

Division - Soil Use and Management | Commission - Soil Fertility and Plant Nutrition

# Reference Values of Grain Nutrient Content and Removal for Corn

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**ABSTRACT:** Unchanged reference values of grain nutrient contents for corn have been used for over 20 years, despite yield increases, the development of new hybrids, and modifications to cropping systems, especially the establishment of in-season second crops and the wide adoption of no-tillage. This study measured macro- and micronutrient contents in corn grains from different regions, in the first (summer) and second (fall) crop, to update the reference values of estimated nutrient removal. A secondary objective was to determine whether there were correlations between grain nutrient contents and grain yields and densities. In this study, 175 corn grain samples of experiments on cultivar evaluation and 22 samples from soil management trials from five states (SP, PR, MG, MT, and MS) were used. Grain nutrient contents were ranked as follows: N > K > P > Mg > S (g kg<sup>-1</sup>) and Ca > Zn > Fe > Mn > B > Cu (mg kg<sup>-1</sup>). Content values for half of the nutrients analyzed were negatively correlated with yield and/or seed weight, whereas grain density was not correlated with nutrient contents. For the first crop of corn, the N, S, and Cu contents clearly decreased with increases in grain yield and seed weight, indicating a lower nutrient removal at higher yields. The great variability of results among environments makes it difficult to differentiate between the first and second crop of corn. The reference values currently in use overestimate the removal of N, P, K, Ca, Mg, S, and Zn grain contents, but underestimate Cu and B in corn. The results of this study can be used to update the reference values of nutrient contents of corn grains to better estimate nutrient removal from the soil.

**Keywords:** corn grains, mineral nutrient contents, grain yield, grain density.

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## INTRODUCTION

Corn production in Brazil has undergone major transformations, including tripling grain yields in the last three decades. The crop has been affected by spatial and temporal changes, with the development and consolidation of second season (off-season) corn as a main cultivation method in the country and, concomitantly, reducing the corn cultivation area in the first season (summer), currently concentrated in regions of high yield potential, especially at high altitudes. The technical changes and crop yield increases were results of the release of new hybrids adapted to different environments and production systems and of the great evolution in crop management. These changes in crop management mainly included the no-tillage system, higher plant density, reduction of row spacing, increase of N fertilization, and, since the end of the 2000's, the application of foliar fungicides and use of transgenic plants (Duarte and Kappes, 2015).

However, the nutrient contents in corn grains used as reference values in Brazil have been practically the same for over 20 years (Raij et al. 1996; Cantarella and Duarte, 2004), and are based on old studies, such as those of Andrade et al. (1975a,b), Hiroce et al. (1989), and Coelho and França (1995). The diversity of plant materials and heterogeneity of management types can influence grain nutrient contents (Carlone and Russel, 1987; Ciampitti and Vyn, 2013; Caires and Milla, 2016). Recent results of grain nutrient contents indicate a possible reduction in N and K (Resende et al., 2012), although the high variation among environments and/or cultivars hampers a joint interpretation that would enable conclusions about the new reference values.

Since the reference values of nutrient contents used in Brazil do not distinguish yield ranges and the mean quantities harvested on fields differ greatly, mainly due to the planting season (from 5 Mg ha<sup>-1</sup> in the second season to 14 Mg ha<sup>-1</sup> in the first season), there may be yield gains at the expense of nutritional quality, and lower nutrient removals. This has been confirmed under North American climate and cultivation conditions, where yields increased in response to a higher plant density (Carlone and Russell, 1987).

This study addressed the determination of macro- and micronutrient contents in corn grain in different corn-producing regions, in the first and second growing seasons, for the establishment of new reference values to support the estimations of nutrient removals. Another objective was to identify correlations between grain nutrient contents and grain yield and grain density.

## MATERIALS AND METHODS

Corn grain samples of experimental assays for cultivar evaluations were used (94 and 81 samples for the first and second growing seasons, respectively). In addition, 12 and 10 additional samples were obtained from soil management studies, resulting in 106 and 91 samples for the first and second growing seasons, respectively, i.e., 197 samples.

The tests were carried out in the 2013/2014 and 2014/2015 growing seasons, in the states of São Paulo, Minas Gerais, Paraná, Mato Grosso, and Mato Grosso do Sul (Table 1). Forty-one representative market cultivars were used, of which three were conventional, and 38 were transgenic hybrids.

Grain yield was corrected to a 13.5 % moisture content for the samples, which were taken from two central rows of an experimental plot consisting of four 5.0 m rows. For the trials installed in São Paulo, the sample was obtained of a mixture of grains from three or four replications, and the mean yields were calculated. The 100-grain weight was determined on a scale (precision accuracy 0.1 g), and grain density was determined by a float test in a sodium nitrate solution, which was measured as percentage of floating grains (Peplinski et al., 1989). Grain weight and density were not determined for the samples from Naviraí-MS, because in some cases the volume was insufficient for these measurements.

**Table 1.** Number and origin of corn grain samples per season, year, institution, and location

| Time                             | Year    | Institution  | State     | Locations | Cultivars <sup>(1)</sup> | Samples |
|----------------------------------|---------|--------------|-----------|-----------|--------------------------|---------|
|                                  |         |              |           | Number    |                          |         |
| Cultivar evaluation              |         |              |           |           |                          |         |
| 1 <sup>st</sup> season           | 2013/14 | IAC          | SP        | 4         | 13                       | 52      |
| 1 <sup>st</sup> season-irrigated | 2014    | IAC          | SP        | 2         | 7                        | 14      |
| 1 <sup>st</sup> season           | 2014/15 | Fundação ABC | PR and SP | 2         | 14                       | 28      |
| 2 <sup>nd</sup> season           | 2014    | IAC          | SP        | 3         | 9                        | 27      |
| 2 <sup>nd</sup> season           | 2014    | Fundação MS  | MS        | 3         | 10                       | 30      |
| 2 <sup>nd</sup> season           | 2015    | Fundação MT  | MT        | 4         | 6                        | 24      |
| Extra samples                    |         |              |           |           |                          |         |
| 2 <sup>nd</sup> season           | 2015    | IAC          | SP        | 2         | 2                        | 4       |
| 1 <sup>st</sup> season           | 2014/15 | Fundação ABC | PR        | 1         | 1                        | 4       |
| 1 <sup>st</sup> season-irrigated | 2014/15 | Embrapa      | MG        | 1         | 4                        | 8       |
| 2 <sup>nd</sup> season           | 2014    | Embrapa      | PR        | 1         | 1                        | 6       |
| Total                            |         |              |           | 23        | 41                       | 197     |

<sup>(1)</sup> Common cultivars evaluated at all locations, except for the extra samples, which were obtained in soil management tests; total number of cultivars is lower than the sum of the column because some cultivars are common to seasons and/or regions.

The grains were oven-dried at 60 °C for 24 h and stored under ambient conditions, without silica gel drying, until grinding for analyses.

Approximately 30 g of grain sample was ground in a smaller Wiley mill than the traditional, carefully sieving (1 mm) all grain fractions without discarding any residue. The coarsest parts of some samples had to be ground by hand in a mortar. The ground material was stored in acrylic bottles under ambient conditions and not subjected to additional drying before weighing for analyses.

The mineral nutrient contents of the samples were analyzed by the Laboratory of Soil Fertility and Plant Nutrition of the Instituto Agronômico in Campinas (IAC), São Paulo, according to the methodology described by Bataglia et al. (1978). The grain samples were digested in a nitric/perchloric acid mixture and the concentration of P, K, Ca, Mg, S, Cu, Fe, Mn, and Zn were determined by ICP-OES (inductively coupled argon plasma-optical emission spectrometry, Varian Model Vista MPX), and K was determined by flame atomic absorption spectrometry (Perkin Elmer 5100 PC). Boron was determined by ashing the sample, then dissolving the residue with chloride acid and analyzing by UV/Vis spectroscopy (Shimadzu UV-2600) using azomethine-H. Nitrogen was evaluated by the Kjeldahl method, using digestion by sulfuric acid as well as catalysts and titrimetry for determination. For N analysis, we used 0.10 g of the ground sample, for boron, we used 0.25 g, and for the other nutrients, we used 0.50 g.

All analyses, except for B, were performed in duplicate and at different post-extraction times. The results of the two analyses were averaged, and in case of discrepant results, a third analysis was performed, eliminating the erratic value.

Nutrient removal was calculated by multiplying nutrient grain contents (average of moisture after grind 11 %) by the grain yield of the experimental plot (moisture content 13.0 %), or in case of composite samples, by the mean yield of the cultivars in the experiment.

All results were used to determine Pearson's correlations between nutrient contents, grain yields, 100-grain weights, and the grain densities, at a significance level of 1 %, with SAS software. The 18 production locations were compared among the cultivar evaluations, and grouped by six environments, according to the growing season, year, and region.

To this end, an analysis of variance was performed, considering each location as a block, which corresponded to the environmental effect.

## RESULTS AND DISCUSSION

### Environmental effect and correlation among variables

All of the evaluated parameters showed great variation among environments, regardless of the sowing season (Table 2). The environmental effect among cultivars was frequent for N and Fe (in five of the six sets) and rare for Mg (only one set).

The grain nutrient contents were ranked as follows:  $N > K > P > Mg > S$ , in  $g\ kg^{-1}$ , and  $Ca > Zn > Fe > Mn > B > Cu$  (Table 2). At most locations, the value of Mg exceeded that of S, except in Mococa and Itararé, where this value was lower than or equal to the first season of 2013/14, respectively.

Half of the nutrients analyzed were correlated with yield (Table 3). The mean yield values were higher in the first season than in the second season (Table 2), which was expected due to the lower yield potential of corn grown in autumn-winter. However, the severe water stress after flowering affected the corn yield in the 2013/14 summer in Mococa, resulting in a mean yield of only  $3.4\ Mg\ ha^{-1}$ . The yields above  $9.0\ Mg\ ha^{-1}$  of the 2015 second-season corn at four locations of Mato Grosso were also noteworthy.

When the corn yield was higher, the content was lower: (1) of Cu, in any growing season; (2) of Fe, in the second season; (3) and of N, S, Mn, and Zn in the first season and across all data. However, the correlation index was relatively low for Mn ( $r \leq 0.25$ ). Since yield was strongly associated with the 100-grain weight ( $r \geq 0.58$ ), this parameter was negatively correlated with N, S, Cu, and B contents in the main season and across all data, especially for N, S, and Cu ( $r \geq 0.44$  in the second season). However, grain density evaluated by the floaters test proved inadequate for the prediction of nutrient contents.

For the first season, there were clear reductions for the N, S, and Cu contents due to the increases in grain yield and weight, and proportionally, in removal at high yields, which confirmed the findings of Carlone and Russell (1987) for corn in North America. Possible explanations for the absence of this outcome for second-season corn were the lower yields and higher heterogeneity of environments and production systems, compared to summer corn.

Moderate correlations ( $r \geq 0.40$ ) were observed between the nutrient contents of the grains: (1) N with S; (2) P with K, Mg, and S; and (3) Mn with Ca and Zn. The nutrients with weak  $r$ -values ( $0.29 \leq r < 0.40$ ) were: (1) P with Fe and Zn, (2) Mg with K and Mn, and (3) Fe with Zn. For some nutrients, the correlation indices were significant and higher for the first season (N with Cu and Zn as well as S with Cu) or for the second season (Mg with S, Fe, and Zn). Nitrogen is a component of the proteins that form the protein matrix surrounding the starch granules in grains and, together with sulfur form the corn-germ, requires Zn and Cu for synthesis. The simultaneous variation of P, K, Mg, S, Fe, and Zn could be related to the fact that the samples were taken from basalt-derived soils (São Paulo and Mato Grosso do Sul), which were clayey and relatively rich in organic matter and nutrients, as well as from less clayey soils with low natural fertility in the Cerrado of Central Brazil (Mato Grosso and Mato Grosso do Sul).

### Nutrient removal

The total nutrient removal increased linearly with grain yield, corresponding to  $23\ kg\ Mg^{-1}$  of grain plus a fixed value of  $6\ kg\ Mg^{-1}$  ( $y = 5.331 + 23.3x$ ) for the yield interval of  $3\text{--}15\ Mg\ ha^{-1}$  that was studied (Figure 1). The mean values of total nutrient removal and grain yield were, respectively,  $183$  and  $8.899\ kg\ ha^{-1}$ , i.e., 2.1 % of nutrients in grains (moisture content 13.0 %).

**Table 2.** Values of yield (Yld), 100-grain weight (GW), grain density by the floaters test (GD), and mineral nutrient contents in function of season and cultivation environment and effect of location within the set of environments in the analysis of variance

| Season  | Year             | Location     | State     | Cult. ‡ | Yld                 | GW             | GD | N                  | P   | K   | Mg                  | S   | Ca   | Fe   | Mn  | Cu  | Zn   | B   |  |
|---|------------------|--------------|-----------|---------|---------------------|----------------|----|--------------------|-----|-----|---------------------|-----|------|------|-----|-----|------|-----|--|
|   |                  |              |           |         | kg ha <sup>-1</sup> | g              | %  | g kg <sup>-1</sup> |     |     | mg kg <sup>-1</sup> |     |      |      |     |     |      |     |  |
| 1 <sup>st</sup> season  | 2013/14          | Capão Bonito | SP        | 13      | 10,355              | 34.8           | 58 | 12.9               | 2.1 | 3.3 | 1.0                 | 0.9 | 44.6 | 12.9 | 4.9 | 1.6 | 17.4 | 4.8 |  |
| 1 <sup>st</sup> season  | 2013/14          | Mococa       | SP        | 13      | 3,428               | 25.9           | 52 | 17.0               | 1.9 | 3.1 | 0.9                 | 1.0 | 45.8 | 13.0 | 5.5 | 2.4 | 22.3 | 5.0 |  |
| 1 <sup>st</sup> season  | 2013/14          | Itararé      | SP        | 13      | 9,635               | 34.9           | 48 | 13.7               | 1.6 | 2.8 | 0.9                 | 0.9 | 40.8 | 12.9 | 4.6 | 1.5 | 13.6 | 5.3 |  |
| 1 <sup>st</sup> season  | 2013/14          | Votuporanga  | SP        | 13      | 8,320               | 26.6           | 52 | 15.8               | 2.5 | 3.5 | 1.1                 | 1.1 | 50.5 | 15.5 | 5.6 | 1.8 | 17.1 | 5.6 |  |
| 1 <sup>st</sup> season  | 2014 - Irrigated | Capão Bonito | SP        | 7       | 11,141              | 33.2           | 86 | 11.1               | 2.5 | 3.6 | 1.1                 | 0.8 | 39.1 | 15.9 | 4.1 | 1.4 | 15.6 | 5.1 |  |
| 1 <sup>st</sup> season  | 2014 - Irrigated | Mococa       | SP        | 7       | 9,919               | 34.7           | 70 | 13.3               | 2.2 | 3.3 | 1.0                 | 0.9 | 26.7 | 11.9 | 4.8 | 1.4 | 17.4 | 5.2 |  |
| 1 <sup>st</sup> season  | 2014/15          | Castro       | PR        | 14      | 13,447              | 38.3           | 69 | 13.3               | 2.0 | 2.8 | 1.1                 | 0.8 | 39.5 | 17.5 | 4.4 | 1.3 | 17.0 | 4.8 |  |
| 1 <sup>st</sup> season  | 2014/15          | Itaberá      | SP        | 14      | 13,334              | 37.2           | 71 | 14.5               | 2.2 | 3.0 | 1.1                 | 0.8 | 45.4 | 16.2 | 4.9 | 1.4 | 17.8 | 3.0 |  |
| Mean  |                  |              |           |         | 9,947               | 33.2           | 63 | 13.9               | 2.1 | 3.2 | 1.0                 | 0.9 | 41.6 | 14.5 | 4.8 | 1.6 | 17.3 | 4.8 |  |
| 2 <sup>nd</sup> season  | 2014             | Mococa       | SP        | 9       | 5,022               | 26.2           | 51 | 12.5               | 1.8 | 2.8 | 1.0                 | 0.8 | 91.7 | 15.6 | 5.9 | 2.8 | 18.7 | 4.3 |  |
| 2 <sup>nd</sup> season  | 2014             | Pedrinhas    | SP        | 9       | 8,163               | 37.4           | 16 | 13.6               | 2.0 | 2.7 | 1.2                 | 1.0 | 56.1 | 13.4 | 5.0 | 2.4 | 20.3 | 4.2 |  |
| 2 <sup>nd</sup> season  | 2014             | Ibirararema  | SP        | 9       | 8,452               | 36.5           | 21 | 13.5               | 1.9 | 2.6 | 1.1                 | 0.9 | 42.0 | 11.5 | 4.7 | 2.4 | 16.8 | 3.5 |  |
| 2 <sup>nd</sup> season  | 2014             | Dourados     | MS        | 10      | 5,502               | 28.7           | 34 | 12.8               | 2.1 | 2.8 | 1.1                 | 0.9 | 75.3 | 15.7 | 5.6 | 2.3 | 16.6 | 3.5 |  |
| 2 <sup>nd</sup> season  | 2014             | Naviraí      | MS        | 10      | 6,408               | <sup>(1)</sup> | -  | 13.5               | 2.1 | 2.8 | 1.1                 | 1.0 | 39.6 | 12.3 | 4.1 | 1.3 | 16.4 | 2.7 |  |
| 2 <sup>nd</sup> season  | 2014             | Sidrolândia  | MS        | 10      | 7,875               | 36.5           | 22 | 12.8               | 2.6 | 3.5 | 1.2                 | 0.9 | 31.5 | 11.6 | 4.0 | 1.4 | 18.2 | 4.0 |  |
| 2 <sup>nd</sup> season  | 2015             | Sorriso      | MT        | 6       | 9,295               | 35.8           | 56 | 13.0               | 2.4 | 3.7 | 1.1                 | 0.9 | 37.8 | 15.4 | 4.1 | 1.2 | 17.1 | 4.4 |  |
| 2 <sup>nd</sup> season  | 2015             | Nova Mutum   | MT        | 6       | 9,115               | 34.9           | 70 | 11.7               | 2.1 | 3.7 | 1.0                 | 0.9 | 85.5 | 12.4 | 5.0 | 1.7 | 20.2 | 3.9 |  |
| 2 <sup>nd</sup> season  | 2015             | Sapezal      | MT        | 6       | 9,295               | 40.8           | 5  | 14.7               | 2.3 | 3.4 | 1.0                 | 0.9 | 34.0 | 11.2 | 4.6 | 1.4 | 17.2 | 2.8 |  |
| 2 <sup>nd</sup> season  | 2015             | Rondonópolis | MT        | 6       | 9,084               | 34.3           | 24 | 12.9               | 2.0 | 3.3 | 0.9                 | 0.8 | 31.5 | 11.6 | 4.1 | 1.4 | 13.3 | 3.9 |  |
| Mean  |                  |              |           |         | 7,821               | 34.6           | 33 | 13.1               | 2.1 | 3.1 | 1.1                 | 0.9 | 52.5 | 13.1 | 4.7 | 1.8 | 17.5 | 3.7 |  |
| F test-Effect of location on each group of cultivars <sup>(1)</sup> |                  |              |           |         |                     |                |    |                    |     |     |                     |     |      |      |     |     |      |     |  |
| 1 <sup>st</sup> season  | 2013/14          | 4            | SP        | 13      | **                  | **             | ns | **                 | **  | **  | **                  | **  | ns   | *    | *   | **  | **   | ns  |  |
| 1 <sup>st</sup> season  | 2014 - Irrigated | 2            | SP        | 7       | **                  | ns             | *  | *                  | *   | *   | ns                  | **  | **   | **   | ns  | ns  | ns   | ns  |  |
| 1 <sup>st</sup> season  | 2014/15          | 2            | SP and PR | 14      | ns                  | ns             | ns | **                 | *   | *   | ns                  | ns  | ns   | ns   | ns  | ns  | ns   | *   |  |
| 2 <sup>nd</sup> season  | 2014             | 3            | SP        | 9       | **                  | **             | ** | **                 | ns  | ns  | ns                  | **  | *    | **   | ns  | *   | **   | ns  |  |
| 2 <sup>nd</sup> season  | 2014             | 3            | MS        | 10      | **                  | **             | ns | Ns                 | **  | **  | ns                  | *   | *    | *    | **  | **  | ns   | **  |  |
| 2 <sup>nd</sup> season  | 2015             | 4            | MT        | 6       | ns                  | **             | ** | **                 | ns  | ns  | ns                  | ns  | ns   | **   | ns  | ns  | **   | ns  |  |

<sup>(1)</sup> 100-grain weight and grain density by the floaters test were not determined in samples from Naviraí-MS because, in some cases, the sample volume was insufficient for these determination. The mineral nutrients were analyzed using the methodology described by Bataglia et al. (1978). ‡ = number of cultivars; \* and \*\* = significant effect at 5 and 1 % probability, respectively; and ns = not significant; SP = São Paulo State; MS = Mato Grosso do Sul State; MT = Mato Grosso State; PR = Paraná State.

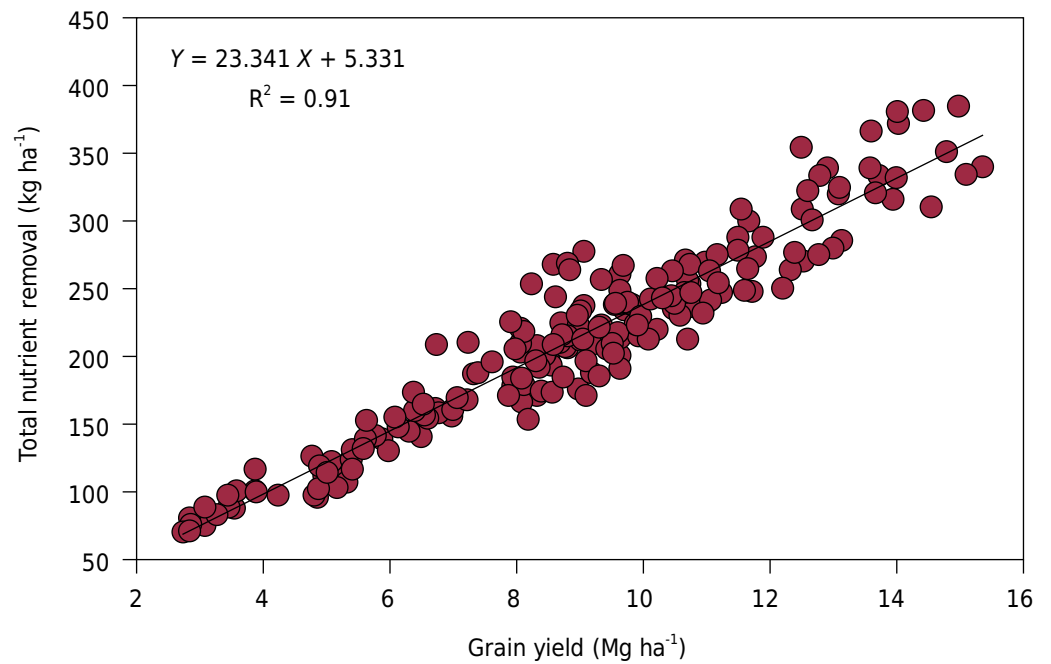
**Table 3.** Pearson's correlations between variables measured for 197 corn grain samples

| Variable            | Season          | GW     | GDI     | N       | P       | K       | Ca      | Mg      | S       | Fe      | Mn      | Cu      | Zn      | B       |
|---------------------|-----------------|--------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Yld. <sup>(1)</sup> | 1 <sup>st</sup> | 0.72** | 0.18*   | -0.56** | 0.13ns  | -0.08ns | -0.03ns | 0.31**  | -0.49** | 0.18*   | -0.25** | -0.60** | -0.39*  | -0.23*  |
|                     | 2 <sup>nd</sup> | 0.64** | -0.15ns | -0.01ns | 0.16ns  | 0.26*   | -0.25*  | -0.16ns | -0.14ns | -0.41** | -0.23*  | -0.37** | 0.07ns  | -0.11ns |
|                     | Total           | 0.58** | 0.24**  | -0.27** | 0.10ns  | 0.07ns  | -0.13*  | 0.08ns  | -0.40** | 0.09ns  | 0.19**  | -0.52** | -0.30** | 0.04ns  |
| GW <sup>(2)</sup>   | 1 <sup>st</sup> |        | 0.25**  | -0.45** | -0.03ns | -0.16*  | -0.15ns | 0.23*   | -0.46** | 0.08ns  | -0.24*  | -0.44** | -0.24*  | -0.26** |
|                     | 2 <sup>nd</sup> |        | -0.22*  | 0.38ns  | 0.17ns  | 0.07ns  | 0.34**  | -0.10ns | 0.13ns  | -0.41** | -0.32** | -0.17ns | 0.07ns  | -0.03ns |
|                     | Total           |        | 0.01ns  | -0.19** | 0.06ns  | -0.05ns | -0.22** | 0.10ns  | -0.23** | 0.8ns   | -0.28** | -0.27** | -0.11ns | 0.19**  |
| GD <sup>(3)</sup>   | 1 <sup>st</sup> |        |         | -0.22*  | 0.18*   | 0.23*   | -0.10ns | 0.08ns  | -0.15ns | 0.08ns  | -0.10ns | -0.23*  | 0.04ns  | 0.07ns  |
|                     | 2 <sup>nd</sup> |        |         | -0.27*  | -0.05ns | 0.24*   | 0.31**  | -0.10ns | 0.06ns  | 0.25*   | 0.19*   | 0.02ns  | 0.23*   | 0.24*   |
|                     | Total           |        |         | -0.10ns | 0.05ns  | 0.24**  | 0.03ns  | -0.06ns | -0.10ns | 0.17*   | 0.05ns  | -0.20** | 0.02ns  | 0.16*   |
| N                   | 1 <sup>st</sup> |        |         |         | 0.38ns  | 0.07ns  | 0.00ns  | 0.01ns  | 0.54**  | 0.06ns  | 0.30**  | 0.48**  | 0.49**  | 0.12ns  |
|                     | 2 <sup>nd</sup> |        |         |         | 0.15ns  | -0.05ns | -0.12ns | 0.03ns  | 0.40**  | -0.06ns | 0.12ns  | -0.12ns | -0.02ns | 0.05ns  |
|                     | Total           |        |         |         | 0.06ns  | 0.04ns  | -0.06ns | -0.02ns | 0.45**  | 0.06ns  | 0.23**  | 0.14*   | 0.30**  | 0.17*   |
| P                   | 1 <sup>st</sup> |        |         |         |         | 0.71**  | 0.08ns  | 0.73**  | 0.42**  | 0.35**  | 0.37**  | 0.02ns  | 0.34**  | 0.02ns  |
|                     | 2 <sup>nd</sup> |        |         |         |         | 0.71**  | -0.25*  | 0.66**  | 0.50**  | 0.34**  | 0.04ns  | -0.39** | 0.36**  | -0.06ns |
|                     | Total           |        |         |         |         | 0.70**  | -0.06ns | 0.70**  | 0.45**  | 0.33**  | 0.21**  | -0.18*  | 0.35**  | -0.02ns |
| K                   | 1 <sup>st</sup> |        |         |         |         |         | 0.09ns  | 0.37**  | 0.42**  | 0.20*   | 0.29**  | 0.13ns  | 0.22*   | 0.10ns  |
|                     | 2 <sup>nd</sup> |        |         |         |         |         | -0.08ns | 0.35**  | 0.21*   | 0.27*   | 0.14ns  | 0.34**  | 0.32**  | 0.04ns  |
|                     | Total           |        |         |         |         |         | -0.00ns | 0.34**  | 0.31**  | 0.22**  | 0.21**  | -0.15*  | 0.25**  | 0.09ns  |
| Ca                  | 1 <sup>st</sup> |        |         |         |         |         |         | 0.15ns  | 0.19*   | 0.23*   | 0.55**  | 0.16*   | -0.03ns | 0.04ns  |
|                     | 2 <sup>nd</sup> |        |         |         |         |         |         | -0.01ns | -0.09ns | 0.32**  | 0.79**  | 0.18*   | 0.17*   | 0.13ns  |
|                     | Total           |        |         |         |         |         |         | 0.09ns  | 0.09ns  | 0.24**  | 0.66**  | 0.19**  | 0.06ns  | 0.04ns  |
| Mg                  | 1 <sup>st</sup> |        |         |         |         |         |         |         | 0.16ns  | 0.33**  | 0.41**  | -0.12ns | 0.38**  | -0.11ns |
|                     | 2 <sup>nd</sup> |        |         |         |         |         |         |         | 0.49**  | 0.50**  | 0.29**  | 0.07ns  | 0.61**  | -0.11ns |
|                     | Total           |        |         |         |         |         |         |         | 0.30**  | 0.36**  | 0.34**  | 0.01ns  | 0.48**  | -0.15*  |
| S                   | 1 <sup>st</sup> |        |         |         |         |         |         |         |         | 0.12ns  | 0.49**  | 0.45**  | 0.34**  | 0.24*   |
|                     | 2 <sup>nd</sup> |        |         |         |         |         |         |         |         | 0.35**  | 0.12ns  | -0.01ns | 0.38**  | 0.09ns  |
|                     | Total           |        |         |         |         |         |         |         |         | 0.17*   | 0.32**  | 0.24**  | 0.36**  | 0.14*   |
| Fe                  | 1 <sup>st</sup> |        |         |         |         |         |         |         |         |         | 0.10ns  | 0.13ns  | 0.30**  | 0.14ns  |
|                     | 2 <sup>nd</sup> |        |         |         |         |         |         |         |         |         | 0.46**  | 0.23*   | 0.41**  | 0.16ns  |
|                     | Total           |        |         |         |         |         |         |         |         |         | 0.22**  | 0.12*   | 0.31**  | 0.18*   |
| Mn                  | 1 <sup>st</sup> |        |         |         |         |         |         |         |         |         |         | 0.25**  | 0.37**  | 0.07ns  |
|                     | 2 <sup>nd</sup> |        |         |         |         |         |         |         |         |         |         | 0.25*   | 0.32**  | 0.05ns  |
|                     | Total           |        |         |         |         |         |         |         |         |         |         | 0.23**  | 0.34**  | 0.07ns  |
| Cu                  | 1 <sup>st</sup> |        |         |         |         |         |         |         |         |         |         |         | 0.41**  | 0.29**  |
|                     | 2 <sup>nd</sup> |        |         |         |         |         |         |         |         |         |         |         | 0.29**  | 0.05ns  |
|                     | Total           |        |         |         |         |         |         |         |         |         |         |         | 0.35**  | 0.09ns  |
| Zn                  | 1 <sup>st</sup> |        |         |         |         |         |         |         |         |         |         |         |         | 0.02ns  |
|                     | 2 <sup>nd</sup> |        |         |         |         |         |         |         |         |         |         |         |         | -0.10ns |
|                     | Total           |        |         |         |         |         |         |         |         |         |         |         |         | 0.04ns  |

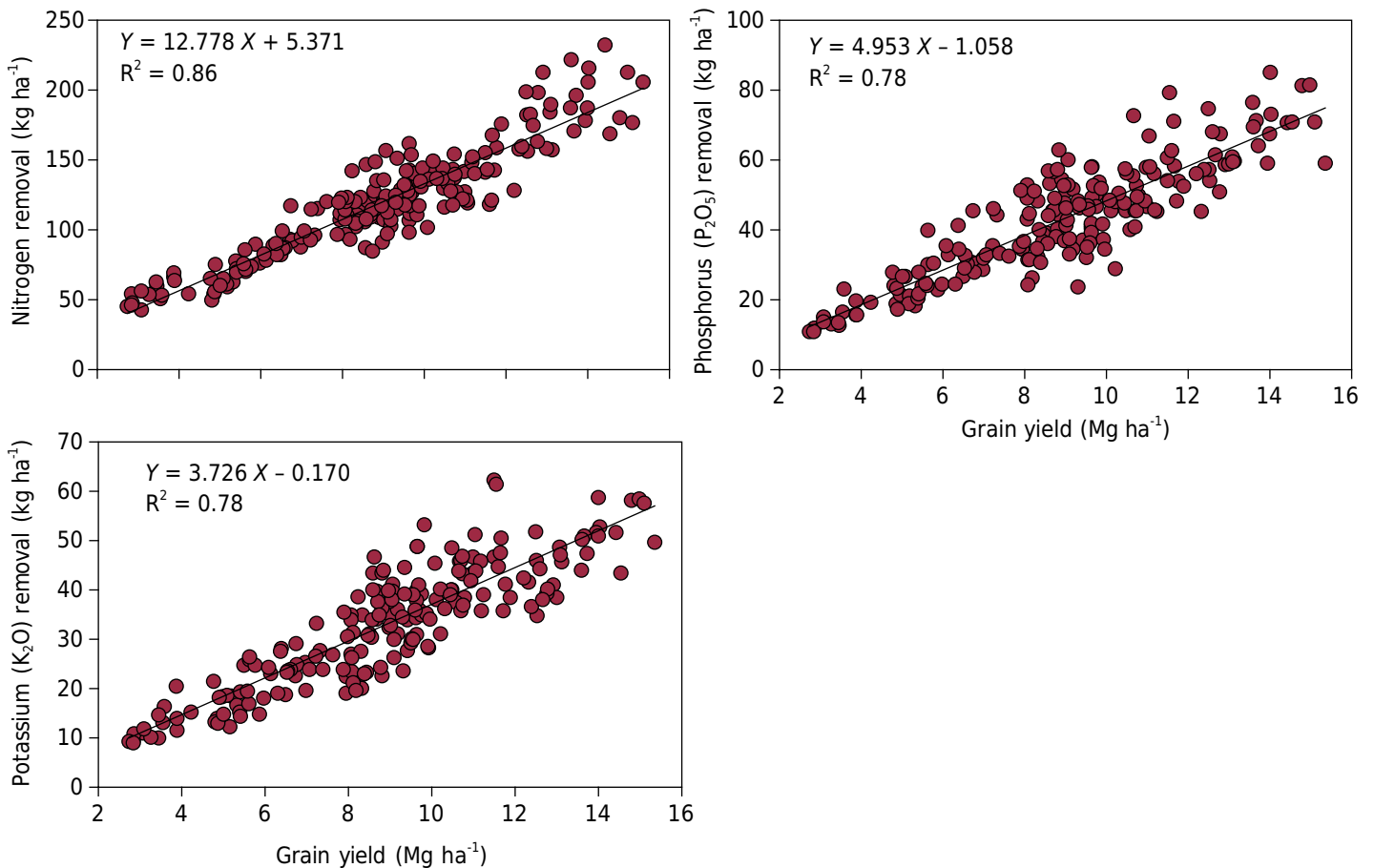
<sup>(1)</sup> Yield. <sup>(2)</sup> 100-grain weight. <sup>(3)</sup> Grain density by the floaters test. \* and \*\* indicate significant effect at 5 and 1 % probability, respectively; ns = not significant.

Nutrient removal values increased linearly with yield for all nutrients, with the exception of Fe (Figures 2, 3, and 4), although the coefficient (r) for Ca was only 0.24 expressed in mg kg<sup>-1</sup>. The values of nutrient removal varied largely among closer yields, even when the coefficient of determination between the two variables was relatively high. For similar yields, the removal amount of a certain nutrient was often twice or more than twice, as high as in a sample of another cultivar from different location.

For N, removal values ranged from 157-232 kg ha<sup>-1</sup> at yields higher than 12 Mg ha<sup>-1</sup> (Figure 2). This is related to the great impact of high yields on the calculation of removals, because it involved multiplication by the different grain N contents. As mentioned above,



**Figure 1.** Total nutrient removal in grains (N, P, K, Ca, Mg, S, Fe, Mn, Cu, Zn, and B) related to corn grain yield.



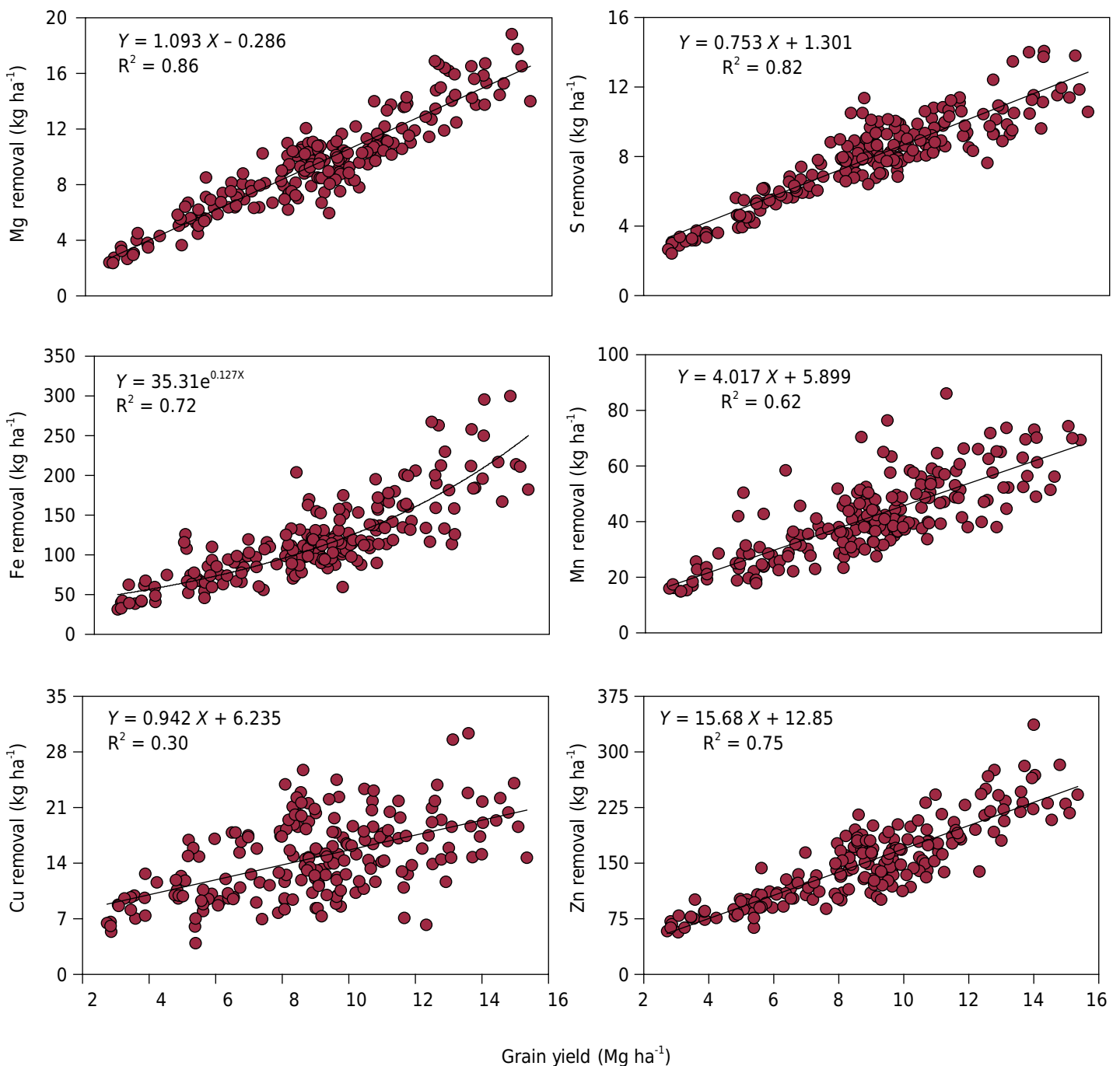
**Figure 2.** Nitrogen, phosphorus (P<sub>2</sub>O<sub>5</sub>), and potassium (K<sub>2</sub>O) removal, respectively, related to corn grain yield.

N content and yield were negatively correlated, specifically in summer corn, with the highest-yielding experimental plots.

The coefficients of determination between the B and Cu removal and grain yield were the lowest among the micronutrients, which could be related to the low contents of these elements in grain. As discussed later, after Ca and B, the ranges between the minimum and maximum contents of Cu, Fe, and Mn were the widest. In this nutrient group, Cu differed the most between production environments.

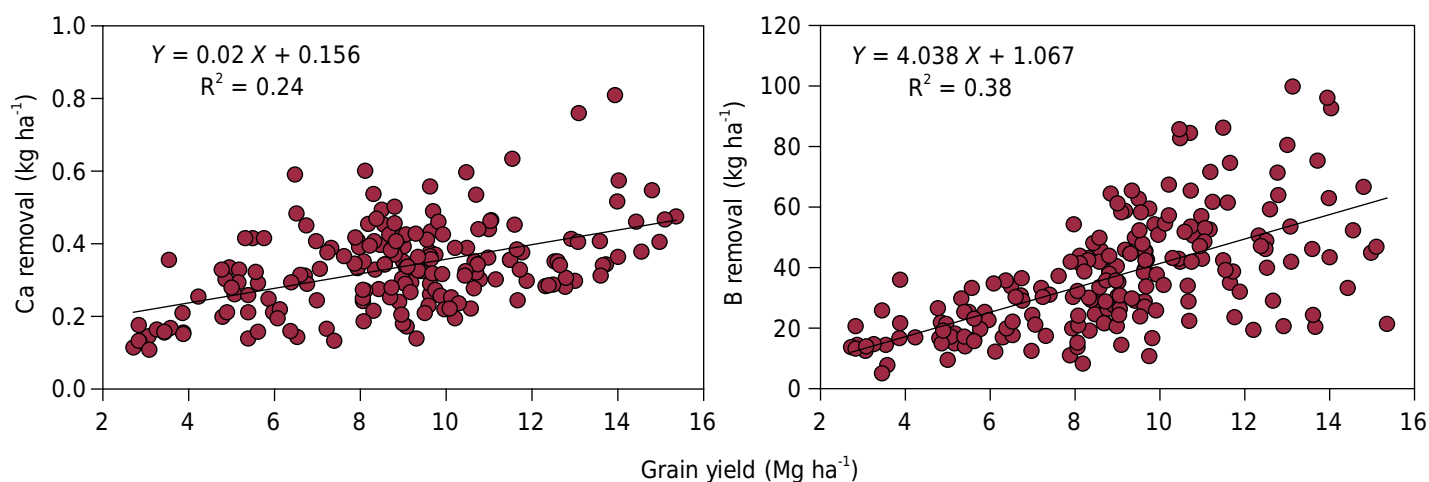
### Reference values

The mean N, P, K, and S contents were lower than the reference values published in Bulletin 100 of the IAC approximately 20 years ago (Raj et al., 1996), based on the knowledge available at the time (Table 4). The contents of Ca, Mg, and Zn were also



**Figure 3.** Removal of magnesium, sulfur, iron, manganese, copper, and zinc related to corn grain yield.





**Figure 4.** Removal of calcium and boron related to corn grain yield.

**Table 4.** Overall and subdivided mean nutrient contents in corn grains for the first and second growing seasons, minimum-maximum intervals, and reference values

| Range                               | g kg <sup>-1</sup> |                  |                  |     |                    | mg kg <sup>-1</sup> |      |     |     |      |     |
|-------------------------------------|--------------------|------------------|------------------|-----|--------------------|---------------------|------|-----|-----|------|-----|
|                                     | N                  | P                | K                | Mg  | S                  | Ca                  | Fe   | Mn  | Cu  | Zn   | B   |
| Set of 197 samples in 2014 and 2015 |                    |                  |                  |     |                    |                     |      |     |     |      |     |
| Overall mean                        | 13.5               | 2.1              | 3.1              | 1.1 | 0.9                | 49                  | 13.8 | 4.8 | 1.7 | 17.4 | 4.2 |
| 1 <sup>st</sup> season mean         | 13.9               | 2.1              | 3.1              | 1.0 | 0.9                | 45                  | 14.3 | 4.9 | 1.6 | 17.2 | 4.6 |
| 1 <sup>2nd</sup> season mean        | 13.1               | 2.1              | 3.0              | 1.1 | 0.9                | 53                  | 13.2 | 4.7 | 1.9 | 17.7 | 3.7 |
| Minimum Range                       | 10.0               | 1.5              | 2.0              | 0.7 | 0.7                | 20                  | 8.0  | 3.0 | 0.9 | 12.0 | 1.0 |
| Maximum Range                       | 17.5               | 3.0              | 4.5              | 1.4 | 1.2                | 150                 | 22.0 | 8.0 | 3.0 | 24.0 | 8.0 |
| Reference values since 1996         |                    |                  |                  |     |                    |                     |      |     |     |      |     |
| Mean                                | 17 <sup>(1)</sup>  | 4 <sup>(1)</sup> | 5 <sup>(1)</sup> | 1.7 | 1.2 <sup>(1)</sup> | 400                 |      |     | 1.1 | 25.1 | 3.1 |

<sup>(1)</sup> IAC Bulletin 100 (Rajj et al., 1996) and the others based on compilation of Cantarella and Duarte (2004), except Fe and Mn. The mineral nutrients were analyzed using the methodology described by Bataglia et al. (1978).

lower than those that were compiled by Cantarella (2004). On the other hand, Cu and B were the only nutrients with higher contents than those obtained until the last decade.

Since the evolution of management and cultivars is continuous, reference values represent the reality of most crops for a given period, and it would be impossible to predict when they could become outdated. Nevertheless, a review of values obtained within a less than 20-year period would be advisable.

For the 45 summer corn samples collected during the 1998/1999 and 2000/2001 growing seasons from different environments in the state of São Paulo, Duarte (2003) determined the following values: 13.7 (N), 3.6 (P), 4.7 (K), 0.1 (Ca), 1.3 (Mg), and 1.0 (S) g kg<sup>-1</sup> as well as 32.3 (Fe), 8.1 (Mn), 4.0 (Cu), 30.1 (Zn), and 6.0 (B) mg kg<sup>-1</sup>. Therefore, in this study, the mean values were lowest for P, K, Fe, Mn, Cu, and Zn. Two of the main differences between production systems in the 15 years that separate the two studies, are the broad implementation of no-tillage systems and the increase of plant densities to at least 10,000 plants ha<sup>-1</sup>. Modern hybrids have far higher yields at high plant densities (more upright leaves) and at high levels of soil fertility (Duvick, 1984; Sangoi, 1990). This is due to a consistent increase in resistances to stem lodging and breaking (Duvick, 1984), and the adjustment of soil fertility to adequate levels to sustain high yields at high planting densities (Sangoi, 1990), which could be related to the use of no-tillage systems. Under these conditions, decreases in grain nutrient contents have been reported (Carlone and Russel, 1987; Ciampitti and Vyn, 2013).

The results were also lower than those that were reported by Resende et al. (2012), in a revision of several Brazilian publications as of 1995, where values were 15.7 (N), 3.1 (P), and 3.7 (K) g kg<sup>-1</sup>. In comparison with a survey of Oliveira Junior et al. (2010), who analyzed hundreds of samples from laboratory routine analyses, the values of this study are similar for K (3.2 g kg<sup>-1</sup>) and lower for P (2.7 g kg<sup>-1</sup>). Since the analysis period for Oliveira Junior et al. (2010) was recent, these results confirmed that the mean K values are close to 3.1 g kg<sup>-1</sup>, i.e., lower than in the past.

In the studies published as of 2000 in North America and Canada, the mean N removal values were between 12-15 g kg<sup>-1</sup> (Hossain, 2006; Binford, 2010; Bender et al., 2013). In these studies, the mean P and mean K values were 3.0 and 3.6 g kg<sup>-1</sup>, respectively, coinciding with the results of Resende et al. (2012) in Brazil. In a survey of Heckman et al. (2003), in five states in the USA (Delaware, Maryland, Massachusetts, New Jersey, and Pennsylvania) during 1998 and 1999, the mean values for P and K were 4.0 and 4.8 g kg<sup>-1</sup>, respectively. This shows that there was also a reduction in the P and K values published after 2000 in North America.

The mean values of Ca, Mg, S, and micronutrients in this study were similar to those reported by Heckman et al. (2003), Hossain (2006), Binford (2010), and Bender et al. (2013), with the exception of Fe, which had the lowest values. It is noteworthy that Ca was only evaluated by Heckman et al. (2003) and Hossain (2006), with means of 300 and 80 mg kg<sup>-1</sup>, respectively.

The individual values of each nutrient were organized in minimum and maximum ranges, by calculating the mean of the 10 samples with the lowest and the highest values, respectively, corresponding to 5 % of the total number of samples in each range (Table 4). The relative difference between the minimum and maximum ranges was very high for Ca and B (10- and 6-fold, respectively), hampering the use of reference values for the calculation of nutrient removals. As already mentioned, the analytical difficulties of Ca and B in grains, due to their very low contents in relation to leaf tissues, must have contributed to this variability. Among the nutrients with extreme amplitudes between minimum and maximum values were Fe, Mn, and Cu (nearly 3-fold variations). For N, P, K, Mg, S, and Zn, which represent the group of nutrients most removed at corn harvest, the ranges of maximum values were approximately twice the minimum values.

## CONCLUSIONS

In summer corn (1<sup>st</sup> season), there was a clear reduction in N, S, and Cu contents with increasing grain yield and weight, indicating that the nutrient removal was proportionally lower at high yields.

The great variability of results between environments, especially for N and Fe, hampers the estimation of nutrient removal based on reference values and prevents the differentiation by season (first and second growing seasons).

The values of grain nutrient contents that have been used for 20 years as references were overestimating for N, P, K, Ca, Mg, S, and Zn and underestimating for Cu and B, compared to the current values determined in this study. This results in misleading calculations for nutrient removal. The results of this study can be used to update the reference values of nutrient contents in corn grains to estimate the amounts of nutrients removed from the soil.

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