

## Article

# Compositional Nutrient Diagnosis Methodology and Its Effectiveness to Identify Nutrient Levels in Yerba Mate (*Ilex paraguariensis*)

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**Abstract:** Yerba mate is a forest species of both cultural and economic importance growing in the subtropical regions of South America, especially in the south of Brazil. Despite its importance, yerba mate has never received enough attention from researchers, so the nutritional sufficiency ranges and critical levels have not yet been determined. This research aimed to establish these parameters for yerba mate to enable its foliar diagnosis. A total of 167 leaf samples were collected from production fields located in the five yerba mate-growing regions in Rio Grande do Sul, and the leaf nutrients were determined by standard chemical methods. The yield of each production field was accessed, and the cutoff value separating low- and high-yield groups was calculated in 16.75 Mg ha<sup>-1</sup>. The multivariate compositional nutrient diagnosis (CND) standards were determined, and nutrient interactions were estimated by correlation and principal component analyses. There was no positive correlation between any single nutrient and yield, even in the high-yield population, evidencing that a higher yield is the outcome of the balance among all nutrients. Excess of B occurred in one-third of the low-yield samples, while deficiency of Cu and K occurred in one-fourth of these samples. Finally, we established the adequate leaf nutrient levels for yerba mate.

**Keywords:** yerba mate; mineral nutrition; sufficiency ranges; foliar analysis; yield; fertilization



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## 1. Introduction

Yerba mate (*Ilex paraguariensis* St. Hil.) is an endemic tree species of subtropical and temperate forest regions of South America, with wild occurrence restricted to northeastern Paraguay, the southern states of Brazil, the northeastern region of Argentina, and Uruguay [1]. Its dried leaves are traditionally consumed in the form of an infusion, a tea-like drink that has been part of the local tradition since the pre-Columbian era [2]. Later on, in the seventeenth century, yerba mate was already one of the most important items of trade in South America [3]. Nowadays, in addition to the usual consumption, there is a growing demand for products derived from yerba mate. Mainly due to its various pharmacological properties, industrialized beverages, cosmetics, and medicines are increasingly being produced, both nationally and internationally [4].

In Rio Grande do Sul, the southernmost state of Brazil, yerba mate is one of the most important agricultural products, resulting in an average monthly revenue of more than USD 5 million [5]. It is estimated that around 35,000 hectares are cultivated with yerba mate in Rio Grande do Sul, a large part of which is destined for export to countries such as Germany, Argentina, Uruguay, and the USA. Indeed, Rio Grande do Sul accounts for about 80% of the Brazilian yerba mate exports to the international market [6].

Despite the socioeconomic and cultural relevance of yerba mate in Rio Grande do Sul, there is a lack of technical information for the plant nutrient management. Unlike other important crops, the sufficiency ranges (SRs) and critical levels (CLs) for the interpretation of foliar analysis results for yerba mate have not yet been determined [7]. It is important to notice that yerba mate is a perennial crop from which large amounts of plant biomass are removed during the harvesting process, making it necessary to quickly replace the nutrients in a balanced way [8,9].

In this context, the nutritional imbalance of plants and the lack of parameters to measure this imbalance are factors that can be contributing to the low productivity of yerba mate in Rio Grande do Sul. Among the different approaches to evaluating the nutritional balance of plants and defining CLs and SRs, compositional nutrient diagnosis (CND) stands out [8,10]. The method is considered one of the best ways to express the balance, deficiency, or excess of nutrients in plant tissue, with advantages over the univariate critical value (CV) or the bivariate diagnosis and recommendation integrated system (DRIS) approaches [11].

Adopting CLs or SRs will contribute to defining when fertilizers must be applied to yerba mate. This approach helps minimize excess nutrient buildup in the soil, which in turn reduces the risk of contaminating the nearby surface and subsurface waters [12]. Additionally, it can help prevent nutrient deficiencies in yerba mate plants, caused by the interaction of nutrients in the soil or solution, which can occur with greater intensity in soils with excess nutrients.

Thus, the cultivation of yerba mate requires parameters that help define the amount and form of replacement fertilization to ensure sustainable productivity in the long term. This research aimed to establish the nutritional sufficiency ranges for yerba mate to enable its foliar diagnosis.

## 2. Materials and Methods

Rio Grande do Sul state has five yerba mate-growing regions, known as *Polos Ervateiros* (Figure 1). The climate of these regions is humid subtropical, predominantly classified as Cfa and as Cfb in the higher altitudes of Alto Taquari, Nordeste Gaúcho, and Alto Uruguai, according to Köppen's classification [13]. Although occupying a smaller territorial area, Cfb is the preferable climate for yerba mate [14]. The altitude is between 400 and 1000 m [14,15]. Soils are preponderantly Leptosols, Regosols, Cambisols, Chernosols, Alisols, and Ferralsols, being derived from basalts, in the lower altitudes, and dacites, in altitudes above 600 m [16].

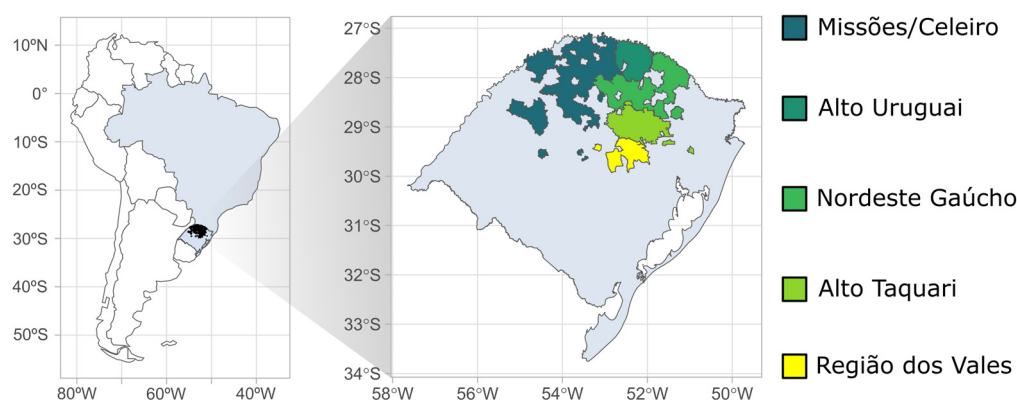


**Figure 1.** *Polos Ervateiros*, the yerba mate-growing regions in the state of Rio Grande do Sul, Brazil.

A total of 167 leaf samples were collected from different production fields, located in the five *Polos Ervateiros*, from 2019 to 2022. On average, the soils where yerba mate was collected had a medium organic matter content, low pH, and high Mn and Al contents (Table 1). Leaf samples were dried in an air-forced oven at 60 °C until constant weight. Then samples were ground and sieved through a 2 mm mesh. Plant tissue chemical analyses were performed by standard methods [17]. Acid digestion was performed with H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub>

for the analysis of N, P, K, Ca, and Mg; and with  $\text{HNO}_3/\text{HClO}_4$  for the analysis of Zn, Cu, Mn, Fe, and S, in addition to burning in a muffle furnace for determination of B. The concentrations of Ca, Mg, Cu, Fe, Zn, and Mn were determined by atomic absorption spectrometry; P, B, and S were determined by visible-light spectrometry; N via  $\text{NH}_3$  distillation; and K by flame spectrometry. Yerba mate yield, in  $\text{Mg ha}^{-1}$ , was informed by farmers, based on the previous harvest.

**Table 1.** Average physicochemical parameters of the sampled soils.

| Parameter | Mean  | Range        |
|-----------|-------|--------------|
| <hr/>     |       |              |
| Clay      | 373   | 27 to 77     |
| OM *      | 33    | 1.4 to 6.9   |
| <hr/>     |       |              |
| P         | 16.4  | 3.7 to 127.6 |
| K         | 152.2 | 23 to 524    |
| Zn        | 4.4   | 0.7 to 32.8  |
| Cu        | 2.6   | 0.2 to 16.1  |
| B         | 0.2   | 0.01 to 0.9  |
| Mn        | 60.6  | 0.2 to 634.8 |
| Fe        | 2.6   | 0.8 to 5.5   |
| pH        | 4.9   | 3.7 to 6.4   |
| <hr/>     |       |              |
| Al        | 1.9   | 0.0 to 9.0   |
| Ca        | 5.8   | 0.4 to 28.6  |
| Mg        | 2.2   | 0.3 to 9.2   |
| CEC **    | 18.6  | 7.0 to 41.9  |

\* OM = organic matter. \*\* CEC = cation exchange capacity.

The step-by-step calculation and rationale of CND are fully detailed in Parent and Dafir [10], Traspadini et al. [18], Rozane et al. [19], Rodrigues et al. [20], Tadayon et al. [11], and González-Vences et al. [21]. In short, the leaf tissue was considered a closed system formed by the sum of the 11 analyzed nutrients (N, P, K, ...), in the same unit of measurement, and non-analyzed plant components (other undetermined elements, carbohydrates, ...), gathered in a term called R. This forms a d-dimensional nutrient arrangement; that is, a simplex ( $S^d$ ) (Equation (1)) arising from the proportions of  $d + 1$  nutrients that include the d elements and a residual value ( $R_d$ ) (Equation (2)):

$$S^d = [(N, P, K \dots R_d): N > 0, P > 0, K > 0 \dots R_d > 0, N + P + K + \dots + R_d = 100], \quad (1)$$

where N, P, K ... are the proportions of nutrients determined in the dry matter, and  $R_d$  is calculated by difference, as follows:

$$R_d = 100 - (N + P + K + \dots), \quad (2)$$

In our case, the nutrients were expressed in  $\text{mg kg}^{-1}$ , and the sum of all plant components totalled 1,000,000. The geometric mean was obtained by calculating the 12th root of the product of the 12 components of the leaf sample (11 analyzed nutrients + R). The multivariate relationship between plant components was obtained by the natural logarithm of the ratio of each component to the geometric mean of the sample. Nutrient proportions become scale invariant after they are divided by the geometric mean (G) (Equation (3)) of  $d + 1$  components, including  $R_d$  [22]:

$$G = [N \times P \times K \dots \times R_d]^{1/(d+1)}, \quad (3)$$

To express each component of the simplex in relation to all the others (interaction study), it is sufficient to define new variables (V) (Equation (4)), which undergo centered

logarithmic transformation (natural or Neperian logarithm); that is, in relation to the geometric mean of the observed values, and are expressed as follows:

$$V_N = \ln(N/G), V_P = \ln(P/G), V_K = \ln(K/G) \dots V_{Rd} = \ln(R_d/G), \quad (4)$$

and, by definition,  $V_N + V_P + V_K + \dots + V_{Rd} = 0$

Next, the database was divided into low- and high-yield groups, using the procedure described by Khiari et al. [23]. CND norms consisted of the mean and standard deviation of the multivariate ratios of the nutrients in the high-yield group, which correspond to the relations of the centered logarithmic transformation of VX of d nutrients for high-yielding plants, i.e.,  $V_N^*, V_P^*, V_K^* \dots V_R^* \dots$  and  $SD_N^*, SD_P^*, SD_K^*, \dots SD_R^*$ , respectively.

CND indices were calculated by subtracting the row-centered log of each plant component from the respective norm mean and then dividing the result by the norm standard deviation (Equation (5)).

$$I_N = (V_N - V_N^*)/SD_N; I_P = (V_P - V_P^*)/SD_P; I_K = (V_K - V_K^*)/SD_K; \dots; I_R = (V_R - V_R^*)/SD_R, \quad (5)$$

where  $V_X^*$  and  $SD_X^*$  are, respectively, the mean and standard deviation of element X in the high-yield subpopulation, and  $I_X$  is the CND index of element X.

Independence among the data is ensured by the centered logarithmic transformation [22]. The CND indices are normed, and the variables made linear as dimensions of a circle ( $d + 1 = 2$ ), a sphere ( $d + 1 = 3$ ), or a large sphere ( $d + 1 > 3$ ), in a dimensional space of  $d + 1$ . The nutritional imbalance index  $r^2$  is distributed as a variable  $x_d^2$  if the CND indices are independent reduced variables [24], and it is calculated by the equation (Equation (6)):

$$r^2 = I_N^2 + I_P^2 + I_K^2 + \dots + I_R^2, \quad (6)$$

At last, the sufficiency range of each nutrient was determined by linear regression analysis between the nutrient content and the respective CND index [11,19]. The critical level was obtained by equating the CND index to zero in the equation, and the sufficiency range was delimited by a 2/3 standard deviation around this value.

Nutrient interactions were estimated by correlation [19] and principal component analyses (PCAs) [11]. Before performing the PCAs, our dataset underwent evaluation through the Kaiser–Meyer–Olkin (KMO) method and Bartlett’s sphericity test utilizing the EFAtools package within R software (version 4.3.1). The KMO value was 0.519, and Bartlett’s sphericity test was significant ( $p < 0.001$ ;  $\chi^2 = 349.31$ ), indicating that the data were suitable for factor analysis. All CND calculations were made using Microsoft Excel software (version Office 365). The correlation and *t*-test analyses were performed using SigmaPlot software (version 11). For the PCA analysis, we used PAST software (version 4.05), adopting the selection criterion (SC) proposed by Collins and Ovalles [25], by which eigenvectors for each PC were considered significant when having a value larger than that calculated using the formula  $SC = 0.5/(\text{PC eigenvalue})^{0.5}$ .

### 3. Results

The yield of the 167 yerba mate production fields from where the leaf samples were collected varied from 3 to 30, with an average of 13.07 Mg ha<sup>−1</sup>. The means and ranges of the plant nutrient contents are shown in Table 2. The correlation analyses between the isolated nutrient content and the plant yield resulted in only one significant result: B was negatively correlated with it (Table 3). It was also possible to verify the significant influence of some single-nutrient leaf concentration on the concentration of other nutrients.

**Table 2.** Leaf nutrient content of yerba mate database.

| Nutrient                  | Mean | Range       |
|---------------------------|------|-------------|
| N (g kg <sup>−1</sup> )   | 21.5 | 7 to 36.3   |
| P (g kg <sup>−1</sup> )   | 1.5  | 0.7 to 4.7  |
| K (g kg <sup>−1</sup> )   | 13.9 | 4.9 to 26   |
| Ca (g kg <sup>−1</sup> )  | 8.2  | 3.0 to 13.5 |
| Mg (g kg <sup>−1</sup> )  | 7.2  | 3.6 to 16.9 |
| S (g kg <sup>−1</sup> )   | 1.9  | 0.4 to 4.4  |
| B (mg kg <sup>−1</sup> )  | 62   | 29 to 141   |
| Cu (mg kg <sup>−1</sup> ) | 14   | 7 to 27     |
| Fe (mg kg <sup>−1</sup> ) | 158  | 63 to 1225  |
| Mn (mg kg <sup>−1</sup> ) | 1836 | 18 to 5034  |
| Zn (mg kg <sup>−1</sup> ) | 96   | 16 to 438   |

**Table 3.** Correlation between leaf nutrient content and yerba mate yield (n = 167).

|       | N     | P      | K        | Ca     | Mg       | S         | B         | Cu        | Fe      | Mn        | Zn       |
|-------|-------|--------|----------|--------|----------|-----------|-----------|-----------|---------|-----------|----------|
| Yield | 0.026 | −0.017 | −0.009   | 0.092  | 0.035    | −0.103    | −0.28 **  | 0.122     | −0.115  | −0.081    | −0.081   |
| N     |       | −0.07  | −0.009   | −0.115 | −0.011   | −0.025    | −0.237 ** | 0.213 **  | 0.153 * | 0.097     | −0.023   |
| P     |       |        | 0.236 ** | 0.017  | −0.067   | 0.023     | −0.167    | 0.218 **  | −0.131  | −0.297 ** | 0.148    |
| K     |       |        |          | −0.117 | −0.596   | 0.064     | −0.209 ** | 0.312 **  | −0.098  | −0.27 **  | 0.154 *  |
| Ca    |       |        |          |        | 0.471 ** | −0.272 ** | 0.007     | −0.107    | −0.02   | 0.149     | 0.246 ** |
| Mg    |       |        |          |        |          | −0.103    | 0.306 **  | −0.241 ** | 0.048   | 0.184 *   | −0.022   |
| S     |       |        |          |        |          |           | −0.095    | 0.117     | −0.02   | −0.029    | 0.069    |
| B     |       |        |          |        |          |           |           | −0.283 ** | −0.006  | 0.326 **  | 0.078    |
| Cu    |       |        |          |        |          |           |           |           | 0.026   | −0.194 *  | 0.093    |
| Fe    |       |        |          |        |          |           |           |           |         | 0.136     | 0.130    |
| Mn    |       |        |          |        |          |           |           |           |         |           | 0.197 *  |

\* Pearson correlation coefficient is significant at  $p < 0.05$ . \*\* Pearson correlation coefficient is significant at  $p < 0.01$ .

The cutoff between the low- and high-yield groups was determined by establishing cubic functions between yerba mate yield and the 12 cumulative variance ratios and equating the second derivative of each equation to zero to find its inflection point, as described by Khiari et al. [23] (Table 4). The cutoff was established at 16.75 Mg ha<sup>−1</sup>, the highest value within the database yield range.

Once the low- and high-yield groups were delimited, correlation analyses between isolated nutrients were performed again, now within each yield group. In the low-yield group, the yerba mate yield was negatively correlated with B, as verified for the whole population (Table 5). In addition, Fe and Mn were also negatively correlated with yield. In turn, in the high-yield group, the yield was negatively correlated with K and S (Table 6). Comparing the average leaf nutrient content between both groups, the only statistically significant difference was the higher level of B in the low-yield group (Table 7). This result reinforces the negative influence of B on the yerba mate yield.

**Table 4.** Estimation of the yield inflection points of cumulative variance functions for row-centered log-ratios in the yerba mate database population.

| Simplex | $F_i^C(V_X) = aY^3 + bY^2 + cY + d$             | R <sup>2</sup>          | Inflection Point (−b/3a)   |
|---------|-------------------------------------------------|-------------------------|----------------------------|
| N       | $y = 0.0011x^3 + 0.1129x^2 - 8.7761x + 143.91$  | R <sup>2</sup> = 0.9791 | −34.21 Mg ha <sup>−1</sup> |
| P       | $y = -0.0015x^3 + 0.3251x^2 - 13.52x + 160.68$  | R <sup>2</sup> = 0.9854 | 7.22 Mg ha <sup>−1</sup>   |
| K       | $y = 0.0119x^3 - 0.4324x^2 - 1.5705x + 120.59$  | R <sup>2</sup> = 0.9794 | 12.11 Mg ha <sup>−1</sup>  |
| Ca      | $y = -0.0051x^3 + 0.4722x^2 - 14.312x + 160.87$ | R <sup>2</sup> = 0.9872 | 30.86 Mg ha <sup>−1</sup>  |
| Mg      | $y = 0.0035x^3 + 0.0609x^2 - 9.8631x + 152.38$  | R <sup>2</sup> = 0.9800 | −5.8 Mg ha <sup>−1</sup>   |
| S       | $y = 0.0005x^3 + 0.0495x^2 - 4.2167x + 119.74$  | R <sup>2</sup> = 0.9846 | −33 Mg ha <sup>−1</sup>    |

Table 4. Cont.

| Simplex | $F_i^C(V_X)=aY^3+bY^2+cY+d$                     | $R^2$          | Inflection Point ( $-b/3a$ ) |
|---------|-------------------------------------------------|----------------|------------------------------|
| B       | $y = 0.0007x^3 - 0.0091x^2 - 0.9839x + 105.31$  | $R^2 = 0.9855$ | $4.33 \text{ Mg ha}^{-1}$    |
| Cu      | $y = 0.0056x^3 - 0.0347x^2 - 8.7314x + 149.28$  | $R^2 = 0.9752$ | $2.06 \text{ Mg ha}^{-1}$    |
| Fe      | $y = -0.0017x^3 + 0.1981x^2 - 8.0993x + 134.99$ | $R^2 = 0.9896$ | $38.84 \text{ Mg ha}^{-1}$   |
| Mn      | $y = -0.0045x^3 + 0.2261x^2 - 4.1263x + 116.62$ | $R^2 = 0.7556$ | $16.75 \text{ Mg ha}^{-1}$   |
| Zn      | $y = 0.0024x^3 + 0.1299x^2 - 11.139x + 158.54$  | $R^2 = 0.9782$ | $-18.04 \text{ Mg ha}^{-1}$  |
| R       | $y = 0.0019x^3 + 0.1448x^2 - 11.001x + 155.51$  | $R^2 = 0.9782$ | $-25.4 \text{ Mg ha}^{-1}$   |

Table 5. Correlation between leaf nutrient content and yerba mate low-yield population (n = 133).

|       | N     | P      | K      | Ca     | Mg        | S         | B         | Cu        | Fe        | Mn        | Zn       |
|-------|-------|--------|--------|--------|-----------|-----------|-----------|-----------|-----------|-----------|----------|
| Yield | 0.013 | 0.056  | 0.044  | 0.045  | −0.078    | 0.020     | −0.289 ** | −0.035    | −0.283 ** | −0.172 *  | −0.085   |
| N     |       | −0.121 | −0.127 | −0.061 | 0.067     | −0.071    | −0.205 *  | 0.178 *   | 0.081     | 0.093     | −0.085   |
| P     |       |        | 0.223  | 0.035  | −0.085    | 0.030     | −0.184    | 0.154     | −0.236    | −0.291    | 0.171    |
| K     |       |        |        | −0.076 | −0.588 ** | 0.007     | −0.200 *  | 0.286 **  | −0.273 ** | −0.313 ** | 0.097    |
| Ca    |       |        |        |        | 0.484 **  | −0.249 ** | −0.010    | −0.111    | 0.110     | 0.105     | 0.245 ** |
| Mg    |       |        |        |        |           | −0.084    | 0.320 **  | −0.232 ** | 0.201 *   | 0.245 **  | 0.021    |
| S     |       |        |        |        |           |           | −0.130    | 0.226 **  | −0.011    | −0.050    | 0.043    |
| B     |       |        |        |        |           |           |           | −0.255 ** | 0.106     | 0.366 *   | 0.075    |
| Cu    |       |        |        |        |           |           |           |           | −0.069    | −0.164    | 0.070    |
| Fe    |       |        |        |        |           |           |           |           |           | 0.239 **  | 0.132    |
| Mn    |       |        |        |        |           |           |           |           |           |           | 0.182 *  |

\* Pearson correlation coefficient is significant at  $p < 0.05$ . \*\* Pearson correlation coefficient is significant at  $p < 0.01$ .

Table 6. Correlation between leaf nutrient content and yerba mate high-yield population (n = 34).

|       | N     | P      | K        | Ca     | Mg        | S        | B         | Cu      | Fe     | Mn      | Zn      |
|-------|-------|--------|----------|--------|-----------|----------|-----------|---------|--------|---------|---------|
| Yield | 0.097 | −0.108 | −0.402 * | 0.211  | 0.274     | −0.373 * | −0.042    | −0.010  | −0.104 | 0.018   | −0.127  |
| N     |       | 0.127  | 0.398 *  | −0.307 | −0.260    | 0.125    | −0.495 ** | 0.337   | 0.264  | 0.114   | 0.163   |
| P     |       |        | 0.325    | −0.074 | 0.027     | −0.021   | −0.111    | 0.574   | 0.011  | −0.336  | 0.044   |
| K     |       |        |          | −0.332 | −0.641 ** | 0.332    | −0.203    | 0.381 * | 0.162  | −0.068  | 0.398 * |
| Ca    |       |        |          |        | 0.416 *   | −0.368 * | 0.202     | −0.135  | −0.246 | 0.358 * | 0.258   |
| Mg    |       |        |          |        |           | −0.181   | 0.311     | −0.301  | −0.175 | −0.076  | −0.181  |
| S     |       |        |          |        |           |          | 0.046     | −0.250  | −0.048 | 0.056   | 0.166   |
| B     |       |        |          |        |           |          |           | −0.290  | −0.296 | 0.092   | 0.079   |
| Cu    |       |        |          |        |           |          |           |         | 0.169  | −0.307  | 0.199   |
| Fe    |       |        |          |        |           |          |           |         |        | 0.011   | 0.157   |
| Mn    |       |        |          |        |           |          |           |         |        |         | 0.255   |

\* Pearson correlation coefficient is significant at  $p < 0.05$ . \*\* Pearson correlation coefficient is significant at  $p < 0.01$ .

Nutrient interactions were also accessed via PCA. In the low-yield group, the first four PCs explained 68.65% of the total variation (Table 8). The A group, formed by K, P, and Cu, was positively loaded on PC1, while PC2 separated Mg from Zn and S. The third PC correlated negatively with P and Zn. Finally, the fourth PC showed a positive correlation with N. The first four PCs explained 74.1% of the total variance in the high-yield group (Table 9). The first PC clustered P, Ca, Mg, and B in the positive quadrant, while locating Zn in the negative quadrant. P, K, and Cu formed a significant cluster located in the positive quadrant of PC2, and located Mn in the negative quadrant. The third PC was positively correlated with S and B, and negatively with N, while the fourth PC was positively correlated with Fe and negatively with Zn.

**Table 7.** Average leaf nutrient content in high and low-yield populations of yerba mate.

| Nutrient                  | High Yield |      | Low Yield |      | T-Test    |
|---------------------------|------------|------|-----------|------|-----------|
|                           | Mean       | SD   | Mean      | SD   |           |
| N (g kg <sup>-1</sup> )   | 21.46      | 5.6  | 21.51     | 4.48 | 0.957     |
| P (g kg <sup>-1</sup> )   | 1.49       | 0.51 | 1.53      | 0.64 | 0.707     |
| K (g kg <sup>-1</sup> )   | 14.34      | 3.61 | 13.64     | 3.89 | 0.327     |
| Ca (g kg <sup>-1</sup> )  | 8.29       | 1.72 | 8.10      | 1.87 | 0.579     |
| Mg (g kg <sup>-1</sup> )  | 7.21       | 2.02 | 7.18      | 2.01 | 0.936     |
| S (g kg <sup>-1</sup> )   | 1.86       | 0.85 | 1.94      | 0.86 | 0.599     |
| B (mg kg <sup>-1</sup> )  | 57         | 14   | 68 **     | 23   | 0.0005 ** |
| Cu (mg kg <sup>-1</sup> ) | 15         | 3    | 14        | 3    | 0.051     |
| Fe (mg kg <sup>-1</sup> ) | 158        | 200  | 159       | 77   | 0.987     |
| Mn (mg kg <sup>-1</sup> ) | 1803       | 1009 | 1868      | 1072 | 0.745     |
| Zn (mg kg <sup>-1</sup> ) | 94         | 77   | 99        | 71   | 0.746     |

\*\* Significantly different by the Student's *t*-test; *p* < 0.01.

**Table 8.** Principal component analysis (PCA) loadings performed on log-transformed data from low-yield group (n = 133).

| Row-Centered Log-Ratio   | PC1      | PC2       | PC3        | PC4       |
|--------------------------|----------|-----------|------------|-----------|
| IN                       | 0.16494  | 0.32548   | 0.38645    | 0.45673   |
| IP                       | 0.45231  | 0.23568   | −0.58274   | 0.16791   |
| IK                       | 0.63399  | −0.021895 | 0.12638    | −0.53837  |
| ICa                      | 0.00328  | 0.34472   | −0.19939   | 0.072897  |
| IMg                      | −0.18117 | 0.41246   | −0.0028109 | 0.18618   |
| IS                       | 0.138    | −0.48307  | 0.38725    | 0.21185   |
| IB                       | −0.24184 | 0.3674    | 0.20799    | −0.60738  |
| ICu                      | 0.37751  | 0.044659  | 0.22622    | 0.10584   |
| IFe                      | −0.17147 | −0.030374 | 0.092964   | 0.063081  |
| IMn                      | −0.26975 | −0.060861 | 0.0014853  | −0.051156 |
| IZn                      | −0.10595 | −0.41729  | −0.44977   | −0.042242 |
| Eigenvalue               | 2.99759  | 1.7473    | 1.40598    | 1.35124   |
| Explained variance (%)   | 27.43    | 15.989    | 12.866     | 12.365    |
| Accumulated variance (%) | 27.43    | 43.419    | 56.285     | 68.65     |
| Selection criterion (SC) | 0.28879  | 0.37826   | 0.42168    | 0.43013   |

**Table 9.** Principal component analysis (PCA) loadings performed on log-transformed data from high-yield group (n = 34).

| Row-Centered Log-Ratio   | PC1      | PC2       | PC3        | PC4        |
|--------------------------|----------|-----------|------------|------------|
| IN                       | 0.00007  | 0.26295   | −0.50489   | 0.30098    |
| IP                       | 0.34684  | 0.35647   | −0.099273  | 0.00081351 |
| IK                       | 0.029684 | 0.5256    | 0.1292     | −0.15567   |
| ICa                      | 0.40363  | −0.30443  | −0.047691  | −0.20405   |
| IMg                      | 0.45897  | −0.30325  | −0.0044752 | 0.18873    |
| IS                       | −0.14951 | 0.10525   | 0.57056    | 0.33524    |
| IB                       | 0.39118  | −0.13429  | 0.40079    | −0.049772  |
| ICu                      | 0.29553  | 0.42536   | −0.18672   | −0.087084  |
| IFe                      | −0.22416 | −0.055658 | −0.022177  | 0.62185    |
| IMn                      | −0.27765 | −0.33909  | −0.38152   | −0.25375   |
| IZn                      | −0.33941 | 0.12157   | 0.22172    | −0.48414   |
| Eigenvalue               | 2.85895  | 2.46246   | 1.57064    | 1.25865    |
| Explained variance (%)   | 25.99    | 22.386    | 14.279     | 11.442     |
| Accumulated variance (%) | 25.99    | 48.37     | 62.65      | 74.10      |
| Selection criterion (SC) | 0.29571  | 0.31863   | 0.39896    | 0.44567    |

The CND norms as means and standard deviations of  $V_N$ ,  $V_P$ ,  $V_K$ ,  $V_{Ca}$ ,  $V_{Mg}$ ,  $V_S$ ,  $V_B$ ,  $V_{Cu}$ ,  $V_{Fe}$ ,  $V_{Mn}$ ,  $V_{Zn}$ , and  $V_R$  for the high-yield group, as well as the critical levels and

sufficiency ranges for each nutrient are presented in Tables 10 and 11. On average, the frequencies of nutritional deficiency, balance, and excess were practically the same between low- (14.5, 67.5, and 15.0%, respectively) and high-yield (16.3, 67.9, and 15.8%, respectively) groups (Figure 2). However, it is interesting to notice that the excess of B occurred in 32.3% of the low-yield samples. The deficiency of K and Cu was observed in 27.1 and 31.6% of the low-yield samples, respectively. Furthermore, when we consider the average of the CND indices, we can see that B, K, and Cu were the nutrients with the highest imbalance, with indices above 0.25 in modulus (Figure 3).

**Table 10.** Compositional nutrient norms based on the high-yield group of yerba mate.

| CND Variable | CND Norm | CND SD |
|--------------|----------|--------|
| $V_N$        | 2.543    | 0.239  |
| $V_P$        | −0.134   | 0.292  |
| $V_K$        | 2.140    | 0.254  |
| $V_{Ca}$     | 1.598    | 0.277  |
| $V_{Mg}$     | 1.448    | 0.323  |
| $V_S$        | 0.022    | 0.444  |
| $V_B$        | −3.390   | 0.305  |
| $V_{Cu}$     | −4.707   | 0.253  |
| $V_{Fe}$     | −2.598   | 0.540  |
| $V_{Mn}$     | −0.156   | 0.866  |
| $V_{Zn}$     | −3.123   | 0.622  |
| $V_R$        | 6.358    | 0.164  |
| $\Sigma V_X$ | 0.000    |        |

**Table 11.** Linear regression between nutrient concentrations in yerba mate leaves from high-yield group and their respective CND indices, coefficient of determination, critical levels (CLs), and sufficiency ranges (SRs) for each nutrient.

| Nutrient | Model                  | R <sup>2</sup> | CL *                     | SR **                         |
|----------|------------------------|----------------|--------------------------|-------------------------------|
| N        | $y = 0.1424x - 3.0545$ | 0.6405         | 21.5 g kg <sup>−1</sup>  | 17.7–25.2 g kg <sup>−1</sup>  |
| P        | $y = 1.6478x - 2.4579$ | 0.711          | 1.5 g kg <sup>−1</sup>   | 1.2–1.8 g kg <sup>−1</sup>    |
| K        | $y = 0.219x - 3.1406$  | 0.6239         | 14.3 g kg <sup>−1</sup>  | 11.9–16.7 g kg <sup>−1</sup>  |
| Ca       | $y = 0.4443x - 3.6819$ | 0.5855         | 8.3 g kg <sup>−1</sup>   | 7.1–9.4 g kg <sup>−1</sup>    |
| Mg       | $y = 0.433x - 3.1241$  | 0.7725         | 7.2 g kg <sup>−1</sup>   | 5.9–8.6 g kg <sup>−1</sup>    |
| S        | $y = 1.0862x - 2.0151$ | 0.8458         | 1.9 g kg <sup>−1</sup>   | 1.3–2.4 g kg <sup>−1</sup>    |
| B        | $y = 0.0588x - 3.3391$ | 0.6907         | 57 mg kg <sup>−1</sup>   | 47–66 mg kg <sup>−1</sup>     |
| Cu       | $y = 0.2235x - 3.3782$ | 0.5701         | 15 mg kg <sup>−1</sup>   | 13–17 mg kg <sup>−1</sup>     |
| Fe       | $y = 0.0099x - 1.3621$ | 0.8429         | 138 mg kg <sup>−1</sup>  | 91–184 mg kg <sup>−1</sup>    |
| Mn       | $y = 0.0008x - 1.4043$ | 0.6177         | 1755 mg kg <sup>−1</sup> | 1082–2428 mg kg <sup>−1</sup> |
| Zn       | $y = 0.0118x - 1.1123$ | 0.8213         | 94 mg kg <sup>−1</sup>   | 43–145 mg kg <sup>−1</sup>    |

\* The critical level was obtained by equating the CND index to zero in the equation. \*\* The sufficiency range was delimited by a 2/3 standard deviation around the critical level.

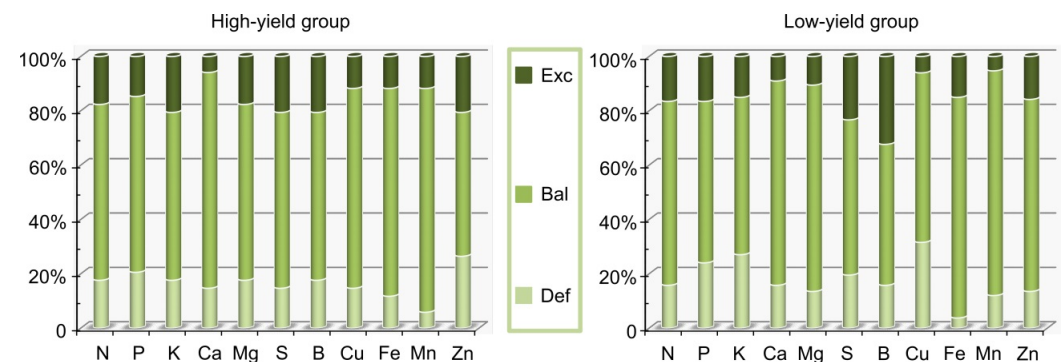


**Figure 2.** Percentage of nutritional deficiency, balance, and excess in high- and low-yield groups of yerba mate, estimated by CND.

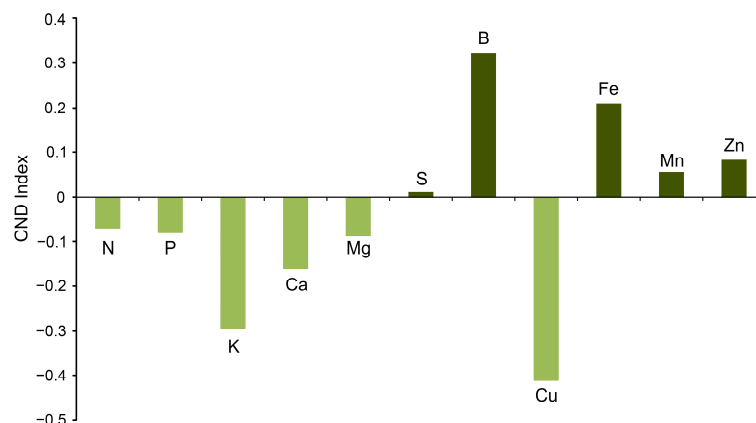


**Figure 3.** Mean values of nutrient indices in the studied yerba mate population (n = 167).

#### 4. Discussion

Establishing the sufficiency ranges and the optimal nutrient levels is crucial to evaluating the nutritional status of a crop. Among the different approaches, CND stands out [11]. Many authors compared CND with other methods, such as DRIS and Mathematical Chance (MCh), and verified its efficiency and precision. Caires et al. [26] assessed the nutritional diagnosis of soybean leaves and seeds using DRIS, MCh, and CND. The authors observed that the optimal nutrient levels estimated by DRIS and CND closely matched the average content in the reference population, whereas the MCh method yielded slightly different values. Santos et al. [27] confirmed the same trend across these three methods in their study on sugar cane. Similar results between CND and DRIS were also observed for corn [28]. CND and DRIS usually produce closely aligned results and are highly correlated [26]. However, CND can produce narrower SRs and establish multivariate relationships among nutrients [28], allowing an accurate association between plant nutrition and yield [19]. These results supported our decision to use the CND method for estimating the SRs and CLs of yerba mate.

As previously mentioned, the yield average of the 167 analyzed yerba mate production fields was  $13.07 \text{ Mg ha}^{-1}$ . This value is higher than the national and the Rio Grande do Sul state average yields in 2019, which were 7.7 and  $10.0 \text{ Mg ha}^{-1}$ , respectively [29]. Although orchard yields above  $12 \text{ Mg ha}^{-1}$  can be considered high [30], yields higher than  $20 \text{ Mg ha}^{-1}$  are not unusual in orchards with high technological levels [31]. Indeed, 68% of the evaluated yerba mate production fields were above the state average yield, while only 20% were considered in the high-yield group delimited by the cutoff established at  $16.75 \text{ Mg ha}^{-1}$ . These observations reinforce the idea that the Brazilian yield is much lower than the potential yield of yerba mate and has been decreasing in the last decades [29], showing the need for research and technological innovation for this productive chain.

Corroborating the findings of Rozane et al. [19] and Krug et al. [9], who applied CND to grapevines and citrus, respectively, there was no positive correlation between any single nutrient and yield, even in the high-yield population. This result evidences that a higher yield is the outcome of the appropriate balance among all nutrients. On the other hand, correlation analyses revealed a negative relationship between leaf B content and yerba mate yield. Moreover, in comparison to the high-yield group, the average B content was significantly higher in the low-yield group. Finally, when estimating the percentage of nutritional deficiency, balance, and excess by CND, it could be noticed that about one-third of the low-yield samples showed an excess of B, and it was the most imbalanced nutrient. It is known that B is a nutrient with a very narrow window between toxicity and deficiency [32]. Although B toxicity is usually associated with saline soils in regions of low precipitation, it can also occur in highly acidic soils, especially if there is an excess of K or a deficiency of Mg [33]. In general, adequate tissue B concentrations for the optimal growth of dicot plants range from 20 to  $70 \text{ mg kg}^{-1}$  [34]. We estimated the normal range

of B for yerba mate to be between 47 to 66 mg kg<sup>-1</sup>. Thus, although yerba mate is a plant well-adapted to soil acidity, capable of tolerating high levels of Al and Mn, and also capable of accumulating high levels of B without showing visual symptoms of toxicity [35], elevated levels of B can be one of the factors that reduces its productivity. Even without causing direct toxicity, the high levels of B may be interfering with the absorption of other nutrients. For instance, Pawlowski et al. [36] found that excess B decreased the levels of Mg and Ca in soybean leaves.

More than 25% of the low-yield samples were classified as deficient in Cu and K. PCA, a multivariate technique that reduces the data dimensionality while preserving the main contributors to variance [37,38], also revealed a similar trend in the levels of K and Cu in the yerba mate leaves. As in the case of B, the availability of Cu is linked to soil characteristics, which mainly depend on its parent material [39]. Soils originating from basic rocks are naturally richer in metals, including Cu. Thus, considering the yerba mate production areas in Rio Grande do Sul, we can state that soils originating from basalts are richer in Cu than soils originating from dacites, which predominate above 600 m in altitude [16,40]. Motta et al. [41], evaluating yerba mate under low input systems in the Brazilian southern states, observed Cu contents in the soil ranging from 0.6 to 10.7 mg dm<sup>-3</sup> and in the leaf from 7.3 to 14.0 mg kg<sup>-1</sup>. In our research, these ranges were even broader (Tables 1 and 2). Those authors emphasized the importance of the soil parent material in the chemical composition of yerba mate. Also, it is important to notice that soil may contain high levels of Cu, but part of the Cu can be retained in the root system of plants, reducing the amount transported to the aerial part [42].

Regarding K, the normal range was estimated by CND to be between 11.9 and 16.7 g kg<sup>-1</sup> (Table 11). As a result, 27% of the low-yield group samples had insufficient K levels. The first study aiming to define the sufficiency range for K in yerba mate was carried out by Reissmann et al. [43], who estimated that the adequate foliar K contents would be between 14 and 18 mg kg<sup>-1</sup>. In the same sense, in a study that evaluated the effect of potassium fertilization on yerba mate, Santin et al. [44] identified that the leaf content of 16 mg kg<sup>-1</sup> was sufficient to obtain high yields. These values are close to those estimated in the present study. The demand for K by yerba mate can be calculated based on the analysis of nutrient exports at harvest. Considering the K export potential in the yerba mate harvest as 15.05 g kg<sup>-1</sup>, determined by Souza et al. [45], and the average yerba mate yield of 13.07 Mg ha<sup>-1</sup> obtained in the present work, it is possible to estimate that about 197 kg K ha<sup>-1</sup>, equivalent to 237 kg K<sub>2</sub>O ha<sup>-1</sup>, are exported in a harvest. This value is proportionally higher as the yield increases, demonstrating that yerba mate is a K-demanding crop. Thus, monitoring K availability in the soil, as well as the nutritional condition of the plants, is fundamental for obtaining and maintaining high yield levels.

Significant correlations were found between the CND indices and the respective nutrient concentrations in plant tissue, but not between productivity and the CND<sup>r2</sup> index (CND- $r^2 = -0.1344 \text{ yield} + 13.856$ ;  $R^2 = 0.0154$ ;  $p = 0.111$ ). A similar result was obtained by Rozane et al. [19] and Krug et al. [9]. Those authors concluded that the nutritional balance would explain only part of the productivity of the vineyards and citrus orchards they evaluated, which were of different cultivars. In our case, in addition to the genetic variability of yerba mate, the evaluated production areas have diverse management systems, with distinct forms of fertilization, plant densities, and pruning frequency, directly interfering with the yield of the orchards. Regardless, this research brings the first definition of CND norms, critical levels, and sufficiency ranges for the leaf nutrient diagnosis of yerba mate. It will contribute to the better nutrition management of a crop with high cultural importance, in regional terms, and of growing economic importance worldwide.

## 5. Conclusions

The CND<sup>r2</sup> indices were effective in establishing the critical levels, sufficiency ranges, and the nutritional status of yerba mate concerning the leaf concentration of the nutrients at deficiency, balance, and excess concentrations.

The CND methodology identified adequate nutrient levels in the leaves, which contributes to establishing the actual need for fertilizer application in yerba mate production fields.

Multi-nutrient associations were found to be more effective than single-nutrient analysis in highlighting the impact of a certain nutrient limitation on the productivity of yerba mate production fields.

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