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Minerals and potentially toxic elements in corn silage from tropical and subtropical Brazil

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ABSTRACT - Our aim was to assess the mineral composition of corn silages produced in four states of Brazil: Goiás, Minas Gerais, Paraná, and Santa Catarina. In total, seventy-three samples were analyzed. Total element content was extracted by HNO_3 and H_2O_2 microwave-assisted digestion, and inductively coupled plasma-mass spectrometry (ICP-MS) was used to determine concentration. Of the 31 elements analyzed (Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Se, Sr, Ti, Tl, U, V, and Zn), 21 had concentrations above equipment detection limits. No elements reached the maximum tolerable concentration, but concentrations of Ca (0.14-0.15%), Cu (3.4-5.6 mg kg^{-1}), P (0.13-0.16%), S (0.06-0.08%), and Zn (13-19 mg kg^{-1}) were below the adequate concentration for good nutritional balance. The strong and consistent correlation observed between Fe and Ti in silage samples indicated contamination by soil. Mean concentrations of Cu, Mn, Mo, P, S, and Zn were different among states, and canonic analyses successfully discriminate samples according to their state of origin. Minerals from corn silage should be considered when formulating balanced cattle diets. To ensure silage quality, farmers must adopt strategies that reduce contamination by soil during the ensiling process.

Keywords: dairy nutrition, elemental composition, *Zea mays* L.

Introduction

Forage conservation techniques are fundamental to increase stocking rate and animal performance, mainly during the dry and cold season. Corn silage has been by far the major conserved forage for dairy cattle in Brazil (Daniel et al., 2019) due to its high yield, quality, and acceptability (Bernardes and Rêgo, 2014; Vieira et al., 2011). According to Daniel et al. (2019), Brazil grows approximately 4 million hectares of corn for silage production each year. Corn silage is produced in all regions of Brazil. There is no official data, but the vast majority of those silages are used for feeding dairy cattle.

The production of well-preserved, high-quality silages depends mainly on the composition of the forage at ensiling and the application of appropriate silage-making practices (Driehuis et al., 2018). Quality parameters of silages could show which nutrient or attribute needs to be improved as well as allow nutritionists and farmers for proper balancing of the diets. It becomes more important since forage composes more than a half of daily dry matter (DM) intake by cows.

Despite major relevance, there is a lack of information about the mineral composition of the corn silage produced in Brazil, with most studies focusing on biochemical aspects (Costa et al., 2017; De Oliveira et al., 2017; Pontes et al., 2018), dry matter production, and presence of mycotoxins (Schmidt et al., 2015). Besides, nutrient concentrations of corn plant results from technological level applied by the producer and breeding evolution (Ferreira et al., 2014; Woli et al., 2019), suggesting a need to constantly update reference values.

Few studies (Buchanan-Smith et al., 1974; Costa et al., 2017) have presented a wide assessment of corn silage mineral composition. Since silage is the main source of energy and fiber for dairy cattle in Brazil (Bernardes and Rêgo, 2014), assessing silage mineral composition is important for understanding silage contributions to the mineral balance in dairy cattle diets. Our objective was to quantify the mineral composition of corn silages produced in the four main dairy-producing regions of Brazil.

Material and Methods

A cross-sectional study was performed using silage samples from 73 farms in Brazil. All the samples came from our previous study (Schmidt et al., 2015). Corn silage samples were collected in four important dairy regions between May and September of 2010: South region of Minas Gerais (MG; n = 20; weather = Cwa – humid subtropical climate), Midwest of Goiás (GO; n = 14; weather = Aw – tropical wet and dry climate), municipality of Toledo - Paraná (PR; n = 19; weather = Cfa – humid subtropical climate), and West of Santa Catarina (SC; n = 20; weather = Cfb). The main criteria for site selection were farms that utilize corn silage and representative farms of regional variability (farm size and technology application). The regional climate was identified according to Alvares et al. (2013) using the Köppen system. Despite the different regions we have visited and the total number of samples taken (n = 73), this survey does not cover all the variability of the Brazilian corn silages.

From chosen farms, approximately 1.1 kg of silage was sampled directly from silo panels, at the point of medium temperature evaluated by infrared thermography, as described by Schmidt et al. (2015). Silage samples were labelled and immediately vacuum-packed (Selveda Orved and Brock, EcoVacuum model) into plastic containers. The maximum period between sampling and transport to the laboratory was three days. Upon arrival at the laboratory, samples were frozen and stored. Prior to further processing and analysis, samples were completely thawed, oven-dried (55 °C for 72h), and milled (< 1 mm). Detailed sampling and processing procedures were previously described by Schmidt et al. (2015).

Samples were digested using a microwave heating system with a 48-vessel capacity (Ethos 1, Milestone SrL, Bergamo, Italy). Vessels were composed of polytetrafluoroethylene (PTFE) with a polyethylethylketone (PEEK) pressure jacket and safety device that activates at 35 bars of pressure. Each run consisted of 42 silage samples (~0.200 mg per sample), two internal standards, and two tomato leaf standards (NIST Tomato 1573a, National Institute of Standards and Technology, NIST, Gaithersburg, MD, USA). In addition, duplicate operational blanks were included in each digestion run. Samples were digested in 2 mL HNO_3 [re-distilled from 69% "Aristar" grade (VWR Ltd, Lutterworth, UK)], 1 mL ultrapure water (18.2 MΩ cm; Fisher Scientific UK Ltd, Loughborough, UK), and 1 mL 30 % H_2O_2 (Trace Select Ultra, Fluka, Gillingham, UK) using the microwave-assisted digestion technique. After cooling, each vessel content was washed into a plastic tube (Greiner Bio-One, Stonehouse, UK), brought to a final volume of 15 mL using Milli-Q water, and stored at room temperature. All digestate was diluted by transferring 2 mL of solution to a vial and adding 8 mL of Milli-Q water. An inductively coupled plasma-mass spectrometer (ICP-MS; Agilent 7500ce, Santa Clara, CA, USA) was used for the following elemental analyses: Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Se, Sr, Ti, Tl, U, V, and Zn. For Se analysis, the hydrogen reaction cell mode was used, while all other elements were analyzed using collision cell mode (He-gas). Extraction and quantification processes were carried out in duplicate.

For each data-point, an element-specific operational blank concentration was subtracted. Data were then multiplied by the initial sample volume, divided by the initial dry mass of silage material, and converted to mg element per kg of dry silage material. Element-specific limits of detection (LODs) were reported as three times the standard deviation of operational blank concentrations (Table 1). Element-specific recoveries from Certified Reference Material (CRM) ranged from 73 to 156 % for 18 elements with certified CRM values, and ranged from 83 to 110% for seven elements with noncertified CRM values (Table 1). From data, ten elements (Ag, As, Be, Co, Cr, Li, Na, Se, Tl, and U) were removed due to their mean concentrations being less than or close to the LOD. For those elements retained for analysis, data for individual silage element concentrations that were below element-specific LOD were replaced with half LOD values. Silage element concentrations > 5 standard deviations (SD) above the global arithmetic mean for each element were also removed (27 out of 4,526 values).

For data analysis of elements measured in silage samples, four groups were considered (MG, GO, PR, and SC). Data displaying normality of the residuals (Shapiro-Wilk test) and homogeneous variances were subjected to analysis of variance (ANOVA), whereas data without normality or homogeneity were submitted to Kruskal-Wallis ANOVA. When significant differences were found between groups ($P<0.05$), parametric data were subjected to Tukey's test ($P<0.05$) and nonparametric data were analyzed with the Dunn's test ($P<0.05$). Pearson correlations were obtained to assess interactions between elements ($P<0.05$). To investigate relationships among the four groups of samples, canonical correlation analyses were performed (Statistica, version 8.0).

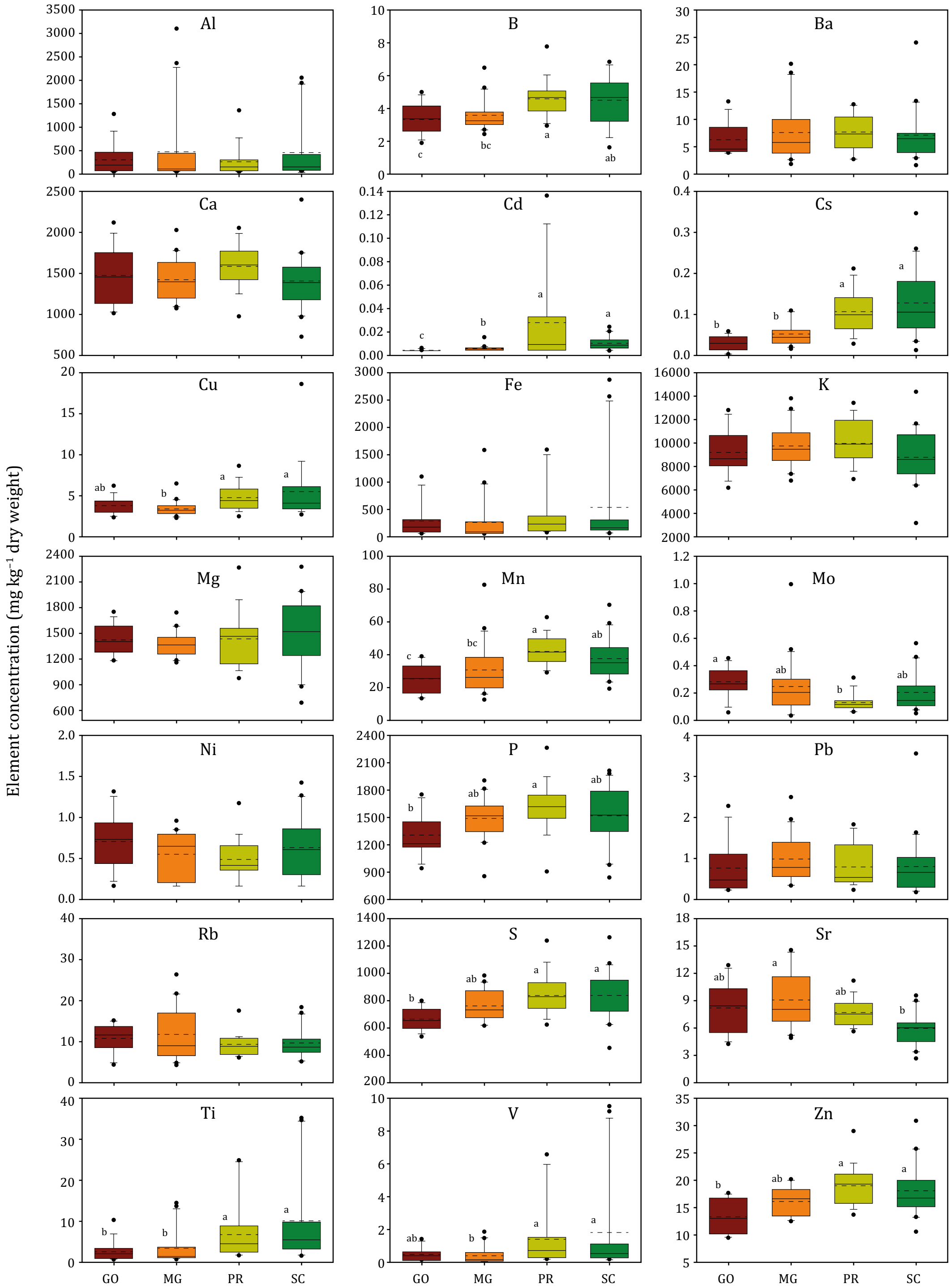
Table 1 - Element-specific limits of detection and recoveries from certified and noncertified reference materials

Element	Limit of detection	Reference value	Recovered value	Recovery
		mg kg^{-1}		%
Ag	0.030			
Al	4.41	598±12	437.00	73.1
As	0.053	0.112±0.004	0.170	152.0
B	2.09	33.3±0.7	29.6	88.9
Ba[1]	0.07	63.00	68.00	107.0
Be	0.010			
Ca	18.6	50500±900	49121.00	97.3
Cd	0.008	1.52±0.04	1.492	98.2
Co	0.09	0.57±0.02	0.52	91.2
Cr	0.94	1.99±0.06	1.71	85.9
Cs[1]	0.001	0.053	0.055	103.0
Cu	0.69	4.70±0.14	3.63	77.2
Fe	11.9	368±7	362.00	98.4
K	7.9	27000±500	26510.00	98.2
Li	0.09			
Mg[1]	18.0	12000.00	10067.00	83.9
Mn	0.91	246±8	225.00	91.5
Mo[1]	0.05	0.46	0.45	97.8
Na	19.5	136±4	94.00	69.1
Ni	0.32	1.59±0.07	1.46	91.8
P	8.86	2160±40	2238.00	104.0
Pb	0.13			
Rb	0.01	14.89±0.27	15.34	103.0
S[1]	240	9600.00	9858.00	102.0
Se	0.012	0.054±0.003	0.084	156.0
Sr[1]	3.56	85.00	94.00	110.0
Ti	0.006			
Tl	0.009			
U[1]	0.0850	0.035	0.029	82.9
V	0.07	0.835±0.010	0.704	84.3
Zn	8.05	30.9±0.7	26.6	86.1

[1] Noncertified leaf concentrations and recovery of tomato leaf certified reference material (Tomato 1573A, NIST, Gaithersburg, MD, USA) and recovery from analysis by ICP-MS.

Results

Of the 31 elements analyzed, 21 were effectively detected and quantified by ICP-MS analysis (Figure 1, Tables 2-6). From this set, 11 nutrients were determined in this study. We were unable to analyze for Cl; and Na concentrations were below detection limits; concentrations of other macronutrients (Ca, Mg, P, K, and S) can be seen in Figure 1.



Boxes represent the mid two quartiles with the median (continuous line) and mean (dashed line); whiskers are the 95% confidence limits plus extremes. Different lowercase letters indicate significant difference by Tukey's (P<0.05) or Dunn's (P<0.05) tests.

Figure 1 - Concentrations of 21 elements in corn silage from four states in Brazil: Goiás (GO; n = 14), Minas Gerais (MG; n = 20), Paraná (PR; n = 19), and Santa Catarina (SC; n = 20).

Table 2 - Average mineral concentration of Brazilian corn silages – summary of nutritional dairy requirement for transition and lactation cows and mineral composition of corn silage on a dry matter (DM) basis according to NRC (2001)

Element	Unit	Average concentration and standard deviation (n = 73)	NRC (2001)					
			Corn silage composition			Maximum tolerable concentration	Dairy requirement	
			< 25% DM[1] (wet)	32-38% DM (normal)	>40% DM (mature)		Transition	Lactation
Ca	%	0.15±0.03	0.29	0.28	0.26	-	0.44-0.48	0.53-0.80
K	%	0.94±0.21	1.30	1.20	1.10	3.0	0.51-0.62	1.00-1.24
Mg	%	0.14±0.03	0.19	0.17	0.16	1.4	0.11-0.16	0.18-0.29
P	%	0.15±0.03	0.24	0.26	0.25	1.0	0.22-0.26	0.32-0.42
S	%	0.08±0.02	0.14	0.14	0.10	0.4	0.2	0.2
Al	mg kg^{-1}	378±589	-	-	-	1000	-	-
B	mg kg^{-1}	4±1	-	-	-	135	-	-
Ba	mg kg^{-1}	7±4	-	-	-	100	-	-
Cd	mg kg^{-1}	0.01±0.02	-	-	-	0.5	-	-
Cs	mg kg^{-1}	0.08±0.06	-	-	-	-	-	-
Cu	mg kg^{-1}	4±2	6	6	6	40	12-18	9-16
Fe	mg kg^{-1}	365±545	157	104	92	1000	13-18	12.3-22
Mn	mg kg^{-1}	34±13	46	36	36	1000	16-24	12-21
Mo	mg kg^{-1}	0.21±0.15	-	-	-	10	-	-
Ni	mg kg^{-1}	0.59±0.33	-	-	-	50	-	-
Pb	mg kg^{-1}	0.82±0.60	-	-	-	30	-	-
Rb	mg kg^{-1}	10±4	-	-	-	-	-	-
Sr	mg kg^{-1}	8±3	-	-	-	2000	-	-
Ti	mg kg^{-1}	6±7	-	-	-	-	-	-
V	mg kg^{-1}	0.96±1.69	-	-	-	50	-	-
Zn	mg kg^{-1}	17±4	29	24	23	1000	21-30	43-73

Element concentrations (Cd, Cs, Cu, Mn, Mo, P, S, Sr, Ti, V, and Zn) varied by ~50% according to state of origin, and the highest concentrations were observed in the states of PR and SC. The high variation observed in some elements (e.g., Al and Fe) may explain the lack of statistical differences among Brazilian states.

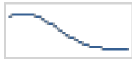
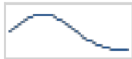
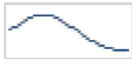
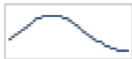
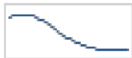
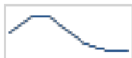
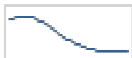
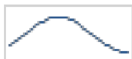
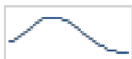
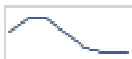
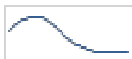
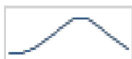
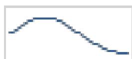
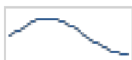
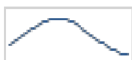
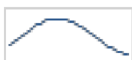
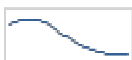
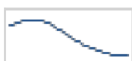
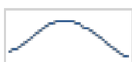
Pearson (Figure 2) and Canonic (Figure 3) analyses emphasized high correlations for Al, Fe, Ti, and V. From the first canonic pair, four groups were clearly formed (one for each state) in the four quadrants of the graph (Figure 3). Analyzing the standardized coefficients for canonical variables, the elements Ti, Fe, Al, and V stood out as the most important. Thus, the canonic variables (Root 1 and Root 2) can be described as follows: Root 1 – samples with high levels of Ti and low concentrations of Al and V; Root 2 – samples with high concentrations of Fe and low concentrations of Al and V.

The first quadrant was mainly occupied by samples from SC and represent samples with high concentrations of Ti and Fe (Figure 3). Samples from PR (second quadrant) presented high Ti and low Fe concentrations. In contrast, samples from GO displayed low Ti and high Fe concentrations. The samples from MG presented low concentrations of Ti and Fe.

Discussion

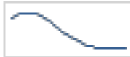
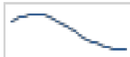
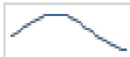
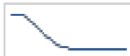
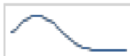
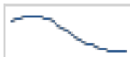
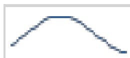
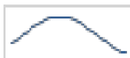
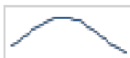
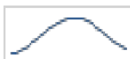
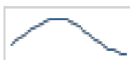
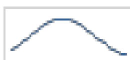
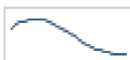
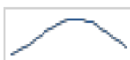
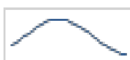
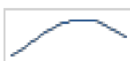
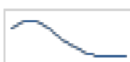
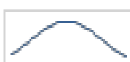
At least 17 minerals are required by cattle (NRC, 2001). Required micronutrients are Cr, Co, Cu, Fe, Mn, Mo, Ni, Se, and Zn. All these elements had average concentrations below those required values listed by NRC (2001). Measured concentrations of Ca, K, Mg, P, and S were 54, 78, 82, 58, and 50% of

Table 3 - Descriptive analysis of the mineral composition of corn silage sampled in Minas Gerais, Brazil

Element	Mean mg kg^{-1}	Median	Min.	Max.	Standard deviation	Variance	Kurtosis	Asymmetry	Normal distribution
					Minas Gerais				
Al	482.19	98.41	39.70	3106.32	830.33	689451.86	4.33	2.30	
B	3.59	3.29	2.35	6.54	1.04	1.07	1.44	1.34	
Ba	7.79	5.86	1.96	21.41	5.09	25.95	0.84	1.28	
Ca	1419.63	1390.24	1041.67	2054.47	253.58	64302.48	−0.11	0.56	
Cd	0.01	0.00	<LOD*	0.02	0.00	0.00	3.74	2.01	
Cs	0.05	0.04	0.01	0.11	0.03	0.00	−0.26	0.97	
Cu	3.38	3.12	2.22	6.49	0.96	0.92	3.78	1.77	
Fe	269.73	108.95	51.62	1596.74	390.09	152168.21	5.14	2.38	
K	9735.28	9434.09	6675.62	13764.64	1805.24	3258899.51	−0.12	0.53	
Mg	1358.98	1354.12	1130.44	1730.27	143.41	20565.80	0.59	0.75	
Mn	30.68	26.41	12.10	86.00	16.03	257.01	3.96	1.80	
Mo	0.23	0.20	<LOD	1.01	0.21	0.04	7.48	2.49	
Ni	0.55	0.63	0.16	0.98	0.29	0.08	−1.46	−0.25	
P	1493.21	1514.76	807.18	1927.25	232.01	53828.66	1.47	−0.76	
Pb	0.98	0.73	0.29	2.49	0.61	0.37	0.40	1.03	
Rb	11.55	8.89	3.94	26.28	6.40	40.97	−0.57	0.78	
S	758.06	727.31	587.78	992.00	109.78	12051.61	−0.87	0.44	
Sr	8.98	7.92	4.74	14.80	2.97	8.83	−1.00	0.45	
Ti	3.36	1.46	0.56	15.58	4.03	16.25	3.25	2.08	
V	0.41	0.15	0.04	1.89	0.54	0.29	1.54	1.67	
Zn	16.16	16.60	12.17	20.53	2.52	6.35	−1.14	−0.07	

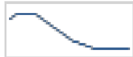
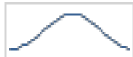
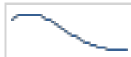
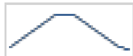
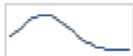
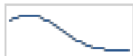
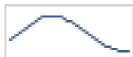
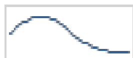
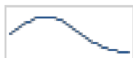
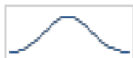
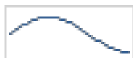
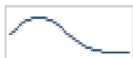
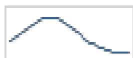
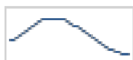
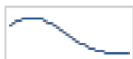
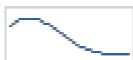
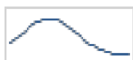
LOD - limit of detection.

Table 4 - Descriptive analysis of the mineral composition of corn silage sampled in Goiás, Brazil

Element	Mean mg kg^{-1}	Median	Min.	Max.	Standard deviation	Variance	Kurtosis	Asymmetry	Normal distribution
					Goiás				
Al	302.65	182.11	44.19	1444.44	326.38	106520.99	5.41	2.19	
B	2.36	2.55	<LOD	5.27	1.86	3.44	−1.40	−0.07	
Ba	6.41	4.74	3.91	14.12	2.92	8.54	0.62	1.22	
Ca	1467.57	1436.26	992.78	2170.82	344.55	118716.42	−1.10	0.23	
Cd	0.00	0.00	<LOD	0.01	0.00	0.00	23.74	4.79	
Cs	0.03	0.03	<LOD	0.06	0.02	0.00	−1.50	0.04	
Cu	3.78	3.78	2.21	8.40	1.16	1.35	8.68	2.28	
Fe	279.82	157.36	50.72	1119.93	298.44	89067.21	2.84	1.92	
K	9154.71	8720.36	6142.04	12843.53	1875.25	3516561.92	−0.37	0.63	
Mg	1413.18	1401.07	1149.55	1742.62	174.83	30566.77	−0.94	0.29	
Mn	25.37	25.00	12.72	39.70	8.47	71.71	−1.25	0.09	
Mo	0.28	0.28	0.05	0.46	0.11	0.01	−0.21	−0.33	
Ni	0.70	0.69	0.16	1.46	0.34	0.12	−0.16	0.43	
P	1310.46	1247.80	888.78	1788.97	233.66	54596.83	−0.49	0.44	
Pb	0.76	0.50	0.20	2.48	0.64	0.41	0.83	1.38	
Rb	10.57	11.43	4.18	15.22	3.45	11.92	−0.79	−0.58	
S	660.73	655.39	529.87	829.05	81.12	6580.16	−0.92	0.08	
Sr	8.13	8.37	4.09	13.28	2.86	8.18	−1.26	0.20	
Ti	2.58	2.07	0.49	11.21	2.43	5.90	7.12	2.56	
V	0.46	0.33	0.08	1.60	0.40	0.16	1.34	1.33	
Zn	13.25	12.92	8.32	18.18	2.97	8.83	−1.30	0.20	

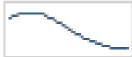
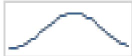
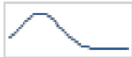
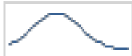
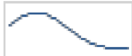
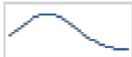
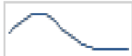
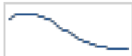
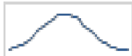
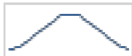
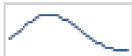
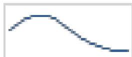
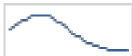
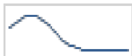
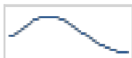
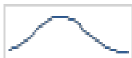
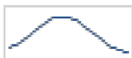
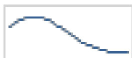
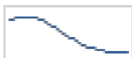
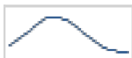
LOD - limit of detection.

Table 5 - Descriptive analysis of the mineral composition of corn silage sampled in Paraná Brazil

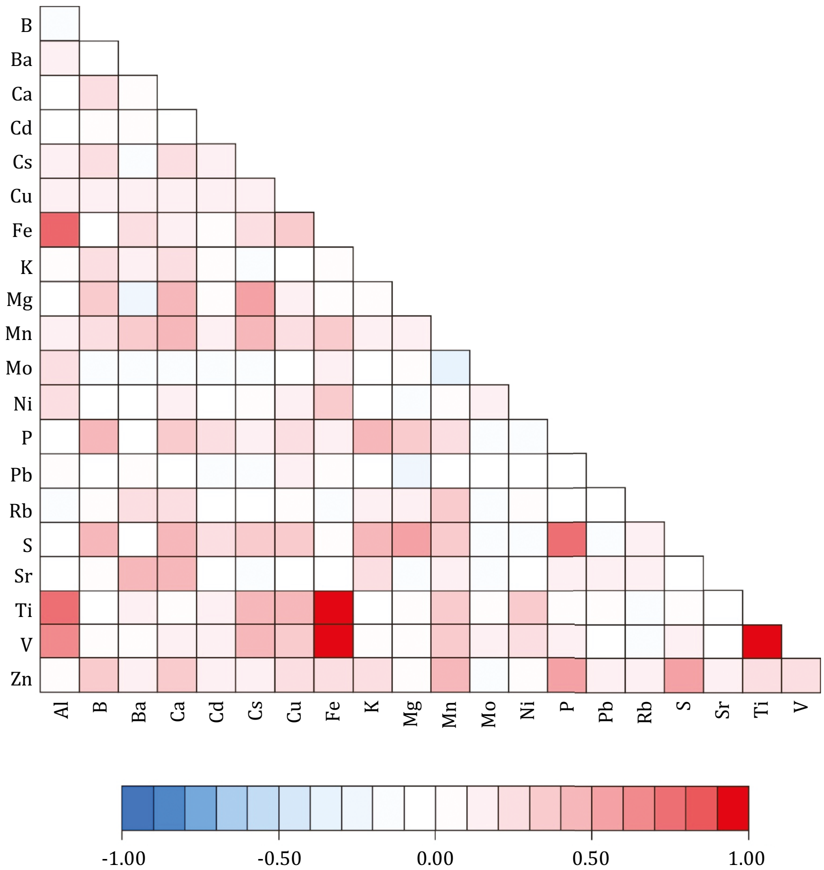
Element	Mean mg kg^{-1}	Median	Min.	Max.	Standard deviation	Variance	Kurtosis	Asymmetry	Normal distribution
					Paraná				
Al	267.90	138.25	46.65	1444.77	324.60	105365.85	5.57	2.36	
B	4.61	4.55	2.86	8.83	1.13	1.29	4.05	1.37	
Ba	7.80	7.46	2.76	13.61	3.32	11.01	−1.16	0.09	
Ca	1578.00	1593.44	947.06	2122.99	258.67	66911.49	0.34	−0.23	
Cd	0.02	0.01	<LOD	0.14	0.04	0.00	3.69	2.17	
Cs	0.10	0.09	<LOD	0.21	0.06	0.00	−0.58	0.27	
Cu	4.77	4.49	2.30	10.19	1.62	2.61	1.90	1.12	
Fe	374.45	225.08	74.86	1767.09	441.02	194495.35	3.71	2.15	
K	9944.63	9735.13	6847.55	13602.31	1924.08	3702085.96	−0.98	0.29	
Mg	1424.92	1434.29	935.14	2297.12	304.01	92422.10	1.35	0.92	
Mn	41.95	40.25	28.28	64.94	9.11	83.01	−0.22	0.63	
Mo	0.13	0.11	0.06	0.32	0.06	0.00	2.66	1.64	
Ni	0.48	0.44	0.16	1.18	0.27	0.07	0.49	0.79	
P	1623.01	1626.19	879.12	2358.45	277.76	77151.94	2.06	−0.23	
Pb	0.80	0.54	0.21	1.91	0.51	0.26	−0.52	0.96	
Rb	9.15	8.83	5.90	18.14	2.61	6.83	3.57	1.51	
S	834.44	815.59	583.05	1298.58	156.03	24345.14	1.04	0.96	
Sr	7.64	7.47	5.47	11.13	1.53	2.34	−0.28	0.60	
Ti	6.81	4.30	1.43	27.94	6.87	47.23	3.22	1.98	
V	1.22	0.65	<LOD	6.55	1.61	2.58	5.80	2.50	
Zn	19.07	19.01	13.22	29.96	3.67	13.50	1.26	0.86	

LOD - limit of detection.

Table 6 - Descriptive analysis of the mineral composition of corn silage sampled in Santa Catarina, Brazil

Element	Mean mg kg^{-1}	Median	Min.	Max.	Standard deviation	Variance	Kurtosis	Asymmetry	Normal distribution
					Santa Catarina				
Al	433.70	153.29	33.68	2126.56	630.74	397832.84	1.72	1.80	
B	4.29	4.57	<LOD	7.70	1.77	3.14	0.42	−0.70	
Ba	6.63	6.35	<LOD	24.03	4.10	16.79	7.50	2.13	
Ca	1403.00	1380.20	714.76	2386.71	337.99	114235.51	2.40	0.77	
Cd	0.01	0.01	<LOD	0.03	0.01	0.00	1.26	1.14	
Cs	0.13	0.10	<LOD	0.36	0.08	0.01	0.96	1.07	
Cu	5.57	4.20	2.50	20.46	3.91	15.32	8.61	2.81	
Fe	516.52	170.516	56.15	2923.08	824.88	680421.8	3.34	2.16	
K	8789.31	8488.26	3001.43	15136.54	2377.79	5653881.39	1.12	0.07	
Mg	1506.59	1503.77	679.15	2261.04	386.31	149234.32	−0.25	−0.21	
Mn	37.33	35.38	18.46	72.16	12.64	159.77	0.77	0.94	
Mo	0.20	0.15	0.05	0.62	0.14	0.02	2.28	1.66	
Ni	0.63	0.58	0.16	1.88	0.41	0.16	1.22	1.03	
P	1520.74	1540.86	801.07	2044.14	320.91	102985.72	−0.41	−0.39	
Pb	0.70	0.62	0.00	3.55	0.64	0.40	9.56	2.55	
Rb	9.51	8.66	4.80	18.24	3.52	12.37	0.98	1.15	
S	832.31	828.17	434.69	1325.72	184.74	34127.77	0.55	0.27	
Sr	5.84	5.91	2.49	9.82	1.84	3.39	−0.06	0.36	
Ti	9.55	5.12	0.91	41.36	10.82	117.15	1.89	1.75	
V	1.56	0.51	<LOD	9.48	2.61	6.81	4.22	2.31	
Zn	18.10	16.74	9.66	31.06	4.78	22.85	1.04	1.02	

LOD - limit of detection.



The correlation coefficients were scaled from −1.00 (blue) to 1.00 (red).

Figure 2 - Pearson correlations between concentrations of 21 elements observed in corn silages from Brazil.

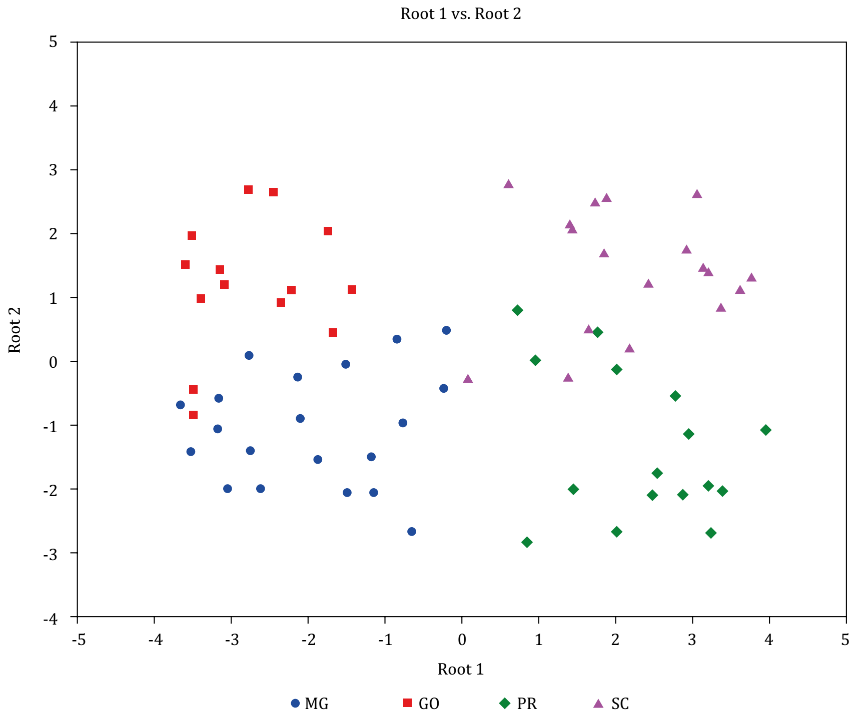


Figure 3 - Canonic analysis of corn silage samples from Minas Gerais (MG), Goiás (GO), Paraná (PR), and Santa Catarina (SC), Brazil.

reference values, respectively. Concentrations of Cu, Mn, and Zn were 67, 94, and 67% of reference values, respectively. However, the concentration of Fe was more than three times the reference (346%). Comparing with the nutrient content databases of the Dairy One Forage Laboratory (Ithaca, NY) for corn silage, the concentration of Mo found in the Brazilian silage is about three times lower than the average value of the samples from United States (Dairy One, 2020). Among potentially toxic trace elements – including Ag, Al, As, Cd, Cs, Pb, etc. – concentrations above toxicity (NRC, 2001) were not detected.

Silage can provide up to 9, 34, 23, 12, and 15% of respective daily requirements of Ca, K, Mg, P, and S for a hypothetical milking cow eating 26 kg of DM per day composed of 40% (10.4 kg DM) corn silage. For micromineral elements, the average corn silage can provide up to 13, 847, 80, and 11% of respective requirements for Cu, Fe, Mn, and Zn.

Regularly, farmers and nutritionists do not emphasize mineral analyses in forages the same way they analyze organic compounds. Since forage mineral analyses are not usually performed, many Brazilian cattle nutritionists may be overestimating contributions from corn silage when balancing rations using NRC values. On the other hand, some nutritionists do not consider mineral contributions from silage, or only consider macrominerals. In fact, it is not uncommon for diets to be supplemented with amounts of trace elements that neglect the concentration already present in the basal diet. An overbalancing of minerals can lead to cost increases and environmental pollution (Weiss, 2017).

Samples used in this trial were first described by Schmidt et al. (2015). They analyzed 327 samples from five Brazilian dairy-producing regions and found highly variable ash content (averaging 3.3% of DM) from 1.1 (minimum) to 10.9% of DM (maximum). De Oliveira et al. (2017) analyzed thirty-two corn silage samples from Minas Gerais, São Paulo, Paraná, and Rio Grande do Sul states and concluded that corn silage produced on intensive dairy farms in Brazil had satisfactory nutritive value for tropical climate conditions, but had greater content of neutral detergent fiber and lower digestibility compared with silages from the United States. Schmidt et al. (2015) reported highly variable chemical composition for all evaluated parameters. Thus, average and table values of forage minerals must be carefully considered when balancing diets for dairy cattle.

Dairy cattle diets are formulated using a variety of feedstuffs (White and Capper, 2014) with forages being the main source of energy and fiber. Despite their role as a main ingredient for feeding dairy cows, corn silages are not the main source for most required minerals. Corn silage was reported to have low concentrations of S (NRC, 2000), Co, Mo (NRC, 2001), Ca, and Cu (Kung Jr. et al., 2015). However, our results confirm that corn silage can be an important source of K, Mg, Fe, and Mn. From economic and nutritional perspectives, feed formulation is essential in the dairy production chain (Alqaisi et al., 2019), and our results suggest that the mineral composition of corn silage should not be underrated.

Corn is widely grown in many parts of the world, with relatively stable yields under a wide variety of environmental and agronomical conditions (Khan et al., 2015). Rayan and Abbott (2015) compared compositional analyses of three genetically modified corn hybrids to a non-genetically modified hybrid corn. These authors reported no significant differences in Ca, P, Na, Zn, Fe, Mn, and Mo values, whereas small differences were found in Mg, S, and Cu. Ridley et al. (2002) assessed the compositional equivalence of glyphosate-tolerant corn and conventional corn grown in the United States and the European Union and found that most nutrient concentrations were statistically similar. Corn appears to have the capacity to absorb and accumulate nutrients independent upon external conditions such as soil type and weather conditions.

The concentrations of Cs, Cu, Mn, Mo, P, S, Sr, Ti, V, and Zn varied according to state of origin. The states of Paraná and Santa Catarina had the highest concentrations of most elements. In these states, dairy production is located in regions with soils predominantly derived from basalt (Silva and Vaine, 2001), which may explain the higher bioavailability of elements for plant uptake (Costa et al., 2002; Ehlers and Arruda, 2014; Melo et al., 2012; Schmidt et al., 2009).

Some elements are not required and can cause toxicity in cattle. Although there are no established minimum concentrations for these elements, there are maximum tolerable concentrations that represent limits above which unsafe residues could be found in human foods derived from animals (NRC, 2000). The average concentrations of Al, B, Ba, Cd, Pb, Sr, and V found in these silage samples can be considered safe for animals. In corn silages from the northeastern United States, Kung Jr. et al. (2015) found concentrations of B ranging from 2 to 3 mg kg^{-1} and concentrations of Ba from 0.9 to 25 mg kg^{-1}. The concentrations of Cs and Rb found in this study were within or close to the range of concentrations reported by Kabata-Pendias (2010).

Although the concentration of Fe in silages was high, the average was below the maximum tolerable concentration. Iron is often found in ruminant diets, and animals display considerable iron tolerance that supports the ingestion of 1000 mg kg^{-1} of Fe in DM (NRC, 2001). However, high Fe in silage has been reported to induce Cu deficiency in lactating cows (Steffil et al., 2009), which may be aggravated by the low Cu concentrations we observed. According to the Nutrient Requirements of Beef Cattle (NRC, 2000), most forages contain from 70 to 500 mg kg^{-1} of Fe. As was observed (Figure 1), Kung Jr. et al. (2015) also pointed out wide Fe variation in corn silage; silage contamination by soil is the most likely explanation for high Fe concentrations (Hansen and Spears, 2009). Martens et al. (2018) highlighted that future investigations must consider if intestinal tissue can tolerate long periods of ferrous iron overload, and if pathogenic microorganism activity alters under such conditions.

In light of the above considerations, silage may be a source of many nutrients. Nutritionists must, therefore, analyze forage for minerals since their concentrations in corn silage can be quite variable. Such information could be critical for optimizing on-farm high precision feed balancing to meet future dairy production demands.

To avoid silage damage and decrease DM losses, applying soil over the plastic film after sealing is a widespread practice on Brazilian dairy farms (Bernardes and Rêgo, 2014). However, this practice may increase the risk of silage contamination by the soil. Soil contamination in silage is a well-known situation (Hansen and Spears, 2009; Pontes et al., 2018; Schmidt et al., 2015) that has three principle causes: field soil on harvested plant material, tractor and vehicles tires carrying soil during the silage making process, and contamination during feed out from soils used to cover the plastic film.

In general, Fe present in soils is mostly in insoluble forms with low absorbability (Martens et al., 2018). However, acids produced by microorganisms during silage fermentation significantly change the chemical dynamics of Fe in the soil-silage mixture. Under such circumstances, soil-bound Fe undergoes reduction (from ferric to ferrous form), which increases bioaccessibility (Hansen and Spears, 2009).

Martens et al. (2018) evaluated the effect of soil contamination on grass silages. The most pronounced difference they observed between contaminated and uncontaminated silages was a 46-72-fold increase in Al when soil was present.

Analyses showed a strong correlation among Fe, Al, Ti, and V, suggesting that Fe and Al found in silage samples was mainly attributable to soil contamination. To confirm this hypothesis and to study the relation of the four sample groups (MG, GO, PR, and SC), a canonic analysis was conducted. This analysis confirmed that concentrations of Ti were significatively higher in SC and PR ($P<0.001$) as noted in ANOVA analysis (Table 7).

Titanium shows a strong lithophilic characteristic, and its content in plants is usually under 7 mg kg^{-1} (Kabata-Pendias, 2010). For this reason, Ti has been identified as a valid indicator of soil contamination in plant samples due to its abundance in soil and negligible uptake by plants (Cook et al., 2009; McIntosh et al., 1995). After a series of experiments, Cook et al. (2009) concluded that Ti concentrations were higher for dust-exposed plants compared with dust-protected plants, lending further validity to Ti as a soil contamination indicator. Thus, observed Ti concentrations indicated soil contamination in our corn silages samples.

Table 7 - Summary of analysis of variance (ANOVA) and Kruskal-Wallis ANOVA results for 21 elements determined in corn silages from Minas Gerais, Goiás, Paraná, and Santa Catarina, Brazil

Element	Test	H or F value	P value
Al	Kruskal-Wallis	0.545	0.909
B	ANOVA	5.463	0.002
Ba	Kruskal-Wallis	1.438	0.697
Ca	ANOVA	1.337	0.270
Cd	Kruskal-Wallis	25.724	<0.001
Cs	Kruskal-Wallis	32.894	<0.001
Cu	Kruskal-Wallis	13.885	0.003
Fe	Kruskal-Wallis	5.728	0.126
K	ANOVA	1.301	0.281
Mg	Kruskal-Wallis	3.014	0.389
Mn	Kruskal-Wallis	19.884	<0.001
Mo	Kruskal-Wallis	14.349	0.002
Ni	ANOVA	1.502	0.222
P	ANOVA	3.653	0.017
Pb	Kruskal-Wallis	3.453	0.327
Rb	Kruskal-Wallis	1.771	0.641
S	ANOVA	5.703	0.002
Sr	Kruskal-Wallis	14.240	0.003
Ti	Kruskal-Wallis	20.632	<0.001
V	Kruskal-Wallis	14.337	0.002
Zn	Kruskal-Wallis	18.944	<0.001

Conclusions

Although corn silage is an important mineral source, mineral composition was highly variable in our study, since there is a large variation among soils and climate conditions. These findings highlight the necessity of silage evaluation as a regular management practice to reach optimum animal nutrition.

The high concentrations of Fe detected suggests the ubiquitous occurrence of soil contamination in corn silages from these dairy-producing regions. This hypothesis was confirmed by the strong correlation between Fe and Ti concentrations observed in our silage samples.

The regions sampled are among the most productive dairy sites in Brazil; however, we acknowledge that our sample set (n = 73) is not enough to cover all the variability expected to the Brazilian condition. However, the mineral analyses of forages in Brazil are scarce, and our manuscript innovates by addressing this issue.

Author Contributions

Conceptualization: A.C.V. Motta and P. Schmidt. Data curation: E.M. Araujo, M.R. Broadley, S.D. Young and J.Z. Barbosa. Funding acquisition: A.C.V. Motta. Methodology: M.R. Broadley and S.D. Young. Resources: M.R. Broadley and S.D. Young. Writing-original draft: E.M. Araujo. Writing-review & editing: A.C.V. Motta, E.M. Araujo, J.Z. Barbosa, S.A. Prior and P. Schmidt.

Conflict of Interest

The authors declare no conflict of interest.

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References

Alqaisi, O.; Moraes, L. E.; Ndambi, O. A. and Williams, R. B. 2019. Optimal dairy feed input selection under alternative feeds availability and relative prices. Information Processing in Agriculture 6:438-453. https://doi.org/10.1016/j.inpa.2019.03.004

Alvares, C. A.; Stape, J. L.; Sentelhas, P. C.; de Moraes Gonçalves, J. L. and Sparovek, G. 2013. Köppen's climate classification map for Brazil. Meteorologische Zeitschrift 22:711-728. https://doi.org/10.1127/0941-2948/2013/0507

Bernardes, T. F. and Rêgo, A. C. 2014. Study on the practices of silage production and utilization on Brazilian dairy farms. Journal of Dairy Science 97:1852-1861. https://doi.org/10.3168/jds.2013-7181

Buchanan-Smith, J. G.; Evans, E. and Poluch, S. O. 1974. Mineral analyses of corn silage produced in Ontario. Canadian Journal of Animal Science 54:253-256. https://doi.org/10.4141/cjas74-037

Cook, L. L.; McGonigle, T. P. and Inouye, R. S. 2009. Titanium as an indicator of residual soil on arid-land plants. Journal of Environmental Quality 38:188-199. https://doi.org/10.2134/jeq2007.0034

Costa, A. C. S.; Almeida, V. C.; Lenzi, E. and Nozaki, J. 2002. Determinação de cobre, alumínio e ferro em solos derivados do basalto através de extrações sequenciais. Química Nova 25:548-552. https://doi.org/10.1590/S0100-40422002000400007

Costa, N. R.; Andreotti, M.; Crusciol, C. A. C.; Lima, C. G. R.; Castilhos, A. M.; Souza, D. M.; Bonini, C. S. B. and Pariz, C. M. 2017. Yield and nutritive value of the silage of corn intercropped with tropical perennial grasses. Pesquisa Agropecuária Brasileira 52:63-73. https://doi.org/10.1590/S0100-204X2017000100008

De Oliveira, I. L.; Lima, L. M.; Casagrande, D. R.; Lara, M. A. S. and Bernardes, T. F. 2017. Nutritive value of corn silage from intensive dairy farms in Brazil. Revista Brasileira de Zootecnia 46:494-501. https://doi.org/10.1590/S1806-92902017000600004

Dairy One. 2020. Interactive Feed Composition Libraries. Available at: <https://dairyone.com/services/forage-laboratory-services/feed-composition-library/interactive-feed-composition-libraries/>. Accessed on: Jan 24, 2020.

Daniel, J. L. P.; Bernardes, T. F.; Jobim, C. C.; Schmidt, P. and Nussio, L. G. 2019. Production and utilization of silages in tropical areas with focus on Brazil. Grass and Forage Science 74:188-200. https://doi.org/10.1111/gfs.12417

Driehuis, F.; Wilkinson, J. M.; Jiang, Y.; Ogunade, I. and Adesogan, A. T. 2018. Silage review: Animal and human health risks from silage. Journal of Dairy Science 101:4093-4110. https://doi.org/10.3168/jds.2017-13836

Ehlers, T. and Arruda, G. O. S. F. 2014. Utilização do pó de basalto em substratos para mudas de *Eucalyptus grandis*. Floresta e Ambiente 21:37-44. https://doi.org/10.4322/floram.2014.002

Ferreira, C. F.; Motta, A. C. V.; Barbosa, J. Z.; Santos, N. Z.; Prior, S. and Gabardo, J. 2014. Maize (*Zea mays* L.) cultivars nutrients concentration in leaves and stalks. Maydica 59:65-71.

Hansen, S. L. and Spears, J. W. 2009. Bioaccessibility of iron from soil is increased by silage fermentation. Journal of Dairy Science 92:2896-2905. https://doi.org/10.3168/jds.2008-1933

Kabata-Pendias, A. 2010. Trace elements in soils and plants. 4th ed. CRC Press, Boca Raton.

Khan, N. A.; Yu, P.; Ali, M.; Cone, J. W. and Hendriks, W. H. 2015. Nutritive value of maize silage in relation to dairy cow performance and milk quality. Journal of the Science of Food and Agriculture 95:238-252. https://doi.org/10.1002/jsfa.6703

Kung Jr., L.; Lim, J. M.; Hudson, D. J.; Smith, J. M. and Joerger, R. D. 2015. Chemical composition and nutritive value of corn silage harvested in the northeastern United States after Tropical Storm Irene. Journal of Dairy Science 98:2055-2062. https://doi.org/10.3168/jds.2014-8621

Martens, S. D.; Majewska-Pinda, A.; Benkmann, A.; Zentek, J.; Spolders, M.; Simon, A.; Schafft, H. and Steinhöfel, O. 2018. Influence of soil contamination before and after ensiling on mineral composition of grass silages, feed intake and carry-over to body tissue of goats. Journal of Animal and Feed Sciences 27:307-316. https://doi.org/10.22358/jafs/99863/2018

McIntosh, P. D.; Loeseke, M. and Bechler, K. 1995. Soil changes under mouse-ear hawkweed (*Hieracium pilosella*). New Zealand Journal of Ecology 19:29-34.

Melo, V. F.; Uchôa, S C. P.; Dias, F. O. and Barbosa, G. F. 2012. Doses de basalto moído nas propriedades químicas de um Latossolo Amarelo distrófico da savana de Roraima. Acta Amazonica 42:471-476. https://doi.org/10.1590/s0044-59672012000400004

NRC - National Research Council. Nutrient requirements of beef cattle. 2000. National Academies Press, Washington, D.C. https://doi.org/10.17226/9791

NRC - National Research Council. Nutrient requirements of dairy cattle. 2001. National Academies Press, Washington, D.C. https://doi.org/10.17226/9825

Pontes, L. S.; Tullio, G. F.; Martins, A. S.; Moletta, J. L. and Porfírio-da-Silva, V. 2018. Corn yield for silage and grains in different integrated crop-livestock systems. Revista Ciência Agronômica 49:315-323.

Rayan, A. M. and Abbott, L. C. 2015. Compositional analysis of genetically modified corn events (NK603, MON88017 × MON810 and MON89034 × MON88017) compared to conventional corn. Food Chemistry 176:99-105. https://doi.org/10.1016/j.foodchem.2014.12.044

Ridley, W. P.; Sidhu, R. S.; Pyla, P. D.; Nemeth, M. A; Breeze, M. L. and Astwood, J. D. 2002. Comparison of the nutritional profile of glyphosate-tolerant corn event NK603 with that of conventional corn (*Zea Mays* L.). Journal of Agricultural and Food Chemistry 50:7235-7243. https://doi.org/10.1021/jf0205662

Schmidt, C. A. P.; Miglioranza, É.; Nagashima, G. and Grecco, F. 2009. Concentrações de metais pesados em grãos de café produzidos em lavouras sobre solos originados do basalto e do arenito Caiuá. Ciência Rural 39:1590-1593. https://doi.org/10.1590/s0103-84782009005000100

Schmidt, P.; Novinski, C. O.; Junges, D.; Almeida, R. and Souza, C. M. 2015. Concentration of mycotoxins and chemical composition of corn silage: A farm survey using infrared thermography. Journal of Dairy Science 98:6609-6619. https://doi.org/10.3168/jds.2014-8617

Silva, D. C. and Vaine, M. E. E. 2001. Atlas geológico do estado do Paraná. Mineropar, Curitiba.

Steffil, M.; Leberl, P.; Schenkel, H. and Amselgruber, W. M. 2009. Iron-induced copper deficiency in dairy cows. Tierärztliche Umschau 64:432-437.

Vieira, V. C.; Moro, V.; Farinacio, D.; Martin, T. N.; Menezes, L. F. G. 2011. Caracterização da silagem de milho, produzida em propriedades rurais do sudoeste do Paraná. Revista Ceres 58:462-469. https://doi.org/10.1590/S0034-737X2011000400009

Weiss, W. P. 2017. A 100-Year Review: From ascorbic acid to zinc—Mineral and vitamin nutrition of dairy cows. Journal of Dairy Science 100:10045-10060. https://doi.org/10.3168/jds.2017-12935

White, R. R. and Capper, J. L. 2014. Precision diet formulation to improve performance and profitability across various climates: Modeling the implications of increasing the formulation frequency of dairy cattle diets. Journal of Dairy Science 97:1563-1577. https://doi.org/10.3168/jds.2013-6859

Woli, K. P.; Sawyer, J. E.; Boyer, M. J.; Abendroth, L. J. and Elmore, R. W. 2019. Corn era hybrid nutrient concentration and accumulation of secondary and micronutrients. Agronomic Journal 111:1604-1619. https://doi.org/10.2134/agronj2018.09.0621