Corn Era Hybrid Nutrient Concentration and Accumulation of Secondary and Micronutrients

Krishna P. Woli,* John E. Sawyer, Matthew J. Boyer, Lori J. Abendroth, and Roger W. Elmore*

ABSTRACT

Studies are limited that focus on change in concentration and accumulation of secondary and micronutrients in corn (Zea mays L.) plant fractions and across corn hybrid development periods. This research was conducted in 2007 and 2008 to evaluate the partitioning of secondary and micronutrients across vegetative and reproductive stages at the plant-fraction level for 1960- and 2000-era hybrids. Two popular hybrids for each era were grown, with measurement of nutrient concentration and content in several plant and grain fractions. Secondary and micronutrient concentrations in plant fractions were lower in 2000- than 1960-era hybrids with most nutrients, except ear shoots and tassels for certain nutrients. However, nutrient content was consistently greater in 2000-compared to 1960-era hybrids in the whole plant and fractions at most development stages, except tassels and ear shoots. In tassels, nutrient content was mostly smaller in 2000-era hybrids, but in ear shoots content was similar. The accumulation rates of most nutrients per growing degree day (GDD) were greater in the reproductive period for 2000-era hybrids, but similar among eras in the vegetative period. Remobilized nutrients from vegetative to reproductive components were similar between era hybrids, except Ca and Fe, and positive except Fe, Mn, and B. It is apparent that greater nutrient content in newer hybrids was driven mainly by associated nutrient uptake rates and greater dry matter (DM). Despite the greater nutrient content with the modern hybrids, removal with grain or stover harvest would still be small for S and micronutrients.

Core Ideas

- We compared 1960- and 2000-era hybrid secondary and micronutrient accumulation and partitioning.
- Nutrient concentrations were mostly lower for 2000- than 1960-era hybrids.
- Whole plant and fraction nutrient content were generally greater for 2000-era hybrids.
- Greater nutrient content in modern hybrids was driven by increased overall plant growth.
(Ciampitti and Vyn, 2013). Secondary and micronutrient deficiency in soil and plants is often a regional or soil specific issue, with severity varying considerably in different regions. For example, in areas of the US Corn Belt, S deficiency has developed into an important issue that requires S application (Rehm, 2005; Sawyer et al., 2011; Kim et al., 2013).

Although nutrient management is a complex process, improving our understanding of uptake timing and rates, partitioning, and remobilization of nutrients by corn plants may help optimize fertilization programs, such as fertilizer rates, sources, and application timings (Bender et al., 2013). Furthermore, it is necessary to understand that a possible decrease in concentration and increase in content associated with removal (when plant parts are harvested) may affect nutrient fertilization need. Increasing the remobilization of nutrients from vegetative organs to grain can effectively increase the nutritional value of grain (Chen et al., 2016). The nutrient content of grain is a function of nutrients accumulated post-silking as well as remobilization of nutrients accumulated in vegetative organs prior to silking (Hirel et al., 2007). In corn, 25 to 82% of grain N is derived from the remobilization of vegetative N accumulated before silking (Ta and Weiland, 1992; Ma and Dwyer, 1998; Mi et al., 2003; Lemaire and Gastal, 2009; Chen et al., 2014). Woli et al. (2018) reported 34 to 36% of grain N, 58 to 68% of P, and 43 to 51% of K remobilized from vegetative parts. In contrast, the nutrient contribution to grain from the remobilization of micronutrients such as Fe, Mn, Cu, and B was reported to be low (Karlen et al., 1988; Brown and Shelp, 1997; Bender et al., 2013).

Nutrient composition values that have historically been available may be different with current production practices, especially newer hybrids. Accurate values for crop nutrient removal in vegetation and grain are an important component of nutrient management planning (Heckman et al., 2003). A recent study reported that vegetative-stage nutrient content averaged 91% (Ca), 51% (Fe), 47% (Zn), and 73% (Mn, Mg, and Cu) of corresponding nutrient contents at maturity (Ciampitti and Vyn, 2013). The concentration of nutrients in corn grain can affect the ability of a seedling to tolerate various biotic and abiotic stresses (Masclaux-Daubresse et al., 2010).

There are a few studies that have compared secondary and micronutrient concentration and accumulation rates among old and modern hybrids with current management practices. Woli et al. (2017) evaluated the accumulation of dry matter (DM) and macronutrient plant nutrients N, P, and K at the whole-plant level, and Woli et al. (2018) assessed the partitioning across vegetative and reproductive stages for historical to modern era hybrids. However, they did not report the partitioning of secondary nutrients Ca, Mg, and S, and micronutrients Fe, Cu, Zn, Mn, and B. The objectives of this study were to evaluate the partitioning of secondary and several micronutrients across vegetative and reproductive stages at the plant-fraction level for hybrids from two eras.

**MATERIALS AND METHODS**

The study was conducted at the Iowa State University Agricultural Engineering and Agronomy Research Farms near Ames, IA; 42°0’41” N, 93°4’32” W in 2007 and 41°59’17” N, 93°40’46” W in 2008, and is a part of the research project that evaluated corn yield and plant nutrition responses across era hybrids. Soil information, fertilizer application, hybrid selection, and agronomic practices are described in detail by Woli et al. (2016). Briefly, soils were Nicollet (fine-loamy, mixed, superactive, mesic Aquic Hapludoll), Harps (fine-loamy, mixed, superactive, mesic Typic Calciaquoll), Clarion loam (fine-loamy, mixed, superactive, mesic Typic Hapludoll), and Canisteo clay loam (fine-loamy, mixed, superactive, calcareous, mesic Typic Endoaquoll). No P or K fertilizer was applied in 2007, because soil test P and K values were in the very high category (Sawyer et al., 2002). In 2008, triple super phosphate (0–46–0) was applied at the rate of 38 kg P ha⁻¹ on 13 May before tillage, because the soil test P (Bray P1, 14 mg kg⁻¹) was low, and no K applied as the soil test K (ammonium acetate, 137 mg kg⁻¹) was optimum. Soil pH was optimal (6.5 and 6.7) and no secondary or micronutrients were applied either year as would be recommended for corn on the soils at the study sites (Sawyer et al., 2002).

Corn was planted on 15 May each year, and ammonium nitrate fertilizer was sidedressed by hand on 5 June 2007 and 10 June 2008 at the V₄ stage with a 168 kg N ha⁻¹ rate within the recommended range in Iowa for corn following soybean (Glycine max (L.) Merr.) (Sawyer et al., 2006). Two popular DuPont Pioneer (Pioneer Hi-Bred International, Johnston, IA) hybrids were selected for 1960 (3206 and 3618) and 2000 (33D11 and 34A15) era-decades, which were recommended by Dr. Don Duvick and Dr. Garren Benson (Pioneer Hi-bred and Iowa State University, respectively; personal communications, 2006 and 2007). The experimental design was a randomized complete block with four replications.

The sampling description for corn development stages and cumulative (from planting date) mean degree Celsius-based growing degree days (GDD) are described by Woli et al. (2017). Plant staging and plant fractionation, along with sample preparation details, are summarized in Woli et al. (2018). Briefly, aboveground whole plant samples were collected at 10 corn development stages ranging from the sixth collar visible (V₆) to physiological maturity (R₆) (Abendroth et al., 2011). Daily Celsius-based GDDs were calculated (Dwyer et al., 1999) from average daily temperature of the nearby weather station that was accessed via the Iowa Environmental Mesonet (2017).

At the V₆ and V₁₀ stages, six plants per plot were collected and analyzed as whole plants. Plant development staging was performed based on the dissection scheme of plants (Fig. 1) throughout the development stages. Plants were separated into three fractions and reported as stalk (stalk + leaf sheaths + ear shoots), leaf, and tassel at the V₁₄ stage. From VT to R₂, plants were separated into four fractions; stalk (stalk + leaf sheaths), leaf, tassel, and ear shoot (shank + husk + cob + grain). Tassels were clipped off from the stalks directly below the lowest tassel branch. Ear shoots, when present, were pulled away from the stalk and clipped from their respective stalk nodes. Any ear shoots visible above the leaf sheath attached to the same node was counted as an ear shoot and cut from the stalk. Beginning at R₃ and continuing until R₅, plants were separated into five fractions; stalk (stalk + leaf sheaths), leaf, tassel, ear shoot (shank + husk + cob), and grain. At the R₆ stage, plant fractionation was similar to the R₃ to R₅ stages except the cobs were separated from the shank and husk fractions of the ear shoots and analyzed separately.

Dissection of plants took place in the field before any artificial drying except for the ear shoots, which were partially dried...
before separating the grain and cobs from the shank and husk. Whole plants taken at V6 and V10 and all plant fractions taken at V14 to R6 were oven-dried at 60°C until they reached a point where weight loss ceased. Biomass dry weights were then determined for all fractioned components. After drying, samples were ground to obtain a subsample for nutrient analysis. Fractioned samples were ground in a Wiley mill (Arthur H. Thomas Co., Philadelphia, PA) until the sample would pass through a 2-mm sieve. The only exception was grain, which was ground through a flour mill (WonderMill Company, Pocatello, ID). After grinding, the samples were thoroughly mixed, and a subsample was analyzed for secondary and micro-nutrient concentrations using the standard methods by AgSource Harris Laboratories in Lincoln, NE (https://www.agsourcelaboratories.com). Plant nutrient content was calculated using plant DM and nutrient concentrations and converted to an area basis by determining the average plant spacing and the associated area that the six sampled plants occupied. The era hybrids whole plant and fractions’ nutrient accumulation rates per cumulative GDD were evaluated for whole plant in the vegetative (V6–R1) and reproductive (R1–R6) periods, and for grain in the reproductive (R1–R6) period. Grain nutrient accumulation rates for the R1 to R6 period were calculated assuming no grain amount at R1. Remobilized nutrients from the vegetative to reproductive components were calculated by the content difference between R1 and R6 vegetative fractions, as in Mueller et al. (2017). Specific components combined for R1 were leaf blades + leaf sheaths + tassel + stalk + ear shoots and combined for R6 were leaf blades + leaf sheaths + tassel + stalk + shanks + husks. Analysis of variance was performed by each corn development stage for whole plant and plant fraction nutrient concentration, nutrient content, nutrient accumulation rate, and remobilized nutrient data with the MIXED procedure in SAS (SAS Institute, 2012) for a randomized complete block design with era fixed and year and block (year) random. As year and year × treatment interaction were not significant, the data was averaged among years. Nutrient concentration and content data were analyzed separately for each sampling date due to range of variances across the sampling dates. The development stage data were tested for normal distribution using the residual statement in PROC MIXED, and PROC UNIVARIATE with the Shapiro-Wilk test, and then confirmed with PROC GLIMMIX using the DIST = LOGN and the default Gaussian comparison. Standard error of the least square means was estimated and reported. Since the standard error of the least square means were same for 1960- and 2000-era hybrids in most cases, the reported values and those in Supplementary Tables S1–S6 are for both hybrids (and noted if different). Differences between the 1960- and 2000-eras are considered significant when the Pr > F was ≤0.05.

RESULTS AND DISCUSSION

Nutrient Concentration Results

Secondary Nutrients

Across development stages, the Ca concentrations in most corn plant fractions tended to change greatly (Fig. 2a–2c). In stalks and ear shoots, there was no consistent pattern across the development stages (Fig. 2a, 2d). In leaves and tassels, Ca concentrations tended to increase to R6 for the 1960- and 2000-era hybrids (Fig. 2b, 2c), whereas grain Ca concentrations across the stages were constant (Fig. 2e). The trend of Ca concentrations across stages was similar for the 1960- and 2000-era hybrids. However, Ca concentrations were different between the 1960- and 2000-era hybrids at most development stages in stalks, leaves, and tassels (Fig. 2a–2c); Ca concentrations were lower in the 2000-era hybrids compared to 1960- in all plant fractions except tassels. Cob Ca concentrations were not different between 1960- and 2000-era hybrids (Table 1).

Magnesium concentrations in stalks and tassels tended to decrease throughout the development stages (Fig. 2f, 2h). In leaves and ear shoots, there was no consistent pattern in Mg concentrations across the development stages (Fig. 2g) in both era hybrids. There was no change in Mg concentrations in grain across the stages (Fig. 2i). At most development stages, Mg concentrations were lower in 2000-era hybrids compared to 1960-in all plant fractions except tassels. Cob Mg concentrations were not different between 1960- and 2000-era hybrids (Table 1).
Table 1. Cob nutrient composition at physiological maturity for the 1960- and 2000-era hybrids. Means considered different at $P \leq 0.05$.

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Concentration 1960 (g kg$^{-1}$)</th>
<th>SE†</th>
<th>$P &gt; F$</th>
<th>Concentration 2000 (g kg$^{-1}$)</th>
<th>SE†</th>
<th>$P &gt; F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>0.753</td>
<td>0.316</td>
<td>0.750</td>
<td>0.964</td>
<td>0.448</td>
<td>0.012</td>
</tr>
<tr>
<td>Mg</td>
<td>0.364</td>
<td>0.061</td>
<td>0.142</td>
<td>0.459</td>
<td>0.096</td>
<td>0.024</td>
</tr>
<tr>
<td>S</td>
<td>0.250</td>
<td>0.05</td>
<td>1.000</td>
<td>0.318</td>
<td>0.065</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Fe</td>
<td>33</td>
<td>2.7</td>
<td>0.489</td>
<td>42</td>
<td>3.7</td>
<td>0.157</td>
</tr>
<tr>
<td>Cu</td>
<td>5.9</td>
<td>0.44</td>
<td>0.100</td>
<td>7.5</td>
<td>0.68</td>
<td>0.582</td>
</tr>
<tr>
<td>Zn</td>
<td>12</td>
<td>0.88</td>
<td>0.293</td>
<td>15</td>
<td>1.5</td>
<td>0.092</td>
</tr>
<tr>
<td>B</td>
<td>118</td>
<td>1.5</td>
<td>0.860</td>
<td>15</td>
<td>2.3</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Mn</td>
<td>3.5</td>
<td>7.5</td>
<td>0.469</td>
<td>4.5</td>
<td>11</td>
<td>0.522</td>
</tr>
</tbody>
</table>

† Standard error of the least squares means.

Fig. 2. Era hybrid plant Ca (a–e) and Mg (f–j) concentration for plant fractions across corn development stages. At each development stage, * indicates significant difference ($P \leq 0.05$) between eras.
Sulfur concentrations in stalks, leaves, tassels, ear shoots, and grain were not consistent across the development stages (Fig. 3a–3e). Sulfur concentrations were consistently lower for 2000-era hybrids in stalks, leaves, tassels, and grain at most development stages, and there was no difference between the 1960- and 2000-era hybrids in ear shoots at all stages and in cobs (Fig. 3a–3e, Table 1).

**Micronutrients**

There were Fe concentration peaks at R1 and R4 in the 1960-era hybrids in stalks, leaves, and tassels (Fig. 3f–3h). Although there was an inconsistent pattern across the development stages, Fe concentrations peaked at R6 in stalks, leaves, and ear shoots (Fig. 3f, 3g, 3i). In tassels, ear shoots, and grain, there was an inconsistent pattern across the development stages in both era hybrids (Fig. 3h–3j). Copper concentrations were consistently lower in 2000-era hybrids at most development stages in stalks, leaves, and tassels; there was no or only minimal difference between the 1960- and 2000-era hybrids in ear shoots, grain, and cobs (Fig. 3a–3e, Table 1).

In stalks, leaves, tassels, and ear shoots, there was no consistent pattern in Zn concentrations across the development stages (Fig. 3f–3j). Iron concentrations were lower in 2000-era hybrids at most development stages and in stalks, leaves, and tassels but not for ear shoots, grain, and cobs (Fig. 3f–3j, Table 1).

There was no consistent pattern in stalk Cu concentrations from V14 to R4, but peaked at R6 in 1960- and 2000-era hybrids (Fig. 4a). In leaves, Cu concentrations remained relatively constant from V14 to R6 (Fig. 4b). In tassels, ear shoots, and grain, there was an inconsistent pattern across the development stages in both era hybrids (Fig. 4c–4e). Copper concentrations were consistently lower in 2000-era hybrids at most development stages in stalks, leaves, and tassels; there was no or only minimal difference between the 1960- and 2000-era hybrids in ear shoots, grain, and cobs (Fig. 4a–4e, Table 1).

In stalks, leaves, tassels, and ear shoots, there was no consistent pattern in Zn concentrations across the development stages (Fig. 4f–4i). In grain, concentrations were consistent from R3 to R4, and then increased to R6 (Fig. 4j). Zinc concentrations in 2000-era hybrids were lower than 1960-era hybrids at all development stages, but only in leaves, whereas there was no difference between 1960- and 2000-era hybrids in cobs and most stages in stalks, ear shoots, and grain (Fig. 4f–4j and Table 1).
The Mn concentrations had a similar trend for the 1960- and 2000-era hybrids throughout the development stages (Fig. 5a–5e). In stalks, Mn concentrations remained constant across the development stages in 2000-era hybrids, while there were peaks at R2 and R4 in 1960-era hybrids (Fig. 5a). Leaf Mn concentrations tended to increase throughout the development stages (Fig. 5b). In tassels, ear shoots, and grain, there was an inconsistent Mn concentration pattern across the development stages (Fig. 5c–5e). Manganese concentrations were lower in the 2000-era hybrids than 1960-era hybrids at most development stages in stalks, leaves, and tassels, but differences only in a few stages in ear shoots and grain, and no difference in cobs (Fig. 5a–5e, Table 1).

Boron concentrations had a similar trend for the 1960- and 2000-era hybrids throughout the development stages (Fig. 5f–5j). In stalks, leaves, tassels, and ear shoots, there were inconsistent patterns across the stages in B concentrations (Fig. 5f–5i). In grain, there was a tendency of decline from R3 to R4 followed by no change to R6 in the 2000-era hybrids, and concentrations remained constant from R3 to R6 in 1960-era hybrids (Fig. 5j). There was no difference in B concentrations for 1960- and 2000-era hybrids at most development stages and all fractions except tassels (Fig. 5f–5j). In tassels, B concentrations were higher at R1 and R2 in 2000-era hybrids, but lower than the 1960-era hybrids at the beginning and later part of the development stages (Fig. 5h). Cob B concentrations were the same for 1960- and 2000-era hybrids (Table 1).

**Discussion of Nutrient Concentration**

For the secondary and micronutrients studied, concentrations remained constant from R3 to R6 in 1960-era hybrids (Fig. 5j). There was no difference in B concentrations for 1960- and 2000-era hybrids at most development stages and all fractions except tassels (Fig. 5f–5j). In tassels, B concentrations were higher at R1 and R2 in 2000-era hybrids, but lower than the 1960-era hybrids at the beginning and later part of the development stages (Fig. 5h). Cob B concentrations were the same for 1960- and 2000-era hybrids (Table 1).
was observed in Mg, S, and Cu. Iron concentrations tended to increase from R5 to R6 but there was no consistent pattern in Zn concentrations in leaves.

In tassels and ear shoots, there was an inconsistent pattern in concentrations of most secondary and micronutrients throughout the growing season. Grain S, Fe, and Cu concentrations tended to decrease in the beginning but increased at maturity, whereas Ca, Mg, and Zn concentrations were similar throughout the development stages or increased at maturity.

Concentration patterns across the development stages in all fractions were similar for 1960- and 2000-era hybrids for all secondary and micronutrients, with only a few exceptions. Nutrient concentrations were lower in 2000- than 1960-era hybrids in most plant fractions at most development stages. The trend of lower nutrient concentrations in most plant fractions across the development stages in 2000- than 1960-era hybrids is consistent with that reported by Woli et al. (2018) for N, P, and K. There are limited studies that report nutrient concentrations in corn plant fractions with which to compare. Of all plant fractions, nutrient concentrations in grain have been most commonly reported for a hybrid period. Across decades, grain N concentration has been often reported to decrease (Duvick and Cassman, 1999; Ciampitti and Vyn, 2013; Haegele et al., 2013; DeBruin et al., 2017; Woli et al., 2018). This is the first study that reports differences in grain concentrations of secondary and micronutrients between a four-decade period. Similar to the results for decreases in grain N, P, and K concentration over time (Woli et al., 2018), grain Mg, S, Cu, and Zn concentrations at R6 were lower in 2000- (1.0, 0.91 g kg⁻¹, 3.1, 18 mg kg⁻¹, respectively) compared with 1960-era hybrids (1.1, 1.05 g kg⁻¹, 3.5, 23 mg kg⁻¹, respectively); there was no difference between 1960- and 2000-era hybrids in Ca, Fe, B, and Mn concentrations (means of 0.56 g kg⁻¹, 20.5, 5.2, and 3.5 mg kg⁻¹, respectively). A study conducted in 2010 in Illinois (Bender et al.,...
2013) reported similar grain concentrations for Mg, S, Cu, Zn, and Fe (1.4, 1.2 g kg\(^{-1}\) and 3.4, 25.7, 20.7 mg kg\(^{-1}\), respectively), whereas much lower B concentration (1.6 mg kg\(^{-1}\)) and much higher Mn concentration (6.0 mg kg\(^{-1}\)), compared with our 1960- and 2000-era hybrids. Vyn and Tollenaar (1998) used six commercial hybrids in Ontario from 1959 and 1988 that were grown during 1986 and 1987, and reported that grain concentrations of Mg, Cu, and Mn were higher in the 1960s hybrids than in 1970s and 1980s, whereas concentrations of Ca and Zn were similar. Watson and Ramstad (1987) reported average concentrations for Cu, Zn, and Mn to be 4.0, 14.0, and 5.0 mg kg\(^{-1}\), which were higher than those reported by Vyn and Tollenaar (1998), but they were comparable with the findings of this study.

### Nutrient Accumulation Results

#### Secondary Nutrients

Whole plant Ca in both era hybrids peaked at R5 (44 and 54 kg Ca ha\(^{-1}\) for 1960- and 2000-era hybrids, respectively) (Fig. 6a). Stalk Ca content peaked at R2 (15 and 18 kg Ca ha\(^{-1}\), respectively, for 1960- and 2000-era hybrids) (Fig. 6b). Similar peaks at R1 for both era hybrids were found in leaves and tassels, and at R2 and R4 in ear shoots (Fig. 6c–6e). In grain,
Table 2. 1960- and 2000-era hybrid nutrient accumulation rates per cumulative Celsius-based growing degree days (GDD) for whole plant vegetative (V6–R1) and reproductive (R1–R6) periods, and for the grain-fill period (R1–R6). Means considered different at *P ≤ 0.05.*

<table>
<thead>
<tr>
<th>Era</th>
<th>Whole plant</th>
<th>Grain</th>
<th>Whole plant</th>
<th>Grain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca</td>
<td>Mg</td>
<td>Ca</td>
<td>Mg</td>
</tr>
<tr>
<td></td>
<td>g ha⁻¹ GDD⁻¹</td>
<td></td>
<td>g ha⁻¹ GDD⁻¹</td>
<td></td>
</tr>
<tr>
<td>1960</td>
<td>70</td>
<td>53</td>
<td>16</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>-5</td>
<td>0.2</td>
<td>6</td>
<td>0.04</td>
</tr>
<tr>
<td>2000</td>
<td>13</td>
<td>1</td>
<td>16</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>7.3</td>
<td>0.3</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>SE†</td>
<td>8</td>
<td>4</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>-0.01</td>
<td>0.01</td>
<td>0.143</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>0.04</td>
<td>0.143</td>
<td>0.03</td>
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<td></td>
<td>0.08</td>
<td>0.06</td>
<td>0.08</td>
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<td></td>
<td>0.16</td>
<td>0.03</td>
<td>0.16</td>
<td>0.03</td>
</tr>
</tbody>
</table>

† Standard error of the least squares means.

Ca accumulation continued to R6, with an increasing difference between era hybrids as development continued (Fig. 6f). Although there was no difference in whole plant Ca accumulation rates on a GDD basis between 1960- and 2000-era hybrids during the vegetative period (Table 2), differences in total Ca content were significant at most development stages (Fig. 6a). The pattern of Ca content was not consistent, however, in all plant fractions. Calcium content at R6 was greater in the 2000- than 1960-era hybrids in whole plant, stalks, leaves, cobs, and grain; but not tassels or ear shoots (Fig. 6a–6f, Table 1). The difference between era hybrids was greatest at later reproductive stages in whole plant, stalks, leaves, and grain (Fig. 6a, 6b, 6c, 6f). Whole plant Ca at R1 was 80 and 71% of the peak total at R5 for the 1960- and 2000-era hybrids, respectively (Fig. 6a).

Whole plant Ca accumulation rates per GDD during the reproductive growth were greater in 2000-era hybrids but they were not different between 1960- and 2000-era hybrids during the vegetative growth (Table 2). Grain Ca accumulation rates were greater for 2000- compared with 1960-era hybrids (Fig. 7a–7c). Whole plant Ca content peaked at R6 in 1960- and 2000-era hybrids (13 and 17 kg S ha⁻¹, respectively). Tassel Ca content peaked at R1 and ear shoot Ca content peaked at R2 in both era hybrids (0.8, 0.4 kg S ha⁻¹ and 2.3, 3.3 kg S ha⁻¹ in 1960- and 2000-era hybrids, respectively) (Fig. 7a–7e). There were inconsistent patterns in Ca content in stalks and leaves across the development stages in both era hybrids (Fig. 7b, 7c). Whole plant S content peaked at R6 in 1960- and 2000-era hybrids (Fig. 7a–7c). There were inconsistent patterns in S content in stalks and leaves across the development stages in both era hybrids (Fig. 7b, 7c). Whole plant S accumulation rate was greater for the 2000-era hybrids compared with 1960-era hybrids (Table 2). There was a tendency of decline in S content at R3 in whole plant, stalks, leaves, and ear shoots and at R2 in tassels in both 1960- and 2000-era hybrids (Fig. 7a–7e). There were inconsistent patterns in S content in stalks and leaves across the development stages in both era hybrids (Fig. 7b, 7c). Whole plant S content was not different between 1960- and 2000-era hybrids during the reproductive period (Table 2). Grain S accumulation rates were greater for 2000- compared to 1960-era hybrids (Table 2).

Micronutrients

Across the development stages, whole plant and grain Fe content tended to increase to R6 in most cases (Fig. 7g, 7h). The whole plant, stalks, leaves, and grain Fe content was greatest at R6 (1316 and 1949 g Fe ha⁻¹, 377 and 418 g Fe ha⁻¹, 676 and 1108 g Fe ha⁻¹, 167 and 245 g Fe ha⁻¹ in 1960- and 2000-era hybrids, respectively) (Fig. 7g, 7h, 7i, 7l). There was no consistent pattern for the difference in Fe content for 1960- and 2000-era hybrids (Fig. 7d). Whole plant Fe content peaked at R6 in 1960- and 2000-era hybrids (13 and 17 kg S ha⁻¹, respectively). The accumulation rates of grain Mg were greater for 2000- compared with 1960-era hybrids (Table 2).

Whole plant Mg content was greater for 2000-era hybrids at most development stages (Fig. 6g). Differences in total Mg accumulation rates were significant only at the vegetative periods (Table 2). Magnesium content at R6 was greater in the 2000- than 1960-era hybrids in whole plant, leaves, cobs, and grain but not stalks, tassels, and ear shoots (Fig. 6g–6l, Table 1). Whole plant Mg Mg accumulation rates per GDD were greater during the vegetative period in 2000-era hybrids, whereas there was no difference between the era hybrids during the reproductive period (Table 2). The accumulation rates of grain Mg were greater for 2000- compared with 1960-era hybrids (Table 2).

There was no difference in whole plant Fe accumulation rates on a GDD basis between 1960- and 2000-era hybrids (Fig. 7a–7e). There were inconsistent patterns in S content in stalks and leaves across the development stages in both era hybrids (Fig. 7b, 7c). Whole plant Mg content peaked at R1 was 79 and 75% of the peak total at R5, respectively, for the 1960- and 2000-era hybrids (Fig. 6g). Whole plant Mg accumulation rates per GDD were greater during the vegetative period in 2000-era hybrids, whereas there was no difference between the era hybrids during the reproductive period (Table 2).
Fe accumulation rates during the reproductive growth period were greater in 2000-era hybrids but the rates were not different between 1960- and 2000-era hybrids during the vegetative period (Table 2). Grain Fe accumulation rates were greater for 2000- compared with 1960-era hybrids (Table 2).

The pattern of Cu content in whole plant, and all fractions except grain, across the development stages was inconsistent in both 1960- and 2000-era hybrids (Fig. 8a–8f). Tassel Cu content at R2 in 2000-era hybrids was nearly zero, possibly due to a sampling error. In whole plant and grain, Cu content increased to R6 but there was a decline at R4 in both 1960- and 2000-era hybrids in whole plant (Fig. 8a, 8f). The stalk and grain Cu content peaked at R6 (26 and 29 g Cu ha$^{-1}$; 28 and 39 g Cu ha$^{-1}$), whole plant and leaves at R5 (89 and 111 g Cu ha$^{-1}$; 31 and 35 g Cu ha$^{-1}$), tassels at R1 (3 and 2 g Cu ha$^{-1}$), and ear shoot at R2 (14 and 19 g Cu ha$^{-1}$) in 1960- and 2000-era hybrids, respectively. There was no consistent pattern of the difference in Cu content for 1960- and 2000-era hybrids in stalks and ear shoot (Fig. 8b, 8e). In whole plant, leaves, and grain, Cu content was greater in 2000- compared with 1960-era hybrids at most development stages (Fig. 8a, 8c, 8f). In tassels, Cu content was smaller in 2000- compared with 1960-era hybrids, but
the difference was significant only at VT, R1, and R2 (Fig. 8d). Cob Cu content was not different between 1960- and 2000-era hybrids (Table 1). Whole plant Cu at R1 was 67 and 60% of the peak total at R6, respectively, for the 1960- and 2000-era hybrids (Fig. 8a). There was no difference in whole plant Cu accumulation rates between 1960- and 2000-era hybrids at both the vegetative and reproductive periods (Table 2), although differences in total Cu content were significant at most development stages (Fig. 8a). Grain Cu accumulation rates were greater for 2000- compared with 1960-era hybrids (Table 2).

Whole plant Zn content tended to increase across the development stages to R6. The pattern of Zn content in all fractions except whole plant and grain across the development stages was inconsistent in both 1960- and 2000-era hybrids (Fig. 8g–8l). In whole plant, Zn content peaked at R5 (263 and 366 g Zn ha$^{-1}$) and in grain at R6 (178 and 230 g Zn ha$^{-1}$) in 1960- and 2000-era hybrids, respectively (Fig. 8g). Stalks and ear shoots peaked at R2 (52 and 69 g Zn ha$^{-1}$), 53 and 77 g Zn ha$^{-1}$) and leaves and tassels at R1 (56 and 70 g Zn ha$^{-1}$; 19 and 15 g Zn ha$^{-1}$) in 1960- and 2000-era hybrids, respectively (Fig. 8h–8k). In whole plant, stalks, leaves, and grain, Zn content was greater in 2000- compared with 1960-era hybrids at most development stages (Fig. 8g, 8h, 8i, 8l). In tassels, Zn content was smaller in 2000- compared with 1960-era hybrids, but the difference was significant only at V14 through R1 (Fig. 8j). Cob Zn content was not different between 1960- and 2000-era hybrids (Table 1). Whole plant Zn at R1 was 58 and 49% of the peak total at R5, respectively, for the 1960- and 2000-era hybrids (Fig. 8g). Although differences in total Zn content were significant at most development stages, there was no difference in whole plant Zn accumulation rates per GDD between 1960- and 2000-era hybrids in both the vegetative and reproductive periods (Table 2) (Fig. 8g). Grain Zn accumulation rates were greater for 2000- compared with 1960-era hybrids (Table 2).

Whole plant Mn peaked at R4 in 1960- (361 g Mn ha$^{-1}$) and at R5 in 2000-era hybrids (344 g Mn ha$^{-1}$) (Fig. 9a). The stalk Mn content peaked at R4 in 1960- (155 g Mn ha$^{-1}$) and R2 in 2000- (134 g Mn ha$^{-1}$) era hybrids (Fig. 9b). In leaves, Mn content peaked at R5 (146 and 150 g Mn ha$^{-1}$), but in tassels peaked at R1 (13 and 7 g Mn ha$^{-1}$) in 1960- and 2000-era hybrids, respectively (Fig. 9c, 9d). Manganese content in ear shoots peaked at R3 (36 g Mn ha$^{-1}$) in 1960- and at R2 (45 g Mn ha$^{-1}$) in 2000-era hybrids (Fig. 9e), whereas grain Mn content peaked at R6 (30 and 39 g Mn ha$^{-1}$) in 1960- and 2000-era hybrids, respectively (Fig. 9f). Manganese content for 1960- and 2000-era hybrids was not different in stalks, leaves, and ear shoots at most development stages (Fig. 9b, 9c, 9e). In tassels, Mn content was smaller in 2000- compared with 1960-era hybrids at most development stages (Fig. 9d). Whole plant Mn at R1 was 81% of the peak at R4 in 1960- and 69% of the peak at R6 in 2000-era hybrids (Fig. 9a). Although there was no difference in total Mn content at all development stages, accumulation rates were greater in 2000- compared with 1960-era hybrids for the reproductive period (Fig. 9a, Table 2). Whole plant Mn accumulation rates per GDD were greater in 2000-era hybrids during the reproductive growth, whereas the accumulation rates were not different in 1960- and 2000-era hybrids during the vegetative growth (Table 2). Grain Mn accumulation rates were not different for 2000- and 1960-era hybrids (Table 2).

The pattern of B content in all fractions except whole plant and grain across the development stages was inconsistent in both 1960- and 2000-era hybrids (Fig. 9g–9i). In whole plant and grain, B content peaked at R6 (132 and 186 g B ha$^{-1}$) in whole plant and R2 (648 and 641 g B ha$^{-1}$) in grain) in 1960- and 2000-era hybrids, respectively (Fig. 9g, 9i). Stalk B content peaked at R6 (42 and 51 g B ha$^{-1}$), but leaf B content remained constant after the peak at R1 (27 and 40 g B ha$^{-1}$) in 1960- and 2000-era hybrids, respectively (Fig. 9h, 9j). Tassel B content peaked at R1 (7 and 6 g B ha$^{-1}$), and ear shoot B content first peaked at R3 (33 and 31 g B ha$^{-1}$) in both 1960- and 2000-era hybrids, respectively (Fig. 9j, 9k). In whole plant and all fractions including cobs, B content was greater in 2000- compared with 1960-era hybrids at most development stages except tassels (Fig. 9g–9l, Table 1). In stalks, B content was smaller in 2000- compared with 1960-era hybrids at most development stages (Fig. 9j). As found in whole plant B content, accumulation rates were also greater in 2000-era hybrids for both the vegetative and reproductive periods (Fig. 9g, Table 2). Whole plant B at R1 was 59 and 53% of the peak total at R6, respectively, for the 1960- and 2000-era hybrids (Fig. 9g). Whole plant B accumulation rates per GDD were greater in 2000-era hybrids during both the vegetative and reproductive periods (Table 2). Grain B accumulation rates were greater for 2000- compared with 1960-era hybrids (Table 2).

**Discussion of Nutrient Accumulation**

In the 1960- and 2000-era hybrids, content of all secondary and micronutrient in grain tended to increase from R3 to R6 and in whole plants S, Fe, and B increased from V6 to R6. On the other hand, the content of Ca, Mg, Cu, Zn, and Mn in whole plants tended to increase from V6 to R5 and then decreased at R6 in both era hybrids. Similar results of a gradual increase in nutrient content until plant maturity in whole plant P, grain N, P, and K and a decrease after R5 to R6 in whole plant N and K were reported in some recent and past studies (Hanway, 1962; Karlen et al., 1988; Bender et al., 2013; Woli et al., 2018).

In stalks in both era hybrids, although all secondary and micronutrient content tended to increase during early vegetative growth and decreased at early reproductive stages, only S, Fe, Cu, and B tended to increase to R6, whereas Ca, Mg, Zn, and Mn decreased to R6. The pattern of secondary and micronutrient accumulation across the development stages in leaves, tassels, and ear shoots was not consistent in both 1960- and 2000-era hybrids. However, a similar pattern of decreasing nutrient content at the late reproductive stages in stalks and ear shoots in all nutrients and in leaves in all nutrients except Fe and B was observed. The pattern of Ca, Mg, Cu, Zn, and Mn in whole plant, stalks, leaves, tassels, and ear shoots across the development stages are consistent with the DM patterns of whole plant and fractions reported by Woli et al. (2018).

Previous studies reported that at maturity, grain contained about two-thirds of the total plant N and P (Sayre, 1948; Hanway, 1962; Woli et al., 2018). For both era hybrids, a similar proportion of total plant content in grain S and Zn was found in this study, whereas approximately only one-third of the total plant Mg, Cu, and B was contained in grain. That proportion
was consistent with the results for total plant K reported by Woli et al. (2018) for the same era hybrids. On the other hand, grain contained approximately one-sixth or less of the total plant Ca, Fe, and Mn.

The whole plant R1 stage content of Ca, Mg, S, Fe, Cu, Zn, B, and Mn, relative to the peak at R5 or R6, was consistently lower for 2000-era hybrids (71, 75, 57, 47, 60, 49, 53, and 69%, respectively) compared with 1960-era hybrids (80, 79, 65, 77, 67, 58, 59, and 81%, respectively) (data not shown). Of the secondary and micronutrients, there was a smallest proportion of whole plant R1 stage or vegetative Fe content (47%) compared with that at maturity in 2000-era hybrids, which was much greater in the 1960-era hybrids (77%) (data not shown). The vegetative Fe contents found in our study in either era hybrids were small compared with that reported for recent hybrids (91% of plant total at R6) by Bender et al. (2013), but for all other nutrients were comparable to that reported by Bender et al. (2013). The result reported by Ciampitti and Vyn (2013) at the whole plant R1 stage compared to plant maturity in recent hybrids for Mg, Fe, Zn, and Mn (73, 51, 47, and 73% of the whole plant at R6, respectively) are comparable with our findings for the 2000-era

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*Fig. 8. Era hybrid plant Cu (a–f) and Zn (g–l) content for whole plant and fractions across corn development stages. At each development stage, * indicates significant difference (P ≤ 0.05) between eras.*
hybrids; while those reported by Ciampitti and Vyn (2013) were much greater for Ca and Cu (91 and 73%, respectively).

All secondary and micronutrient accumulation rates per GDD were consistently greater during the vegetative growth compared with the reproductive growth and grain production. Accumulation rates per GDD of Ca, S, Fe, Mn, and B during the reproductive growth were greater in 2000- compared with 1960-era hybrids. All grain nutrient accumulation rates, except Mn, were greater in 2000- than in the 1960-era hybrids.

The Ca, Mg, Zn, and Mn contents in stalks and in most secondary and micronutrients in tassels and ear shoots at the late reproductive stages are consistent with those reported by Woli et al. (2018), Hanway (1962), and Karlen et al. (1988) for N, P, and K. The calculated remobilized nutrients from vegetative to reproductive components (Table 3) were positive for secondary and micronutrients in both 1960- and 2000-era hybrids, except were negative for Fe and B, and negative for Mn in 2000-era hybrids, indicating translocation of nutrients into the developing ear shoot and then to the grain for most nutrients except Fe, B, and Mn.

Some nutrients such as N and K have high relative mobility, allowing them to be assimilated in one location, and then later remobilized to another tissue (Bender et al., 2013; Woli et al., 2018).
The potential need of more fertilization with greater nutrient content and removal with harvest will vary by the specific soil system's ability to supply adequate secondary and micronutrients. A recommendation would not be to generally add development stages, although similar between era hybrids, was not the same for all nutrients. Like the decrease in grain N, P, and K concentrations reported in prior research across hybrid eras, Mg, S, Cu, and Zn concentrations in grain were lower in 2000- compared with 1960-era hybrids. However, concentrations of Ca, Fe, B, and Mn in grain for 1960- and 2000-era hybrids were different. Differences in leaf nutrient concentrations between 1960- and 2000-era hybrids were greatest for Ca, Mg, S, Cu, Zn, Mn and Mn, but little to no difference was found for Fe and B. In stalks, concentration differences between era hybrids were greatest for Mg and Mn; in tassels, differences were greatest for Ca, Fe, and Mn; and in ear shoots and cob, little to no difference was found for all nutrients studied.

Secondary and micronutrient content in grain for both era hybrids increased from R3 to R6, concurrent with DM accumulation. Although the whole plant nutrient content increased across development stages, there was no consistent pattern between nutrients and for several nutrients reached a maximum content at the R5 stage. For both the 1960- and 2000-era hybrids, grain contained about two-thirds of the whole plant S and Zn, about one-third of Mg, Cu, and B, and only one-sixth of Ca, Fe, and Mn. The calculated remobilized nutrients were positive for most secondary and micronutrients, except Fe and B in both 1960- and 2000-era hybrids, and Mn in the 2000-era hybrids. This remobilization indicates translocation of some accumulated nutrients to reproductive components.

Total plant content of all nutrients studied, except Mn, was greater in 2000- compared with 1960-era hybrids, despite the mostly lower concentrations in the 2000-era hybrids. Secondary and micronutrient content was also greater in the 2000- compared with 1960-era hybrids in most plant fractions, except tassels where nutrient content was smaller. This is a similar pattern previously found for DM. Also, nutrient accumulation rates per cumulative GDD for the whole plant vegetative R1–R6, and grain-fill periods were greater in 2000- compared with 1960-era hybrids for all nutrients except Mg and Zn in the whole plant, but not different between era hybrids in the V6–R1 vegetative period (Mg and B the exceptions).

As found for the macronutrients, secondary and micronutrient content in newer hybrids was mainly due to increased nutrient uptake rate and DM accumulation, especially in grain. Nutrient removal in grain harvest would be increased with newer hybrids; however, the amount would still be small, approximately 7 to 12 kg ha⁻¹ for the secondary nutrients and in the 39 to 245 g ha⁻¹ range for the micronutrients. The fraction of total plant nutrient in vegetative plus cob material at R6 varied greatly between nutrients, ranging from 34 to 84% for secondary nutrients and 37 to 87% for micronutrients. Therefore, the impact of grain vs. stover harvest on potential secondary or micronutrient removal in modern hybrids would need to be determined individually for yield and specific nutrient. In addition, the negative remobilization for some micronutrients (Fe, Mn, and B), and the low percentage of total plant nutrients in grain, most notably Ca, Fe, and Mn, have implications for nutritional quality of modern hybrid corn grain.

### Table 3. Amount of nutrients remobilized from the vegetative to reproductive components for the 1960- and 2000-era hybrids. Means considered different at \( P \leq 0.05 \).

<table>
<thead>
<tr>
<th>Era</th>
<th>Ca</th>
<th>Mg</th>
<th>S</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Mn</th>
<th>B</th>
<th>SE†</th>
<th>P &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1960</td>
<td>7.6</td>
<td>8.2</td>
<td>3.8</td>
<td>–151</td>
<td>5.8</td>
<td>56</td>
<td>37</td>
<td>–4.8</td>
<td>0.050</td>
<td>0.499</td>
</tr>
<tr>
<td>2000</td>
<td>1.8</td>
<td>10</td>
<td>3.8</td>
<td>–769</td>
<td>7.2</td>
<td>82</td>
<td>–16</td>
<td>–6.8</td>
<td>0.002</td>
<td>0.812</td>
</tr>
<tr>
<td></td>
<td>3.8</td>
<td>1.4</td>
<td>0.5</td>
<td>123</td>
<td>8.9</td>
<td>22</td>
<td>22</td>
<td>24</td>
<td>0.097</td>
<td>0.959</td>
</tr>
</tbody>
</table>

† Standard error of the least squares means.

CONCLUSIONS

Overall, the pattern of change in concentration for secondary and micronutrients across corn development stages were similar for the 1960- and 2000-era hybrids. However, concentrations in plant fractions were mostly lower in the 2000-era hybrids. Also, the increase or decrease in nutrient concentrations across...
secondary or micronutrients to all fields just because corn uptake and removal with harvest may be greater with modern hybrids; instead, follow appropriate application guidelines developed in respective states or regions. What is important to know is: (i) whether or not plant component concentrations have decreased, and then if tissue critical test levels should be re-investigated; and (ii) are there corn yield responses to secondary or micronutrients occurring now that may have not been before. Therefore, rather than a suggestion to simply apply secondary or micronutrients, correlation or calibration of nutrient composition should be investigated due to the potential effect of greater removal with modern hybrids.

ACKNOWLEDGMENTS

We express our sincere thanks to DuPont Pioneer for providing the era hybrid seed. We also would like to thank Nick Kastler, Wade Kent, Stephanie Bowden, and Liz Boyer for processing samples and helping determine appropriate plant populations, to Donald Duvick (deceased) for selecting hybrids for the eras that would be representative, and to Paul White and the Iowa State University Corn Breeding Group for their time and equipment used for planting and mechanically harvesting corn.

REFERENCES


