.8^{a}	2.6^{a}	2.7^{a}	2.04^{a}	2.050^{a}
	SD	1.6	1.4	-	0.82	0.071
	Min	n.d.	n.d.	2.7	0.80	2.000
	Max	4.9	4.7	2.7	3.50	2.100
	Median	3.1	2.9	2.7	2.10	2.050
Turanose	*n*	12	15	1	8	2
(g/100 g honey)	Mean	2.27^{a}	2.06^{ab}	1.50^{ab}	1.71^{ab}	1.30^{b}
	SD	0.82	0.48	-	0.54	n.d.
	Min	0.50	1.50	1.50	1.10	1.30
	Max	3.20	3.10	1.50	2.80	1.30
	Median	2.30	1.90	1.50	1.75	1.30
Erlose	*n*	12	15	1	8	2
(g/100 g honey)	Mean	0.12^{a}	0.23^{a}	0.20^{a}	0.25^{a}	0.10^{a}
	SD	0.18	0.18	-	0.37	0.14
	Min	n.d.	n.d.	0.20	n.d.	n.d.
	Max	0.50	0.50	0.20	0.90	0.20
	Median	n.d.	0.30	0.20	n.d.	0.10

Abbreviations: See Table 2.
Different letters within each row indicate significant differences according to Fisher's test ($p < 0.05$).

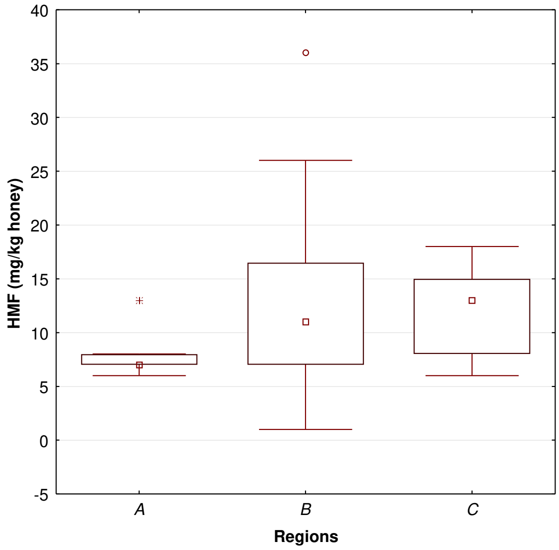


Figure 4 • Box and whisker plots of the HMF content of honeys according to regions of the vegetation units (VUs) of the Phytogeographic Provinces (PP), i.e. VU-9 of PP Chaqueña and VU-23 of PP Monte, located in Catamarca and La Rioja (Argentina).

Table 5 • Physicochemical Parameters of Honeys from the Subregions of the Vegetation Units (VUs) of the Phytogeographic Provinces (PP) Chaqueña and the PP Monte Located in Catamarca and La Rioja (Argentina)

		Phytogeographic Province				
		PP Chaqueña			**PP Monte**	
Physicochemical		**VU-9**			**VU-23**	
Parameter		**A-Catamarca**	**B-Catamarca**	**B-La Rioja**	**C-Catamarca**	**C-La Rioja**
Moisture	***n***	21	31	39	13	5
(%)	**Mean**	18.1[a]	16.7[b]	16.2[b]	16.3[b]	18.4[a]
	SD	1.8	1.4	1.1	1.7	1.1
	Min	15.4	13.8	13.8	12.0	16.8
	Max	22.6	19.9	19.2	18.8	19.8
	Median	18.0	16.6	16.0	16.4	18.4
EC	***n***	21	34	39	14	5
(µS/cm)	**Mean**	575[ab]	548[abc]	589[b]	438[ac]	345[c]
	SD	179	289	207	211	71
	Min	228	223	306	206	257
	Max	963	1,325	1,167	847	448
	Median	584	460	540	411	347
Ash content	***n***	21	34	39	14	5
(mg/100 g honey)	**Mean**	331[ac]	315[abc]	338[c]	251[ab]	198[b]
	SD	103	166	119	121	41
	Min	131	128	176	118	147
	Max	553	761	671	487	257
	Median	336	264	310	236	199
Free acidity	***n***	21	35	39	14	5
(meq/kg honey)	**Mean**	39[a]	35[a]	25.0[b]	33.1[ab]	25.9[ab]
	SD	14	20	8.3	8.9	5.6
	Min	12	11	13.4	19.3	19.7
	Max	78	93	51.5	52.0	32.0
	Median	39	30	24.3	33.9	24.8

		Phytogeographic Province				
		PP Chaqueña			PP Monte	
Physicochemical		VU-9			VU-23	
Parameter		A-Catamarca	B-Catamarca	B-La Rioja	C-Catamarca	C-La Rioja
pH	*n*	19	30	39	11	5
	Mean	4.22[a]	4.25[a]	5.0[b]	3.92[a]	3.567[a]
	SD	0.32	0.45	1.2	0.34	0.076
	Min	3.79	3.45	3.6	3.48	3.485
	Max	4.91	5.01	7.9	4.46	3.650
	Median	4.27	4.32	4.6	3.80	3.540
Color	*n*	21	35	39	14	5
(mm Pfund)	Mean	85[a]	81[a]	66[b]	83[ab]	35.9[c]
	SD	21	35	19	40	8.5
	Min	45	32	34	41	26.8
	Max	120	150	113	150	45.3
	Median	89	79	67	67	36.8
Total soluble	*n*	20	31	39	13	5
Content (°Brix)	Mean	80.6[a]	81.6[b]	81.9[b]	82.0[b]	79.88[a]
	SD	1.3	1.3	1.1	1.2	0.97
	Min	77.7	78.4	79.0	79.6	78.71
	Max	82.8	84.2	84.3	84.5	81.28
	Median	80.5	81.6	82.2	81.9	79.71
HMF	*n*	9	14	22	5	-
(mg/kg honey)	Mean	7.7[a]	13.4[a]	11.0[a]	12.0[a]	-
	SD	2.1	6.2	8.4	4.9	-
	Min	6.0	6.0	1.0	6.0	-
	Max	13.0	26.0	36.0	18.0	-
	Median	7.0	13.0	9.5	13.0	-

Abbreviations: See Table 3.
Different letters within each row indicate significant differences according to Fisher's test ($p < 0.05$).

3.2.2. Electrical conductivity

Electrical conductivity (EC) is directly related to the concentration of minerals and salts in the soil, the organic acids and proteins of the nectar from the botanical species, and the pedoclimatic characteristics of each area; therefore, the EC of honey can be related to its phytogeographical origin [9, 10, 24, 26, 27]. The Codex Alimentarius standard establishes that the EC of honey should not exceed 800 µS/cm, except for honeydew honey and certain unifloral blossom honeys [1]. The EC measured for the honeys studied confirmed that most of the honeys were blossom honeys (**Tables 3** and **5, Figure 3**). Significant differences were observed between the mean EC of honeys from VU-9 (region A, 575 µS/cm; region B, 570 µS/cm) and VU-23 (425 µS/cm). Similarly, honey from La Rioja followed the same trend; honeys from VU-9 under semiarid climate (589 µS/cm) exhibited significantly higher average EC than those from VU-23 under arid climate (345 µS/cm). These observations reflect the influence of the botanical species and pedoclimatic characteristics of each VU, and its subregions on EC of honey.

3.2.3. Ash content

The ash content in honey is mainly determined by soil and climatic characteristics and the flora physiology of the area, since certain nitrogen compounds, minerals, vitamins, pigments, and aromatic substances contribute to this parameter [26], which has been usually used for honey classification in blossom, mixed, or honeydew honey [7]. According to the Mercosur (Mercosur – Res. Nº 89/99, 1999) and the Argentinian National (Código Alimentario Argentino Ley 18284, Res. MSyAS N° 003, 1995) regulations, the ash content of honey should not be higher than 600 mg/100 g, except for honeydew honey or blends of honeydew and blossom honeys. Only five samples, which also met the established Codex limit for CE, displayed higher ash contents than the standard threshold. The parameters such as ash content and EC of honeys are directly correlated [5, 10]; therefore, the ash content of the honeys studied followed the same trends observed for their EC and confirmed their blossom origin (**Tables 3** and **5, Figure 3**). The significantly highest average ash contents were observed for honeys from VU-9 (331 and 328 mg/100 g honey for A and B regions, respectively) compared with respect to those from VU-23 (244 mg/100 g honey). This difference is particularly marked in honeys from La Rioja, showing 338 and 198 mg/100 g honey for VU-9 and VU-23, respectively, whereas no significant differences were observed among honeys from both VUs in Catamarca.

3.2.4. Free acidity

Free acidity of honey is due to the presence of organic acids in equilibrium with their corresponding lactones or internal esters, and some inorganic ions [24]. The organic acids present in honey vary according to the characteristic flora in each phytogeographical region [4]. Free acidity is an important quality criterion, since fermentation of honey causes an increase in acidity [5]. Honey fermentation is favored by high moisture contents; therefore, free acidity can be correlated with the humidity of the honey and the environment [20, 25]. In fact, the increase of honey acidity may be due to the fermentation of its sugars to alcohol by microorganisms and further oxidation to carboxylic acids [28]. The Codex Alimentarius standard for honey fixed the free acidity at 50 meq of acid/kg of honey [1]. The average free acidity of the honeys analyzed was within the limits established by international standards, except for 14%, 9%, and 5% of the honeys from regions A, B and C, respectively, which exceeded the Codex threshold (**Tables 3** and **5, Figure 3**). Among these noncompliant samples, three of them presented free acidity close to the limit (<54 meq/kg honey) and accomplished all other quality parameters; two of them presented moisture contents above the limit, as mentioned above; and seven samples from region B of VU-9 also exhibited CE higher than the established Codex limit to be blossom honeys. Honeys collected in region A of VU-9 presented the highest average free acidity (39 meq/kg honey), in agreement with the high moisture contents measured in these samples. The mean free acidity of honeys from this region was significantly different from those of honeys from region B (30 meq/kg honey), which contained lower humidity. Within samples from VU-9 under hot semiarid climate (region B), honeys from Catamarca (35 meq/kg honey) showed significantly larger average free acidities than those from La Rioja (25 meq/kg honey). This can be related to their moisture content and the average annual rainfalls, which are higher in Catamarca [13, 14]. The honeys from La Rioja, both VU-9 (25 meq/kg honey) and VU-23 (26 meq/kg honey), exhibited the lowest mean free acidity values, probably due to the hot semiarid and arid climates with annual rainfall under 400 mm.

3.2.5. pH

The pH of honey is affected by extraction and storage conditions and microorganism's growth, which can change the texture, stability, and shelf life of honey. Therefore, this parameter is considered as an index of freshness of honey [24, 27, 29]. The IRAM 15938 (1995) standard for honey establishes pH between 3.5 and 4.5 for blossom honey, and between 4.5 and 5.5 for honeydew honey. Indeed, low pH values, even lower than pH 3.5, are associated with blossom honeys, while high pH values are associated with honeydew honeys [21, 24, 30]. Most of the honeys from VU-23 (pH 3.5–4.5) and VU-9 in Catamarca (region A, pH 3.8–4.9; subregion B-Catamarca, pH 3.5–5.0) presented pH values in the range of blossom honeys (**Tables 3** and **5, Figure 3**). The average pH of the honeys from these regions (pH 3.8–4.3) was not significantly different. In contrast, the mean pH of the honeys from subregion B-La Rioja of VU-9 (pH 5.0) was significantly higher than those of honeys from the other regions and subregions. This was due to the fact that nine samples harvested in 2017 from subregion B-La Rioja presented high extreme pH values between 5.7 and 7.9. Among these honeys, those with pH lower than 7.2 were blossom honeys, according to their EC and ash content, while the two samples with pH close to 7.9, even though they complied with other quality parameters, exceeded the EC limit established by Codex Alimentarius standard to be blossom honeys, presenting characteristics of honeydew honey or a particular floral honey [1]. Concerning the honeys from Catamarca, the average pH of honeys from VU-9 (pH 4.2) was significantly higher than that of VU-23 (pH 3.9), probably due to the different botanical species growing in these VUs (**Table 6**).

Table 6 • Physicochemical Parameters of Honeys from the Vegetation Units (VUs) of the Phytogeographic Provinces (PP) Chaqueña and PP Monte Located in Catamarca (Argentina)

		Phytogeographic Province	
Physicochemical		**PP Chaqueña**	**PP Monte**
Parameter		**VU-9**	**VU-23**
Moisture	***n***	52	13
(%)	**Mean**	17.3[a]	16.3[a]
	SD	1.7	1.7
	Min	13.8	12.0
	Max	22.6	18.8
	Median	17.0	16.4
EC	***n***	55	14
(μS/cm)	**Mean**	559[a]	438[a]
	SD	251	211
	Min	223	206
	Max	1,325	847

	Median	497	411
Ash content	***n***	55	14
(mg/100 g honey)	**Mean**	321[a]	251[a]
	SD	144	121
	Min	128	118
	Max	761	487
	Median	286	236
Free acidity	***n***	56	14
(meq/kg honey)	**Mean**	37[a]	33.1[a]
	SD	18	8.9
	Min	11	19.3
	Max	93	52.0
	Median	36	33.9
pH	***n***	49	11
	Mean	4.24[a]	3.92[b]
	SD	0.40	0.34
	Min	3.45	3.48
	Max	5.01	4.46
	Median	4.27	3.80
Color	***n***	56	14
(mm Pfund)	**Mean**	82[a]	83[a]
	SD	30	40
	Min	32	41
	Max	150	150
	Median	83	67
Total soluble	***n***	51	13
content (°Brix)	**Mean**	81.2[a]	82.0[a]
	SD	1.4	1.2
	Min	77.7	79.6
	Max	84.2	84.5
	Median	81.3	81.9
HMF	***n***	23	5
(mg/kg honey)	**Mean**	11.2[a]	12.0[a]
	SD	5.7	4.9
	Min	6.0	6.0
	Max	26.0	18.0
	Median	8.0	13.0

Abbreviations: See Table 2; EC, electrical conductivity and HMF, 5-hydroxymethyl-2-furaldehyde.
Different letters within each row indicate significant differences according to Fisher's test ($p < 0.05$).

3.2.6. Color

Honey color depends on its alkalinity, ash content, and antioxidant compounds, such as polyphenols, terpenes, and carotenoids [31]. In general, light honeys have lower total phenol contents than dark honeys [32]; therefore, honey color is considered as an index of its antioxidant activity [33]. These antioxidant compounds come from the flowers that feed honeybees; hence, honey color provides information related to its botanical origin [31]. Agricultural practices and production methods can also influence honey color [34]. Honeys from both VUs in Catamarca did not show significantly different colors, exhibiting an average color of 82 mm Pfund (light amber) and a large color variability from white to dark (32–150 mm Pfund) (**Tables 3** and **5**, **Figure 3**). In contrast, regarding honeys from La Rioja, honeys from VU-9 (66 mm Pfund, light amber) presented significantly darker colors than those from VU-23 (36 mm Pfund, extra light amber). Moreover, the former, with colors from extra light amber to amber (34–113 mm Pfund), displayed larger variability than the latter, with colors from white to extra light amber (27–45 mm Pfund). Honeys from La Rioja were significantly lighter than those from Catamarca.

3.2.7. Total soluble solid content

The total soluble solid content expressed as grams of sucrose in 100 g of honey (°Brix) represents the total sugar content in honey, which typically contains about 83 °Brix (°Bx) [22–24, 35]. All honeys studied presented 81–82 °Bx on average (**Tables 3** and **5**, **Figure 2**). As previously reported [22–24], the total soluble content of honey is inversely proportional to its moisture ($r2 = -0.93$, $p < 0.05$). In this sense, the highest average °Bx value was observed in honeys of region B (82 °Bx) and the lowest in samples from subregion C-La Rioja (80 °Bx) in agreement with their mean moisture content. Regarding VU-9, honeys from region A presented significantly lower °Bx values than those from region B, which also agreed with the rainfall regimes of these regions. In fact, the higher the average annual rainfall, the higher the moisture content in honey, the greater the dilution of the sugars, and, therefore, the lower the °Bx value. Moreover, the higher the moisture content in honey, the greater the probability that sugar fermentation occurs during honey storage, which also can lead to lower °Bx values [36]. Regarding honeys from Catamarca, honeys from region A of VU-9 (81 °Bx) showed significantly lower average °Bx values than those from subregion B of VU-9 and subregion C of VU-23 (82 °Bx). This fact was related with the precipitation patterns of these regions (**Table 2**). Significant differences were found in the total soluble contents of honeys from VU-23. Thus, honeys from Catamarca exhibited higher mean °Bx values (82 °Bx) than those from La Rioja (80 °Bx), in accordance with their average annual rainfalls.

3.2.8. HMF content

Hydroxymethylfurfural (HMF) is formed by the decomposition of monosaccharides during the Maillard reaction, which occurs during storage, more or less slowly depending on the pH of the honey and the storage temperature, and quickly when honey is heated [5, 29]. Therefore, the HMF content in honey indicates the degree of honey deterioration [37]. The Codex Alimentarius established a maximum content of 40 mg HMF/kg for honey from nontropical regions and 80 mg HMF/kg for honey from tropical regions [1, 10]. HMF was determined in the honeys collected in the 2015 and 2017 harvests (**Tables 3** and **5, Figure 4**). All of them presented HMF contents within the limits defined by Codex standards, indicating that the honeys were of good quality, fresh and unprocessed, and suggesting good practices by beekeepers. No significant differences were found in the HMF contents of honeys, neither between the VUs nor among the regions and subregions studied. The highest HMF contents and variability were observed for honeys of region B (1–36 mg/kg honey).

4. Discussion

The physical and chemical quality parameters of the majority of the honeys analyzedwere in compliance with the national (Código Alimentario Argentino Ley 18284, Res. MSyAS Nº 003, 1995) and the international regulations established by the Codex Alimentarius Commision [1], EU Council (Council Directive 2001/110/EC, 2001), and Mercosur (Res. Nº 89/99, 1999), except for a low percentage of samples, which presented moistures, free acidities, pH, and/or CE higher than the established limits. The parameter values found in these samples could be due to special botanical species grown under certain pedoclimatic conditions of a particular area, since only one or two of the physicochemical parameters did not conform to the standards.

The honeys from VU-9 presented significantly lower mean contents of fructose (38% for region A and 39% for region B), glucose (31% for region A and 32% for region B), and F + G (69% for region A and 70% for region B) than those from VU-23 (40% fructose, 35% glucose, and 74% F + G). Regarding only the honeys from Catamarca of these VUs, the same tendency was observed (**Table 7**). Besides, the average concentrations of glucose in honeys from VU-23 under hot arid climate (37%) were significantly higher than in those under cold arid climate (34%); however, no significant differences were found due to cold and hot semiarid climates in VU-9 (32%). Honey from all regions and subregions of VU-9 and VU-23 contained higher average amounts of fructose (38%–40%) than those reported for honeys from Córdoba, under arid (37%, $n = 19$) and Pampean (36%, $n = 56$) climates [7], and the PP Pampeana (35%, $n = 6$) [38] and similar to clover honeys from the PP Pampeana (40%, $n = 53$) [39] and Spanish honeys (40%, $n = 40$) [40]. The mean concentrations of glucose in honeys from VU-23 (34%–37%) were similar to those of honeys from the SE of Buenos Aires (33%, $n = 24$) [41], and clover ($n = 53$) and eucalyptus ($n = 28$) honeys from the PP Pampeana (34%) [39]. The average contents of glucose in honeys from VU-9 (31%–32%) were similar or higher than in honeys from Córdoba under Pampean (31%, $n = 56$) and arid (29%, $n = 19$) climates [7], the PP Pampeana (27%, $n = 6$) [38], and Spain (27%, $n = 40$) [40]. The mean F + G of honeys from the subregion of VU-9 (69%–70%) and VU-23 (74%–75%) were lower than those from the Argentinean province of Corrientes (75%–78%, $n = 141$) [27] and higher than those from the Argentinean province of La Pampa (68%, $n = 38$) [42]; and similar to those from Serbia (72%, $n = 32$) [43].

Table 7 • Sugar Composition of Honeys from the Vegetation Units (VUs) of the Phytogeographic Provinces (PP) Chaqueña and PP Monte Located in Catamarca (Argentina)

		Phytogeographic Province	
Physicochemical		**PP Chaqueña**	**PP Monte**
Parameter		**VU-9**	**VU-23**
Fructose	***n***	53	14
(g/100 g honey)	**Mean**	38.2[a]	39.7[b]

		Phytogeographic Province	
Physicochemical		**PP Chaqueña**	**PP Monte**
Parameter		**VU-9**	**VU-23**
	SD	2.2	1.3
	Min	34.3	37.7
	Max	46.0	41.4
	Median	38.4	39.6
Glucose	***n***	53	14
(g/100 g honey)	**Mean**	31.4[a]	34.2[b]
	SD	2.7	1.4
	Min	26.0	32.0
	Max	36.2	36.1
	Median	31.4	34.1
F + G	***n***	53	14
(g/100 g honey)	**Mean**	69.6[a]	73.8[b]
	SD	3.9	2.4
	Min	61.4	69.7
	Max	76.3	77.1
	Median	69.8	73.6
F/G ratio	***n***	53	14
	Mean	1.23[a]	1.162[b]
	SD	0.11	0.040
	Min	1.03	1.086
	Max	1.58	1.220
	Median	1.21	1.175
Sucrose	***n***	54	14
(g/100 g honey)	**Mean**	0.26[a]	0.34[a]
	SD	0.25	0.50
	Min	0.00	0.00
	Max	1.20	1.80
	Median	0.30	0.10
Maltose	***n***	27	8
(g/100 g honey)	**Mean**	2.7[a]	2.04[a]
	SD	1.5	0.82
	Min	0.0	0.80
	Max	4.9	3.50
	Median	2.9	2.10
Turanose	***n***	27	8
(g/100 g honey)	**Mean**	2.15[a]	1.71[a]
	SD	0.65	0.54
	Min	0.50	1.10
	Max	3.20	2.80
	Median	2.00	1.75
Erlose	***n***	27	8

		Phytogeographic Province	
Physicochemical		PP Chaqueña	PP Monte
Parameter		VU-9	VU-23
(g/100 g honey)	Mean	0.18[a]	0.25[a]
	SD	0.19	0.37
	Min	0.00	0.00
	Max	0.50	0.90
	Median	0.30	0.00

Abbreviations: n, number of samples; SD, standard deviation; Min, minimum; Max, maximum; nd, not detected; F + G, total content of fructose and glucose; and F/G ratio, fructose/glucose ratio.
Different letters within each row indicate significant differences according to Fisher's test ($p < 0.05$)

The average sucrose amounts found in honeys from the subregions of VU-9 and VU-23 in Catamarca (0.24%–0.34%) were close to those exhibited in honeys from the PP Pampeana (0.27%, *n* = 6) [38] and lower than that from Buenos Aires (1.0%–1.6%, *n* = 24) [41] and Spain (0.60%, *n* = 40) [40].

The mean concentrations of turanose and maltose in honeys from VU-9 (region A: 2.3% turanose, 2.8% maltose; region B: 2.0% turanose, 2.6% maltose) and VU-23 (1.6% turanose, 2.0% maltose) were higher than those reported for honeys from the PP Espinal (0.98% turanose and 1.8% maltose, *n* = 6) and the PP Pampeana (1.0% turanose, 1.3% maltose, *n* = 6) [38].

Honeys from regions B (16.4%) and subregion C-Catamarca (16.3%) exhibited similar mean moistures to Spanish thyme honeys (16.3%, *n* = 25)—a floral genus also grown in these Argentinian regions [24]. The average humidity of honeys from subregion B-Catamarca (16.7%) was similar to those found in honeys from Buenos Aires (17.0%, *n* = 24) [41], the SE of Corrientes (16.8%, *n* = 60) [27] and the north of Córdoba (17.4%, *n* = 19) [7], in clover (*n* = 53) and eucalyptus (*n* = 28) honeys (17.1% and 17.3%, respectively) from the PP Pampeana [39], and unifloral and multifloral honeys from Argentina (17.0%, *n* = 16) [44] and Italy (17.4%, *n* = 40) [22]. Honeys from region A (18.1%) showed mean moistures similar to those found in honeys from the north of Corrientes (17.9%, *n* = 81) [27], the south of Córdoba (18.3%, *n* = 56) [7], Spain (18.1%, *n* = 40) [40], and all over the world (17.9%, *n* > 1,000) [45].

The average EC of the honeys studied (425–575 µS/cm) agreed with that reported for Spanish blossom honeys (470 µS/cm, *n* = 53) [21]. However, they were lower than those found in honeys from Corrientes (470–790 µS/cm, *n* = 141) [27] and in honeys sampled all over the world (640 µS/cm, *n* > 1,000) [45] but higher than in honeys from different phytogeographical regions of Buenos Aires (200–370 µS/cm, *n* = 144 (*30*); 140–221 µS/cm, *n* = 24 [41]) and in Spanish thyme honeys (395 µS/cm, *n* = 25) [24]. The honeys analyzed from the VU-9 and VU-23 displayed EC values in the range of 206–1,325 µS/cm, which was within the range reported for more than 1,000 honeys collected worldwide (150–1,640 µS/cm) [45]. The median EC of the honeys from subregion B-Catamarca (548 µS/cm) were similar to those of honeys from the Argentinean province of Misiones (550 µS/cm, *n* = 13) and honeys from subregion C-Catamarca (438 µS/cm) to those from the Argentinean province of Formosa (430 µS/cm, *n* = 10) [29].

The mean ash content of honeys from the subregion C-Catamarca in VU-23 (251 mg/100 g honey) was close to that reported before for honeys from Catamarca (260 mg/100 g honey, *n* = 39) [3]. The average ash contents of honeys from the different regions and subregions studied (198–338 mg/100 g honey) were lower or similar to those of honeys from the Argentinean province of Jujuy (240–430 mg/100 g honey, *n* = 58) [46] and higher than those of honeys from different PPs in Buenos Aires (59–148 mg/100 g honey, *n* = 144) [30], La Pampa (110 mg/100 g honey, *n* = 38) [42] and the Argentinean province of Chubut (110 mg/100 g honey, *n* = 62) [25], and clover honeys from the PP Pampeana (160 mg/100 g honey, *n* = 148) [39].

Honeys from both VUs in Catamarca (33–39 meq/kg honey) and La Rioja (25–26 meq/kg honey) showed higher average values than those from Córdoba (20–23 meq/kg honey) (7), Buenos Aires (17–21 meq/kg honey, *n* = 144 [30]; 17–23 meq/kg honey, *n* = 148 [47]; 17 meq/kg honey, *n* = 24 [41]), the PP Pampeana (20 meq/kg honey, *n* = 30) [48], and the SE of Corrientes (21 meq/kg honey, *n* = 60) [27] and Portugal (23 meq/kg honey, *n* = 20) [6]. The same trend was observed for honeys from Catamarca compared to the previous reports on honeys from this province (26 meq/kg honey, *n* = 39) [3]. The mean free acidities of honeys from La Rioja were close to those observed for honeys from the north of Corrientes (25–26 meq/kg honey, *n* = 81) [27] and Spanish thyme honeys (27 meq/kg honey, *n* = 25) [24].

The average pH of honeys from VU-9 in Catamarca (pH 4.2) was similar to that found in honeys from the north of Córdoba (pH 4.1) [7], whereas that of honeys from VU-23 (pH 3.6–3.9) were in the range of honeys from different phytogeographical regions of Buenos Aires (pH 3.4–3.9, *n* = 144 [30]; pH 3.3–3.7, *n* = 30 [48]). In particular, the honeys from the subregion C-La Rioja belonging to the PP Monte (pH 3.57) exhibited an average pH close to honeys from the same PP in Buenos Aires (pH 3.66, *n* = 10) [30]. The pH values of the honeys studied were lower than those measured in honeys from Corrientes (pH 4.4–4.7, *n* = 141) [27]. Most of the analyzed honeys showed pH values in the range of 3.4–5.0, similar to Spanish blossom honeys (3.5–4.7, *n* = 53) [21].

The mean colors of honeys from VU-9 and VU-23 in Catamarca (81–85 mm Pfund) were darker than those from different regions in Corrientes (68–76 mm Pfund, *n* = 141) [27] and the PPs in Buenos Aires (9–56 mm Pfund, *n* = 144 [30]; 42–66 mm Pfund, *n* = 24 [41]). Similar average colors were observed in honeys from the VU-9 in La Rioja (66 mm Pfund) and the north of Corrientes (68 mm Pfund, *n* = 29) [27]. Consumers commonly associate honeys with lighter colors to delicate flavors, and honeys with darker colors with strong flavors and less attractive appearance. Taking into account that organoleptic properties of honey can undergo changes, including darkening, during transport and storage, color is a very relevant quality parameter for the ranking of honey and determines the commercial price of honey in the world market [27, 47].

The average °Brix values of honeys from region A of VU-9 (80.6 °Bx) and subregion C-Catamarca of VU-23 (79.9 °Bx) were close to those reported for honeys from Italy (80.9 °Bx, n = 40 (*22*); 81.0 °Bx, n = 69 [23]); and honeys from region B of VU-9 (81.8 °Bx) and subregion C-Catamarca of VU-23 (82.0 °Bx) to those of Spanish thyme honeys (81.9 °Bx, n = 24) [24].

The mean HMF content of honeys from region A in VU-9 (7.7 mg/kg honey) was slightly higher than those measured in clover (6.7 mg/kg honey, n = 53) and eucalyptus (7.1 mg/kg hone, n = 28) honeys from the PP Pampeana [39], and in honeys from SE of Buenos Aires (6.0 mg/kg honey, n = 19) [41] and Spain (4 mg/kg honey, n = 40) [40]; and barely lower than those observed in honeys from Portugal (9 mg/kg honey, n = 38) [49]. The median HMF content in all honeys (7–13 mg/kg honey) was close to those observed in honeys from Corrientes (11 mg/kg honey, n = 16) [29] and Misiones (6 mg/kg honey; n = 13); and lower than those found in honeys from Formosa (33 mg/kg honey, n = 10) and Chaco (28 mg/kg honey, n = 10). Regarding the honeys from Catamarca, the average HMF content (7.7–13.4 mg/kg honey) was lower than those reported previously in honeys from this province (20 mg/kg honey; n = 39) [3]. The contents of water and HMF in honey also depend on the method used for extraction, processing and storage of honeys; therefore, these parameters cannot be considered as completely representative of the nature of honey but rather as indicators of freshness [7].

In general, the analytical results disclosed that the honeys from the different VUs of the main beekeeping regions in Catamarca and La Rioja were high-quality honeys obtained under adequate beekeeping and processing practices. Several parameters, such as F + G content, F/G ratio, EC, ash content, and pH, indicated the blossom origin of most of the honeys studied. The contents of sucrose, water, and HMF evidenced the good maturity and freshness of the honeys, which had been harvested in the proper time and season. The moisture and free acidity measurements revealed the absence of undesirable fermentation in the honeys. Low EC and contents of HMF and sucrose were indicative of a high control of production, good beekeeping practices, and good preservation state of samples. The present study demonstrated the influence of the different VUs and climates, in particular, the rainfall regime of each area on the physical and chemical parameters of the honeys from Catamarca and La Rioja. In this sense, honeys from VU-9 and VU-23 presented significantly distinctive physico-chemical parameters; the contents of glucose and F + G were higher in honeys from VU-23, whereas their EC, ash contents, F/G ratio, and the amounts of turanose and maltose were lower. Besides, honeys from VU-23 in La Rioja also exhibited characteristic lighter colors, and lower pH and contents of total soluble solids and turanose. In contrast, honeys from VU-9 in La Rioja showed the highest pH values. Honeys from Catamarca, in particular those from region A of VU-9, were typified by high free acidities and amounts of turanose. However, none of the physical and chemical parameters measured were completely discriminant among the honeys according to the phytogeographical origin, i.e., the VU that it belongs to. To the best of the authors' knowledge, data related to the contents of major and minor sugars, and total soluble solids, moisture, pH, EC, and color of honeys from the different VUs of the PP Chaqueña and the PP Monte located in Catamarca and La Rioja, as well as HMF in honeys from this last province, are published here for the first time.

The relevance of this work lies in the extended knowledge generated with the study of the set of traceable and representative honey samples from the different PPs and VUs located in the main beekeeping regions in Catamarca and La Rioja. Honeys were collected along four harvests including seasonal variability, which is a requirement to characterize any agricultural food product. The typification of the honeys from each of the phytogeographical regions studied will give them added value, will allow them to access newer markets, and will promote beekeeping activities in these regions little exploited for apiculture. Furthermore, typified honey has a higher commercial value than standard-quality honey. Indeed, there is currently a growing global demand for differentiated products. In this framework, the importance of having typified honeys is evident, and the contribution of this study to the characterization of honeys from Catamarca and La Rioja is noteworthy.

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Author contributions

Conceptualization: RA; validation: ME and RA; formal analysis: AP, IA and VR; investigation: AP, IA, ME, VR and RA; resources: ME, SF and RA; data curation: RA, writing – original draft: AP and RA; writing – review & editing: AP, IA, ME, SF and RA; supervision: RA; funding acquisition: SF and RA. All authors approve of this work and take responsibility for its integrity.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability statement

Data supporting these findings are available within the article, at or upon request.

Institutional review board statements

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