Composition and thermal properties of starch in flint maize (*Zea mays*, L.) kernels: location and crop management effects

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ABSTRACT

Flint maize kernels are processed by the dry-milling industry to produce the flaking grits used thereafter in the corn flakes industry. Flaking-grit yield during milling depends on kernel hardness whereas corn flakes production involves starch gelatinization. Starch composition influences both characteristics of maize kernels. The objective of this work was to analyze the effect of different crop environments and management practices on starch composition of kernels and its thermal properties. Two flint maize hybrids (Cóndor and Morgan, 306) were grown at three locations (Balcarce, Pergamino and Paraná, located in a latitudinal transect of 6°) with different plant densities (7.5 and 9 plants/m^2), sowing dates (early and late), and fertilizing rates (with and without additional N and S-fertilizer near silking) during two growing seasons (2003-2004 and 2004-2005). Crop biomass accumulated from silking to physiological maturity was measured and mean kernel weigh was calculated at harvest. Kernel hardness was estimated by mean of the test weight and percent floaters. Amylose and starch concentration in kernels were determined. Starch thermal properties were analyzed by differential scanning calorimetry and endotherm parameters were calculated. Cropping conditions modified starch composition of kernels. Amylose/starch ratio decreased as air temperature decreased from the north to the south and by delaying sowing date. Deposition of amylose in the endosperm of the kernels increased as growing conditions for crop growth improved during kernel filling. Starch thermal properties were also modified by these changes in starch composition. The onset and peak temperatures, gelatinization enthalpy, and peak height index were positively associated with amylose concentration and amylose/starch ratio, whereas the gelatinization temperature range was negatively associated with both kernel attributes. The results reported herein would contribute to foresee the effect of location and agricultural practices on kernel quality of flint maize, and to make appropriated management adjustments to obtain a product that meets the market needs.

Keywords: flint-maize, kernel hardness, starch composition, starch thermal properties.

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RESUMEN

Los granos de maíz flint son procesados por la industria de la molienda seca para producir los flaking grits que son utilizados luego en la industria de corn flakes. El rendimiento de flaking grits durante la molienda depende de la dureza del grano, mientras que la producción de corn flakes involucra la gelatinización del almidón. La composición del almidón influencia ambas características del grano de maíz. El objetivo de este trabajo fue analizar el efecto de diferentes ambientes de producción y prácticas de cultivo sobre la composición del almidón y sus propiedades térmicas. Dos híbridos de maíz flint (Cóndor y Morgan, 306) fueron cultivados en tres localidades (Balcarce, Pergamino y Paraná, ubicadas en una transecta latitudinal de 6°) con diferentes densidades de plantas (7,5 y 9 plantas/m^2), fechas de siembra (temprana y tardía), y dosis de fertilización (con y sin agregado adicional de fertilizante con N y S cerca de la floración) durante dos campañas agrícolas (2003-2004 y 2004-2005). Se midió la biomasa acumulada desde floración hasta madurez fisiológica y se estimó el peso medio del grano en la cosecha. La dureza del grano se estimó a través del peso hectolítrico y el porcentaje de flotación. Se determinó la concentración de amilosa y almidón. Las propiedades térmicas del almidón se evaluaron por calorimetría diferencial de barrido y se estimaron los parámetros de las endotermas. Las condiciones de crecimiento modificaron la composición del almidón de los granos. La relación amilosa/almidón se redujo a medida que la temperatura del aire descendió de norte a sur y por retraso de la siembra. La deposición de amilosa en el endosperma de los granos aumentó cuando las condiciones para el crecimiento del cultivo mejoraron durante el llenado de los granos. Las propiedades térmicas del almidón también se modificaron con estos cambios en la composición del almidón. Las temperaturas de inicio y pico de gelatinización, la entalpía de gelatinización y el índice de altura de pico se asociaron positivamente con la concentración de amilosa y la relación amilosa/almidón, mientras que el rango de temperatura de gelatinización se asoció negativamente con ambos atributos del grano. Los resultados aquí reportados pueden contribuir a prever los efectos de la localidad y prácticas de cultivo sobre la calidad de maíz flint y hacer los ajustes de manejo del cultivo apropiados para obtener un producto final que satisfaga las necesidades del mercado.

***Palabras clave:** maíz flint, dureza de grano, composición del almidón, propiedades térmicas del almidón.*

INTRODUCTION

Dry-milling industry processes kernels of maize to provide the flaking grits used in the corn flakes industry (Orthoefer and Eastman, 2004). Flaking-grit yield during milling depends on kernel hardness. Flaking-grit yield of flint maize is greater than those of dent or semi-dent maize because of higher kernel hardness. Kernel hardness is related to the proportion of horny endosperm of higher density (Kljak *et al.*, 2018). Robutti *et al.* (2000) reported that the horny endosperm presented higher amylose concentration than the floury endosperm. Kernel endosperm is mainly composed of protein and starch. Starch represents ~70% of the maize endosperm and it consists of two types of carbohydrate chains, amylose and amylopectin. Amylose is predominantly composed of linear chains of glucans, whereas amylopectin has branched chains. The starch is contained in granules immersed in the protein matrix of the endospermic cells (Sabelli and Larkins, 2009). Endosperms with high amylose/starch ratio are more compressible by the protein matrix during grain-filling period and therefore become denser and harder at harvest than endosperms with a high proportion of amylopectin (Dombrink-Kurtzman and Knutson, 1997). In turn, flaking grits obtained by the dry-milling industry are cooked in boiling syrup to elaborate the corn flakes. Through this procedure, the flaking grits achieve a softening and translucent aspect as the result of water intake and starch gelatinization (Fast, 2001; Farroni and Buera, 2012). Resulting gelatinized grits are then immediately pressed and toasted and, after that, the resulting corn-flakes become ready for packing (Johnson *et al*., 2011). It would be expected that differences in starch composition will also modify the onset, extend, and energy requirement of the gelatinization process and, then, would affect the energy requirement for cooking during the elaboration of corn flakes.

The starch composition is an heritable attribute of maize kernels (Robutti *et al*., 2000; Sandhu *et al*., 2005; Chen *et al*., 2006; Liu *et al*., 2006; Srichuwong and Jane, 2007; Popescu *et al*., 2010; Ali *et al*., 2016). Kernel starch composition may vary depending on the type of maize. The normal maize starch contains ~23-25% of amylose, but there is a broad range among maize types. In fact, while the waxy maize has only ~0-1% of amylose, the amylose-extender maize presents ~50-70% of amylose (Singh *et al*., 2005). The cropping conditions also affect starch composition of maize kernels. Recently, Martinez *et al*. (2017) reported crop environment and management effects on starch composition of kernels for maize hybrids of different hardness. In turn, genotype (Ji *et al*., 2003; Scott and Duvick, 2005; Tziotis *et al*., 2005) and environment (Ng *et al*., 1997; Ji *et al*., 2004a; Lenihan *et al*., 2005; Lu *et al*., 2014) effects on the starch structure and thermal properties were reported in the literature. Nevertheless, there is still scarce information about the influence of the environment and the cropping conditions on starch composition of maize kernels and its thermal properties. The objective of this work was to analyze the effect of locations and crop management practices on starch composition and its thermal properties in two commercial orange-flint hybrids grown in the main maize-production area of Argentina.

MATERIALS AND METHODS

Field experiments

Two commercial hybrids of flint maize were evaluated: (i) Cóndor (from Syngenta Agro S.A.), which is a modern hybrid with high grain yield potential but with unstable flint-type expression, and (ii) Morgan 306 (from Dow AgroSciences S.A.), which is an old hybrid with limited grain yield potential but with strong flint-type expression. Field experiments were conducted in the Argentina's main maize-production area. We selected three representative locations along a south to north transect: (i) Balcarce (latitude 37° 50' S, longitude 58°15' W) with the lowest thermal and radiation conditions; (ii) Pergamino (latitude 33° 53' S, longitude 60°34' W), with intermediate temperature and radiation levels; and (iii) Paraná (latitude 31°43' S, longitude 60°32' W), with the highest temperature and radiation regimes. Experiments were conducted during two cropping seasons (2003–2004 and 2004–2005). Four different crop management treatments were imposed at each location: (i) *control*: early sowing date (mid-October) with a population of 7.5 plants/m^2; (ii*) high density*: early sowing date (mid-October) with a population of 9 plants/m^2; (iii) *refertilization*: early sowing date (mid-October) with a population of 7.5 plants/m^2 and nitrogen (N, 10 g/m^2) and sulfur (S, 4 g/m^2) addition to the soil at pre-silking (at V_{15} to V_T crop stage; Ritchie *et al*., 2008); and (iv) *late sowing*: late sowing date (mid-December; except for Paraná in the second season when sowing took place on January 3rd) with 7.5 plants/m^2. At each location, treatments were arranged in a split-plot design with three replicates. Crop management treatments were assigned to the main plots and the hybrids to the sub-plots. In all experiments, each sub-plot had 35 m^2 (5 rows, 0.70 m apart, and 10 m long). Every plot was fertilized at the crop stage V_6 (Ritchie *et al*., 2008) with 4 to 8 g N/m^2 (source: urea) according to local expert estimates for maize production. Phosphorus fertilizer was also added into the top layer of the soil by pre-sowing application of 3 g P/m^2 (source: calcium triple super-phosphate). Potassium soil levels were naturally high at all evaluated locations. Insects, weeds, and diseases were appropriately controlled. Plots were hand-planted at three seeds per hill, and thinned to the desired plant population at V_3 (Ritchie *et al*., 2008). Water stress was prevented by means of sprinkler irrigation, keeping available soil water content over 50% in the uppermost 1 m of soil throughout the growing season. Rain accumulation throughout the crop growing cycle ranged across locations from 422 to 644 mm for the early sowings and from 270 to 951 mm for the late ones. Daily rain, mean air temperature and incident solar radiation data were obtained from standard weather stations installed not farther than 500 m from each experimental site.

Kernel weight, post-silking biomass and source-sink ratio

At harvest time, all plant ears in 4 m of each of the three central rows were sampled in each plot (total surface: 8.4 m^2). Resulting kernel samples were weighed, their moisture was determined, and the weight was corrected to kernel moisture of 140 g/kg and expressed by m^2. Kernel weight (KW) in dry basis (db) was determined by weighing samples of 500 kernels per plot, previously dried at 60-65ºC for 20 days until constant weight. Kernel number (KN) per unit area was calculated as the quotient between grain yield expressed in db and KW. Post-silking biomass (BIOM) accumulation was determined by taking plant samples at silking (i.e., when 50% of the plants reached silking) and physiological maturity (i.e., when 50% of the plants reached 75% milk line in kernels from the mid portion of ears) from the three central rows of each plot. The sample size was 10 plants per plot, leaving appropriate border rows and border plants within the sampled rows. Plants were cut at ground level, grinded, dried in an air-forced oven at 60-65ºC for 10 days and weighed. Mean plant weight of samples and plant density were used to calculate dry matter per square meter. Post-silking biomass accumulation was calculated as the difference between biomass at physiological maturity and at silking. Post-silking source-sink ratio (SSR; in mg/kernel) was calculated as the ratio between BIOM accumulation and KN per unit area. The source-sink ratio was used as an estimator of photo-assimilates availability per growing kernel during grain-filling period.

Kernel hardness estimation

Kernel hardness was estimated by the determination of test weight (TW) and percent floaters (PF) in pooled samples from each experimental unit. Test weight was determined in kernel samples of ≈400 g from each harvested plot, using a Tripette & Renaud TR-77400 instrument. Values were expressed in kg/hl. Higher TW values are generally related to flintier kernels (Robutti *et al*., 2000). Percent floaters values were determined according to Lepes *et al*. (1976). One hundred of whole kernels from each harvested plot were placed in a 250 ml beaker with ≈170 ml of carbon tetrachloride and kerosene mixture with a 1.305 g/cm^3 density at 25ºC. After being briefly stirred with a glass rod, the floating kernels were counted. Values were expressed in percentage. Lower values of this test indicate flintier kernels (Robutti *et al*., 2000).

Amylose and starch determination

Amylose (Am, %) and starch concentration (St, %) in kernels were determined by spectrophotometry. The Knutson (1986) method modified by Robutti et al. (2000) was used for amylose determination. Starch was solubilized in dimethylsulfoxide (DMSO) at 70ºC during 48 hr. Absorbance of amylose-iodine complex was measured at 600 nm. Starch concentration in kernel was analyzed by the method of Dubois et al. (1956) and absorbance for starch was measured at 490 nm. Single measurements for both variables were performed on pooled samples from each harvested plot and results were expressed in db. Amylose/starch ratio (Am/St, %) was calculated as the quotient between both variables. The amylose (Am, mg) and starch content (St, mg) per kernels was obtained by multiplying their concentration by the mean KW (data of KW was reported in Cirilo *et al*., 2011).

Starch thermal properties measurement

Differential scanning calorimetry (DSC) methodology was used to analyze starch thermal properties (Seetharaman *et al*., 2001; Yu and Christie, 2001; Ai and Jane, 2018) on pooled samples for each harvested plot from the field experiments. A DSC Perkin-Elmer Pyris 6 (Perkin-Elmer, Norwalk, CT) was used. Starch extraction was performed according to the procedure described by White *et al*. (1990) procedure with modifications introduced by Ji *et al*. (2004b). Briefly, five whole mature kernels were selected and incubated in 15 ml tubes with 2 ml of sodium metabisulfite 0.45% w/v at 45°C for 48 ± 4 hr. Then, the germ and pericarp were manually extracted using bistoury and histology nippers. Endosperms were placed in 50 ml centrifuge tubes with 25 ml of distilled water and were homogenized in a tissue homogenizer (Ultra-Turrax T25, 600 W, Tekmar, Cincinnati, OH) at 1,600 rpm in two periods of 30 sec. Then, the homogenized liquid was filtered through a 30 µm pore size nylon membrane. The preparation was decanted in a 250 ml beaker at 4ºC during 2 hr. After that, water was discharged, and starch was dried at room temperature for 4 hr under fan air current. Finally, the starch was removed with a spatula and it was temporarily stored in glass vials. Starch samples (3 to 6 mg) were weighted on aluminum pans and water was added at 1:2 starch/water ratio. Pans were sealed and allowed to stand for 30 min at room temperature. A linear temperature gradient from 30 to 120ºC at a heating speed of 10ºC/min was used for starch gelatinization and corresponding endotherms were obtained. Previously, Indio and Zinc standards were used to calibrate the equipment. Thermograms were analyzed using Pyris software for Windows (v2.04, Perkin-Elmer, Norwalk, CT) to characterize starch thermal properties: gelatinization onset temperature (T_{oG}) is the temperature at which the gelatinization process starts; gelatinization peak temperature (T_{pG}) is the temperature at which the process achieves its maximum; gelatinization enthalpy (DH_G) was calculated from area under the endotherm curve and is the amount of energy needed to complete the gelatinization process; gelatinization range (R_G) is the range of temperatures over which gelatinization occurs and was calculated as $2^*(T_{pG} - T_{oG})$. Narrow values for R_G would reveal that the granule size distribution is homogeneous and hence starch gelatinization progress rapidly. In turn, lower values for T_{oG} as well as for DH_G indicate less energy required for starch gelatinization. The gelatinization peak temperature (T_{pG}) indicates the change of state for the starch, and the peak height index (PHI), expressed as the ratio between the energy needed and the half of the temperature range for the process, gives a measure of the

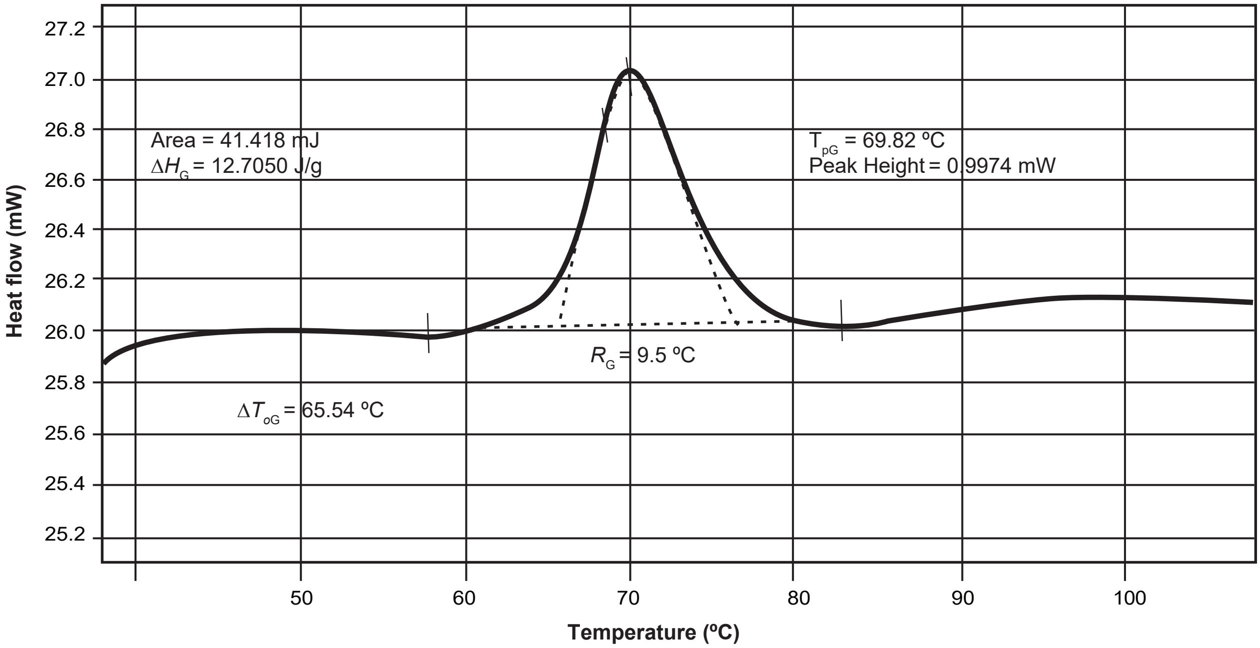

Figure 1. Starch gelatinization endotherm corresponding to hybrid Cóndor grown under the control management at Pergamino in the 2003-04 growing season. A linear temperature gradient at a heating speed of 10ºC/min was used. The bold line represents the heat flow during the process. Dotted lines indicate the software simplification over the curve to make parameter calculations.

uniformity of starch gelatinization (Krueger *et al.*, 1987). figure 1 shows an example of an endotherm graph obtained during starch gelatinization of a sample.

Statistical analysis

Combined analysis of variance over locations and years were made to evaluate the effects of hybrids, locations, crop managements and their interactions on the response variables. Locations and years were assumed as fixed effects in the analyses. The Tukey's test ($p<0.05$) was used for mean comparisons. Partial correlation coefficients among variables were calculated. All statistical analyses were performed using the InfoStat statistical software (Di Rienzo *et al.*, 2012).

RESULTS

Air temperature and incident solar radiation during grain-filling period at the field

Mean temperature and mean daily incident radiation during the grain-filling period (from silking to physiological maturity) varied according to location and sowing dates (table 1). For more details view Cirilo *et al.* (2011).

Crop post-silking biomass and source-sink ratio

Growth location and crop management significantly affected the BIOM, no significant differences between hybrids were found. Mean values for this variable were higher at Pergamino compared to the northern and southern locations (1437 vs.1074 g/m^2 for Pergamino and the other locations, respectively). Late sowing date markedly decreased crop dry matter accumulation from silking to physiological maturity. Post-silking biomass accumulated in late sown plots reached nearly 60% of that corresponding to early sown ones (797 vs.1328 g/m^2 for late and early sowings, respectively). This effect was more noticeable during the second season because of the unusual behavior of late sown crops at Paraná. The post-silking biomass had a significant positive association with mean daily incident radiation during the post-silking period ($r^2=0.58$, $n=12$, $p<0.01$), which varied according to sowing date and location.

Variations in the BIOM accumulated during the post-silking period and in the KN harvested per unit area (data not shown) generated a wide range of SSR during grain-filling period. Values of this ratio ranged from 272 to 582 mg/kernel in 2003-04, and from 154 to 617 mg/kernel in 2004-05. The hybrid Morgan 306 always showed higher post-silking SSR compared to Cóndor (405 vs. 342 mg/kernel, respectively). This difference resulted from the low KN set by Morgan 306 and the similar BIOM production between hybrids. In turn, SSR values were higher at the intermediate location of Pergamino (419 mg/kernel) compared to the northern and southern locations (mean of 355 mg/kernel). This variable was significantly affected by crop management. Late sowings showed very low values because the reductions in BIOM production were larger than those in kernel set when sowing was delayed. Nevertheless, significant interactions between crop management, year, and location were found. In fact, the high BIOM accumulation during the post-silking period in the first growing season at Paraná, and the low kernel set in the second season at Pergamino contributed to explain those interactions.

Kernel weight and hardness

Kernel weight was affected by the treatments. Morgan 306 showed weightier kernels than Cóndor (251 vs. 243 mg, respectively). In turn, kernel weight in Pergamino was always higher compared to the other locations. Weightiest

Location	Sowing date	Daily mean air temperature (°C)		Daily mean incident solar radiation (MJ/m^2)	
		2003-04	2004-05	2003-04	2004-05
Balcarce	Early sowing	20.0 ± 3.4 [a]	18.3 ± 3.9	17.3 ± 5.4	15.7 ± 5.4
	Late sowing	17.2 ± 4.6	15.8 ± 3.6	12.7 ± 5.0	12.4 ± 3.6
Pergamino	Early sowing	22.1 ± 3.0	22.1 ± 3.8	24.7 ± 5.0	21.9 ± 6.0
	Late sowing	21.0 ± 2.6	19.2 ± 3.3	19.8 ± 5.6	16.7 ± 5.3
Paraná	Early sowing	23.4 ± 3.3	24.2 ± 3.5	23.4 ± 6.5	22.8 ± 6.5
	Late sowing	20.7 ± 4.4	17.7 ± 4.3	16.7 ± 6.8	13.1 ± 6.4

Table 1. Mean temperature and mean daily incident radiation averaged from silking to physiological maturity of two orange-flint maize hybrids grown at three locations with four different crop managements without water restrictions during 2003–2004 and 2004–2005 growing seasons (previously reported in Cirilo *et al.,* 2011).

[a] Data shown are means ± standard deviation.

kernels were harvested when maize was sown earlier, at low plant density and refertilized near silking. Late sowing date produced kernels with lower weight in most cases. Kernel weight for late sowings at Paraná showed an opposite behavior in both years. In fact, it was as high as that obtained in early sowings in the first year but also low in the second year. Reductions in weight per kernel in response to late sowings were more pronounced at Balcarce than at the other locations for both years (27 vs. 19% in 2003-04, and 19 vs. 6% in 2004-05).

Kernel hardness was also affected by the treatments. The hybrid Morgan 306 always recorded higher TW than Cóndor (average of 80.5 vs. 78.2 kg/hl, respectively). In turn, maize kernels achieved the highest TW value at Pergamino (i.e., 80.5 kg/hl, mean for both hybrids), whereas the lowest one was obtained at the southern location of Balcarce (i.e., 78.1 kg/hl). Crop management practices also significantly affected TW. In fact, the highest TW value was measured when early-sown maize was refertilized (average of 80.0 kg/hl), whereas the lowest one was obtained at late sowings (i.e., 78.1 kg/hl). The difference between both crop managements was more evident at Balcarce (79.3 vs. 75.2 kg/hl, average of both hybrids and years). These responses revealed that while the old hybrid Morgan 306 matched the dry-milling industry requirement for premium quality (i.e., 79 kg/hl) in almost all situations, the new high-yielding hybrid hardly achieved that requirement.

The hybrid Morgan 306 presented lower PF values than Cóndor (average of 1.2 vs. 17.0%, respectively for each hybrid), but these differences were more noticeable at Balcarce and Paraná. In turn, refertilization of early-sown maize decreased PF for hybrid Cóndor, reducing the differences between hybrids). This effect was more evident in Balcarce and Paraná than in Pergamino. Moreover, delayed sowing and high plant density resulted in increments in this variable for Cóndor, with larger effects in Balcarce (for both years) and Paraná (only for the second year) compared to Pergamino. Almost 40% of the data corresponding to Cóndor (mainly from late sowing date and high density at the southern and northern locations) exceeded that limit, whereas all data from Morgan 306 were below it (Cirilo *et al.*, 2011).

Starch and amylose in kernels and amylose/starch ratio

Starch concentration in kernels was slightly lower at Pergamino than at the other locations (i.e., 71.6% at Pergamino and an average of 75.2% for the other two locations, table 2). Starch content per kernel varied according to cropping conditions. Kernels from Pergamino showed the highest starch content in comparison to the other locations. When fertilizer was added close to silking, the amount of starch accumulated in kernels increased significantly. Nevertheless, significant interactions were found between location and crop management in both growing seasons, mainly because of the lower starch deposition in kernels when maize was sown late at the southern location (Balcarce). Cóndor hybrid generally showed higher starch concentration than Morgan 306 (74.6 vs. 73.3%, respectively). However, higher starch accumulation was observed for Morgan 306 only during the second season, resulting in a significant interaction effect between year and hybrid.

Amylose concentration in kernels increased from Balcarce, the coldest location situated at the highest latitude, to Paraná, the warmest location at the lowest latitude. This trend was more noticeable during the 2004-05 growing season (table 2). Nevertheless, kernels from Pergamino showed higher Am (mg) than kernels from other locations. On the other hand, Am (mg) was lower for late sowing dates, but this trend was less important for Paraná in the first season and for Pergamino in the second one, revealing a significant interaction between growing location and crop management. In turn, Am (mg) in kernels was higher during the 2003-04 growing season, but important effects of cropping conditions were evident for each season. In fact, the refertilization treatment increased amylose accumulation in kernels; however, late sowing dates reduced said concentration compared to the other crop managements. Hybrid Cóndor showed higher Am (%) than Morgan 306.

Amylose/starch ratio was higher in 2003-04 and increased from Balcarce to Paraná (i.e., 32.2 and 33.7%, respectively, as means for both years; table 2). The delay in sowing date significantly reduced this ratio in the 2004-05 growing season (32.6 vs. 31.1%, as means for early and late sowings, respectively).

Starch thermal properties

Starch thermal properties varied according to year, location, crop management and hybrid (table 3). T_{oG}, T_{pG}, and R_G were slightly higher for the first growing season, but significant interaction was found with the remaining sources of variation (i.e., location, crop management, and hybrid). In turn, DH_G, and PHI were slightly lower for the first season. T_{oG} and T_{pG} increased as latitude decreased from Balcarce to Paraná (from 63.8 to 66.4ºC for T_{oG}, and from 68.7 to 70.7ºC for T_{pG}, respectively, as average across both growing seasons).

Contrarily to T_{oG} and T_{pG}, R_G decreased from Balcarce to Paraná (from 9.9 to 8.6ºC, respectively as average for both growing seasons). In 2003-04, hybrid Cóndor showed lower R_G values than Morgan 306 (9.0 vs. 9.8°C, respectively). Calculated PHI increased from Balcarce to Paraná (2.41 to 2.79 J/g.°C, respectively as means of both years), and the hybrid Cóndor always showed higher PHI values than Morgan 306 (2.68 vs. 2.55 J/g.°C, respectively).

Late sowing date significantly reduced T_{oG} in comparison to early sowings (63.9 vs. 65.6ºC and 68.1 vs. 70.1ºC for the first and second growing seasons as means across locations and hybrids, respectively). In turn, refertilization increased the value of T_{pG} compared with the control management plots (70.2 vs. 69.6ºC, respectively in 2003-04, and 65.7 vs. 64.9ºC, respectively in 2004-05).

When comparing corn hybrids, T_{oG} tended to show lower values for Cóndor than for Morgan 306, but this difference was significant only during 2004-05 growing season *(*64.9 vs. 65.4°C, respectively; table 3). T_{pG} was also lower for hy-

Hybrid	Location	Crop management	Amylose content (mg/kernel)		Starch content (mg/kernel)		Amylose concentration (%)		Starch concentration (%)		Amylose/starch ratio (%)	
			2003-04	2004-05	2003-04	2004-05	2003-04	2004-05	2003-04	2004-05	2003-04	2004-05
Cóndor	Balcarce	Control	61.6±2.4[a]	63.8±2.2	193.5±4.5	200.2±16.8	24.2±0.4	24.3±0.7	76.0±1.5	76.1±1.9	31.8±0.6	32.0±1.7
		High density	61.9±3.7	64.1±1.9	187.4±7.3	195.4±5.3	24.7±0.6	24.1±0.3	74.9±0.5	75.0±1.8	33.0±0.7	32.8±0.5
		Refertilization	67.5±4.1	67.0±0.6	208.4±17.5	213.4±15.0	24.7±0.7	23.9±0.6	76.3±4.2	76.5±4.2	32.5±0.9	31.5±2.4
		Late sowing	48.2±1.1	42.1±4.6	143.9±3.4	143.0±18.0	24.6±0.1	24.3±0.2	73.5±2.3	77.6±1.9	33.5±1.0	29.5±1.0
	Pergamino	Control	66.1±2.8	64.6±1.3	190.3±8.5	193.9±3.6	25.6±0.3	24.4±0.2	73.8±1.1	71.3±0.2	34.8±0.3	33.3±0.2
		High density	65.2±2.9	64.8±3.2	192.1±7.7	189.8±3.2	25.6±0.3	25.5±0.9	75.4±0.5	70.3±2.2	33.9±0.2	34.2±2.1
		Refertilization	71.2±3.0	65.4±2.5	212.4±8.8	202.0±2.0	24.8±1.0	24.5±1.1	74.1±4.2	70.8±1.4	33.6±1.7	32.4±0.9
		Late sowing	54.5±1.7	52.9±4.1	163.7±2.9	165.6±10.6	25.1±0.6	24.9±1.0	75.4±1.5	73.3±2.2	33.3±1.0	31.9±0.5
	Paraná	Control	63.1±2.1	56.1±6.8	180.0±9.6	174.4±20.0	25.6±0.3	25.6±0.7	72.9±2.1	77.5±1.6	35.1±1.2	32.2±0.3
		High density	56.8±6.9	53.2±3.8	161.5±15.9	165.5±6.9	26.0±0.3	25.9±0.3	74.1±4.8	76.0±1.7	35.2±1.9	32.1±1.1
		Refertilization	68.6±0.6	62.0±5.4	202.8±8.0	190.3±20.6	25.3±0.2	25.3±0.3	74.7±2.1	76.5±3.0	33.8±1.1	32.6±1.5
		Late sowing	65.4±1.5	37.6±2.5	184.3±5.3	118.4±6.2	25.3±0.2	25.3±0.2	71.2±2.9	74.4±1.9	35.5±1.2	31.8±0.5
Morgan 306	Balcarce	Control	64.2±3.0	63.0±0.6	193.8±8.7	194.3±2.2	24.3±0.4	23.7±0.9	73.5±1.2	73.2±2.9	33.1±0.1	32.4±0.5
		High density	64.3±1.7	59.4±3.9	193.6±6.7	186.9±5.2	24.6±0.8	23.8±1.3	72.6±3.8	74.9±0.9	33.2±1.9	31.8±1.3
		Refertilization	67.7±3.8	63.1±3.1	214.8±19.9	193.3±10.1	24.0±0.5	23.8±1.1	75.9±4.2	72.8±2.4	31.6±1.3	32.7±1.2
		Late sowing	54.5±3.9	46.6±2.4	164.4±14.4	153.1±13.0	22.8±0.2	23.3±0.6	73.4±2.3	76.4±2.5	33.2±1.3	30.5±1.6
	Pergamino	Control	66.6±2.5	62.8±1.3	199.9±10.7	194.6±4.1	23.7±0.3	23.4±0.4	73.3±2.0	72.7±1.5	33.3±1.1	32.3±0.4
		High density	63.7±3.4	64.1±4.0	186.4±11.1	199.4±3.9	24.0±0.6	23.2±1.0	73.2±1.1	72.1±1.0	34.2±0.3	32.1±1.8
		Refertilization	70.7±2.6	62.5±3.4	207.1±2.9	192.8±9.7	22.9±1.0	23.1±1.2	71.8±0.2	71.3±3.1	34.1±1.5	32.5±2.1
		Late sowing	60.1±3.8	59.7±2.2	178.2±11.7	189.9±3.3	23.4±0.8	22.2±0.3	73.7±2.4	70.7±0.9	33.7±0.2	31.4±0.7
	Paraná	Control	62.0±4.3	63.7±5.7	178.6±20.1	190.3±19.8	24.9±0.2	25.1±0.9	73.5±4.1	74.9±2.5	34.8±1.7	33.5±0.8
		High density	56.6±3.4	55.9±0.3	164.8±6.6	164.9±8.5	24.4±0.9	25.1±1.4	75.4±4.2	73.9±3.2	34.3±0.9	34.0±2.0
		Refertilization	65.4±0.7	60.1±2.7	189.4±2.1	181.8±13.8	24.9±0.3	24.4±0.6	73.3±1.8	73.9±4.2	34.5±0.8	33.2±2.7
		Late sowing	62.2±0.9	38.8±6.9	178.3±3.9	124.0±22.8	23.6±0.5	23.0±0.8	72.5±1.8	73.4±1.2	34.9±0.5	31.3±0.6
Year (Y)			(1.6)***,[b]		(5.5)*		(0.3)***		ns		(0.4)***	
Location (L)			(2.4)***		(8.2)***		(0.4)***		(1.8)*		(0.6)***	
Crop management (C)			(2.3)***		(7.3)***		(0.5)***		ns		(0.8)*	
Hybrid (H)			ns		ns		(0.2)**		(0.8)*		ns	
Y*L			(4.3)**		(14.6)*		(0.7)**		(3.2)*		ns	
Y*C			(3.9)***		(12.3)***		(0.8)*		ns		(0.1)**	
Y*H			ns		ns		ns		ns		ns	
L*C			(5.2)***		(16.3)***		ns		ns		ns	
L*H			ns		ns		ns		ns		ns	
C*H			(2.9)***		(10.6)**		ns		ns		ns	
Y*L*C			(8.3)***		(26.0)***		ns		ns		ns	
Y*L*H			(3.9)**		(14.1)*		ns		ns		ns	
Y*C*H			ns		ns		ns		ns		ns	
L*C*H			(6.1)*		ns		ns		ns		ns	
Y*L*C*H			ns		ns		ns		ns		ns	

Table 2. Amylose and starch content and concentration, and amylose/starch ratio (in db) of two orange-flint hybrids sown at three locations with four different crop managements without water restrictions during 2003–2004 and 2004–2005 growing seasons. The data in the table are the mean of the three field replications. Only significant interactions are shown.

[a] Data shown are means ± standard deviation.

[b] Statistical significance of main effects and interactions at 5% (*), 1% (**), and 0.1% (***) levels are included (ns: no significant). Values between brackets are Tukey's (p< 0.05) values for mean comparison.

Hybrid	Location	Crop management	T_{oG} (°C)		T_{pG} (°C)		R_G (°C)		ΔH_G (J/g)		PHI (J/g.°C)	
			2003-04	2004-05	2003-04	2004-05	2003-04	2004-05	2003-04	2004-05	2003-04	2004-05
Cóndor	Balcarce	Control	63.4±1.0[a]	64.1±0.7	68.4±1.0	68.8±0.6	10.0±0.3	9.3±0.8	11.5±0.2	11.9±0.2	2.30±0.04	2.56±0.24
		High density	63.2±0.5	64.6±0.6	68.0±0.6	69.3±0.3	9.6±0.4	9.4±0.5	11.8±0.3	11.7±0.1	2.46±0.14	2.51±0.16
		Refertilization	64.1±0.4	64.2±0.2	68.9±0.2	69.3±0.3	9.5±0.8	10.1±0.2	12.1±0.4	12.0±0.2	2.56±0.25	2.38±0.01
		Late sowing	64.7±0.1	61.6±0.5	69.0±0.3	66.3±0.2	8.8±0.5	9.4±0.8	11.6±0.2	11.4±0.1	2.65±0.18	2.45±0.22
	Pergamino	Control	65.1±0.5	64.6±0.8	69.8±0.3	69.4±0.5	9.2±0.5	9.5±0.8	11.9±0.4	11.7±0.2	2.59±0.21	2.47±0.22
		High density	65.7±0.4	64.9±1.0	70.2±0.1	69.3±0.7	9.2±0.6	8.7±0.8	11.5±0.1	12.4±0.4	2.52±0.15	2.87±0.25
		Refertilization	65.7±0.4	65.3±0.3	70.1±0.2	69.6±0.5	8.9±0.3	8.4±0.4	11.7±0.4	12.4±0.4	2.65±0.16	2.95±0.20
		Late sowing	65.5±0.4	64.2±0.2	69.9±0.1	68.2±0.3	8.9±1.0	8.0±0.8	11.4±0.6	12.1±0.9	2.60±0.28	3.08±0.56
	Paraná	Control	66.1±0.3	66.6±0.1	70.2±0.2	70.5±0.2	8.1±0.4	7.7±0.2	11.7±0.3	12.1±0.8	2.88±0.13	3.14±0.20
		High density	65.7±0.2	67.0±0.1	70.0±0.2	70.8±0.1	8.6±0.1	7.7±0.4	11.5±0.5	11.9±0.3	2.67±0.09	3.09±0.09
		Refertilization	66.6±0.4	66.7±0.5	70.8±0.3	71.2±0.2	8.3±0.6	8.9±0.7	12.0±0.3	11.7±0.5	2.90±0.17	2.62±0.31
		Late sowing	65.7±0.5	64.7±0.2	70.3±0.4	69.1±0.2	9.2±0.9	8.6±0.5	11.7±0.6	12.1±0.3	2.55±0.33	2.81±0.23
Morgan 306	Balcarce	Control	64.0±1.1	64.5±1.3	68.4±0.7	69.8±0.7	8.9±0.9	10.7±1.4	11.2±0.7	12.3±0.2	2.52±0.28	2.32±0.27
		High density	63.3±0.8	63.9±1.0	68.2±0.8	69.3±0.8	9.7±0.4	10.8±0.9	11.8±0.3	11.5±0.0	2.43±0.16	2.14±0.19
		Refertilization	64.0±1.0	64.6±0.4	69.0±0.9	70.1±0.5	10.0±0.6	10.9±0.5	11.2±0.3	12.1±0.4	2.24±0.15	2.21±0.17
		Late sowing	63.1±0.2	62.3±1.4	69.4±0.5	66.4±0.4	12.7±0.6	8.2±2.5	11.2±0.1	11.6±0.1	1.76±0.10	3.02±1.02
	Pergamino	Control	65.3±0.9	65.5±0.5	70.7±0.2	69.8±0.4	10.7±1.8	8.6±0.2	11.4±0.1	12.0±0.6	2.16±0.38	2.80±0.16
		High density	64.6±1.2	65.7±0.9	70.3±0.7	70.1±0.8	11.5±1.5	8.8±0.2	11.6±0.4	11.8±0.4	2.05±0.36	2.68±0.14
		Refertilization	66.4±0.6	65.8±0.5	71.0±0.5	70.2±0.7	9.3±0.8	8.8±0.5	11.7±0.3	12.0±0.4	2.55±0.27	2.72±0.20
		Late sowing	65.7±0.9	64.7±0.8	70.3±0.7	68.8±0.7	9.2±0.5	8.3±2.8	11.5±0.0	11.7±0.2	2.51±0.12	3.14±1.35
	Paraná	Control	66.1±0.2	67.9±0.3	70.7±0.4	71.9±0.4	9.2±0.4	7.9±0.2	12.0±0.0	12.4±0.7	2.59±0.09	3.15±0.21
		High density	66.2±0.2	67.1±0.3	70.5±0.4	71.3±0.1	8.8±0.4	8.4±0.6	11.6±0.2	11.9±0.4	2.65±0.14	2.84±0.19
		Refertilization	67.2±0.2	66.9±0.6	71.4±0.2	71.9±0.1	8.3±0.4	10.0±1.1	12.0±0.7	12.3±0.5	2.89±0.16	2.48±0.36
		Late sowing	66.4±0.2	65.9±0.5	71.0±0.1	70.0±0.3	9.1±0.3	8.4±0.3	11.7±0.2	11.9±0.8	2.56±0.13	2.84±0.25
Year (Y)			ns		(0.2)*		(0.2)**		(0.2)**		(0.11)**	
Location (L)			(0.3)***[b]		(0.3)***		(0.4)***		ns		(0.17)***	
Crop management (C)			(0.5)***		(0.3)***		ns		ns		ns	
Hybrid (H)			(0.2)**		(0.1)***		(0.3)***		ns		(0.11)*	
Y*L			(0.6)*		(0.5)***		(0.7)*		ns		ns	
Y*C			(0.8)***		(0.6)***		(1.0)**		ns		(0.35)*	
Y*H			(0.4)*		ns		ns		ns		ns	
L*C			ns		ns		(1.3)*		ns		ns	
L*H			ns		ns		ns		ns		ns	
C*H			ns		ns		ns		ns		ns	
Y*L*C			ns		(1.2)***		(2.0)*		ns		ns	
Y*L*H			ns		ns		ns		ns		ns	
Y*C*H			ns		ns		ns		ns		ns	
L*C*H			ns		ns		ns		ns		ns	
Y*L*C*H			(2.0)*		ns		(3.0)***		ns		(1.16)*	

Table 3. Starch thermal properties (gelatinization onset and peak temperature, range and enthalpy) of two orange-flint hybrids grown at three locations with four different crop managements without water restrictions during 2003–2004 and 2004–2005 growing seasons. The data in the table are the mean of the three field replications. Only significant interactions are shown.

[a] Data shown are means ± standard deviation.

[b] Statistical significance of main effects and interactions at 5% (*), 1% (**), and 0.1% (***) levels are included (ns: no significant). Values between brackets are Tukey's ($p < 0.05$) values for mean comparison.

brid Cóndor than for Morgan 306 (69.6 vs. 70.1ºC in 2003-04 and 69.3 vs.70.0ºC in 2004-05, respectively).

Correlation between analyzed variables

Partial correlation coefficients among variables calculated for the whole data set are shown in table 4. Total amylose deposition in the endosperm of kernels appeared to be significantly and positively associated with the amount of BIOM produced by the crop after silking. Nevertheless, the correlation coefficient was higher for Am (mg) than for Am (%). The same trend was found for starch deposition. Then, weightier kernels appeared to be strongly associated with St (mg), mainly explained by amylose deposition. A high and significant correlation coefficient was found between Am/St (%) and amylose deposition in kernels, in terms of both content and concentration. Thereafter, amylose/starch ratio in kernels was significantly correlated with both the crop BIOM produced during the post-silking period and the SSR for kernels established for the same period. Amylose content of kernels also strongly correlated to hardness-associated properties of kernels. In fact, a positive association was found between the Am (mg) and the TW, whereas the association was negative with the PF. These correlations indicate that kernel became flintier when Am (mg) increased. On the other hand, the variations in amylose deposition in kernels, promoted by locations and crop management, also showed significant associations with some starch thermal properties. In fact, T_{oG} and $T_{pG,}$ were strong and positively correlated with Am (%) and Am/St (%) of kernels. As expected, T_{oG} was strongly associated with T_{pG}, and both temperatures were negatively correlated to R_G. Similarly, T_{oG} showed significant correlation coefficients with ΔH_G and PHI. The PHI, which involved both components in the calculation, appeared to be better explained by the difference between T_{oG} and T_{pG} than by variations in ΔH_G. Finally, narrow values for R_G were associated with high values of ΔH_G.

DISCUSSION

Variations in crop environment due to location and crop management modified the crop growing condition during the reproductive period after silking. Late sowing date markedly decreased crop dry matter accumulation from silking to physiological maturity, particularly during the second growing season when reductions in incident radiation and temperature were more pronounced (table 1). The low SSR established in delayed sowing dates (325 vs. 390 mg/kernel as general means for late and early sowings, respectively) limited the supply of assimilate to support grain filling demand, as was previously proposed for Bonelli *et al*. (2016) and Zhou *et al*. (2017). In fact, kernels produced in late sowing date were

	KW [a]	BIOM	SSR	TW	PF	Am, mg	St, mg	Am, %	St, %	Am/St, %	T_{oG}	T_{pG}	R_G	ΔH_G	PHI
KW	1.00														
BIOM	0.70 ***,[b]	1.00													
SSR	0.59 ***	0.74 ***	1.00												
TW	0.49 ***	0.36 ***	0.48 ***	1.00											
PF	-0.54 ***	-0.36 ***	-0.43 ***	-0.63 ***	1.00										
Am, mg	0.95 ***	0.74 ***	0.59 ***	0.45 ***	-0.52 ***	1.00									
St, mg	0.96 ***	0.66 ***	0.51 ***	0.38 ***	-0.47 ***	0.93 ***	1.00								
Am, %	-3.4E-03	0.22 **	0.09	-0.01	-0.01	0.32 ***	0.07	1.00							
St, %	-0.22 **	-0.19 *	-0.30 ***	-0.41 ***	0.31 ***	-0.13	0.07	0.23 **	1.00						
Am/St, %	0.16	0.33 ***	0.30 ***	0.28 ***	-0.24 **	0.37 ***	2.7E-03	0.69 ***	-0.54 ***	1.00					
T_{oG}	0.10	0.12	0.16	0.46 ***	-0.17 *	0.20 *	0.06	0.35 ***	-0.14	0.40 ***	1.00				
T_{pG}	0.20 *	0.21 *	0.23 **	0.56 ***	-0.29 ***	0.32 ***	0.17 *	0.40 ***	-0.14	0.44 ***	0.90 ***	1.00			
R_G	0.18 *	0.16	0.10	0.06	-0.21 *	0.17 *	0.20 *	-4,0E-03	0.03	-0.02	-0.49 ***	-0.06	1.00		
ΔH_G	0.07	-0.07	-0.10	0.08	-4.4E-03	0.05	0.05	-0.07	-0.06	-0.02	0.28 ***	0.17 *	-0.29 ***	1.00	
PHI	-0.16	-0.20 *	-0.09	-0.04	0.17 *	-0.18 *	-0.19 *	-0.06	-0.05	-0.02	0.46 ***	0.06	-0.93 ***	0.48 ***	1.00

Table 4. Partial correlation coefficients between kernel weight, biomass accumulation and source-sink ratio after silking, hardness associated properties (test weight, and percent floaters), starch and amylose content and concentration, amylose/starch ratio, and starch thermal properties (gelatinization onset and peak temperatures, gelatinization range and enthalpy, and peak height index), of two flint hybrids of maize grown at three locations with four different crop managements without water restrictions during 2003–2004 and 2004–2005 growing seasons. Data for kernel weight, post-silking biomass, post-silking source-sink ratio, test weight, and percent floaters were reported in Cirilo *et al.,* 2011.

[a] *References:* KW (kernel weight), BIOM (post-silking biomass), SSR (post-silking source-sink ratio), TW (test weight), PF (percent floaters), Am, mg (amylose content per kernel), St, mg (starch content per kernel), Am, % (amylose concentration), St, % (starch concentration), Am/St (amylose/starch ratio), T_{oG} (gelatinization onset temperature), T_{pG} (gelatinization peak temperature), R_G (gelatinization range), ΔH_G (gelatinization enthalpy), PHI (peak height index).

[b] * Significance at 5% level; ** significance at 1% level;*** significance at 0.1% level.

markedly lighter than those corresponding to early sowings (216 vs. 258 mg/kernel as general means for late and early sowings, respectively). The shortage in assimilate supply during grain-filling period would particularly affect amylose deposition in the endosperm since the proportion of amylose in the starch gradually increase toward the last phase of grain development in maize (Guo *et al*., 2006). The significant relationship found between Am (mg) or Am/St (%) with the BIOM produced after silking (figure 2) supports this assumption and highlights the importance of favorable growing conditions during grain-filling period in maize to promote increases in the Am (mg) into the kernel, enhancing the Am/St (%) of the endosperm.

Those cropping conditions that allowed the crops to achieve higher grain yields (data not shown) together with weightier kernels also produced flintier kernels. Recently, analyzing the behavior of several maize hybrids in different locations from a broad area of the maize production region of Argentina, Cerrudo *et al*. (2017) reported a strong association between the environment potential sources to supply assimilates to fill the kernels and its hardness at harvest. Robutti *et al*. (2000) reported that flintier maize kernels had higher amylose proportion than floury ones. Endosperms with starch having higher amylose content would be more compressible during the maturing stage at the field. Then, these endosperms would achieve higher density and, consequently, higher hardness than endosperms with fewer amylose content (Kljak *et al*., 2018). In fact, we found a significant correlation between the Am/St (%) and hardness-associated properties like TW (r=0.28, p<0.001) and PF (r=-0.24, p<0.01; table 4). Kernel hardness in maize results from the whole endosperm biochemical composition, and the interaction established between stored protein and starch was proposed to account for the differences in endosperm texture of the kernels (Robutti *et al*., 2000). The negative correlation between Am/St (%) and St (%) shown in table 4 (r=-0.54, p<0.001) reflected the increase in protein deposition in the endosperm (data not shown) when assimilate availability per kernel during the grain-filling period increased as was reported by Borrás *et al*. (2002). Then, with improved conditions during grain-filling period, the protein matrix of the endosperm would become stronger. A strong protein matrix would compress the starch that would also become rich in amylose and more compressible under those conditions. This assumption is supported by significant correlation coefficients calculated between hardness-associated properties and the Am (mg) of kernels (r=0.45 and -0.52, p<0.001, for TW and PF, respectively; table 4).

Crop growth environment varied across locations and sowing dates. Daily mean air temperature and incident radiation during the grain-filling period increased from Balcarce, the southern location at higher latitude, to Paraná, the northern location at lower latitude, when comparing similar sowing dates (table 1). Accordingly, variations in starch composition were observed. In fact, positive and significant relationships between Am (%) ($r^2 \geq 0.37$, n=12, p≤0.01) or Am/St (%) ($r^2 \geq 0.36$, n=12, p≤0.01) and mean air temperature during the grain-filling period were found when all data for each hybrid were analyzed (figure 3). Lenihan *et al*. (2005) proposed that increases in temperature in maize reduce the activity of the starch branching enzyme which catalyses the α-1,6 links in the starch. This enzymatic response to temperature would consequently reduce the production of branch-chains of amylopectin, consequently increasing the Am/St (%) (table 3). The increase of amylose in response to temperature was also reported for barley (Savin and Nicolas, 1999) and wheat (Hurkman *et al*., 2003). Evaluating kernels from several maize hybrids of different endosperm texture grown in Argentina, Martinez *et al*. (2017) recently reported that both Am (%) and Am/St (%) were increased in response to increases in mean air temperature during the grain-filling period.

In turn, starch thermal properties also varied across locations according to the thermal environment registered

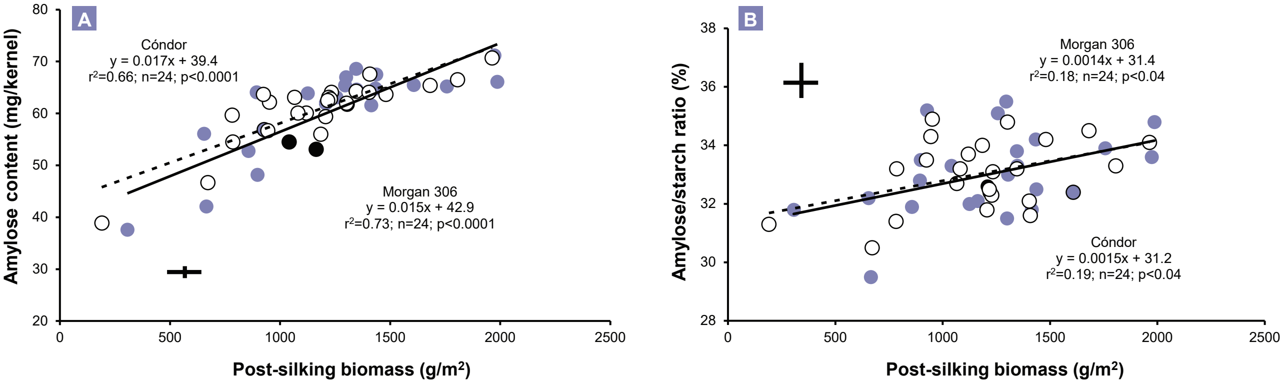

Figure 2. Amylose content in kernels as a function of post-silking biomass for two flint maize hybrids: Morgan 306 (open symbols) and Cóndor (close symbols), grown at three locations (Balcarce, Pergamino and Paraná) with four different crop managements (control, high density, refertilization and late sowing) during two growing seasons (2003-04 and 2004-05). Each symbol corresponded to the mean of three replications for both hybrids. Bars in cross represent the value of the standard error for each variable. The lines represent the fitted regressions for Cóndor (bold line) and Morgan 306 (dotted line) hybrids. The inserts show details for the corresponding equations.

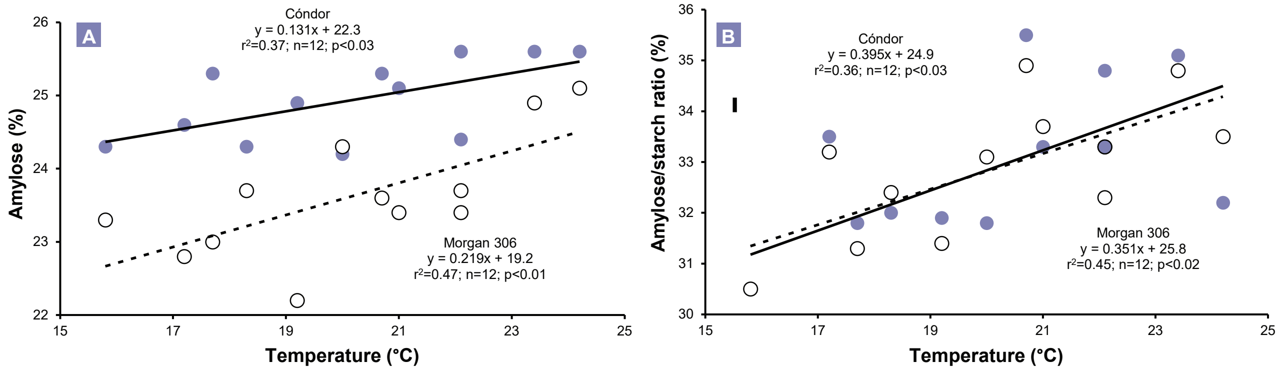

Figure 3. Amylose concentration (A) and amylose/starch ratio (B) in kernels as a function of air mean temperature for the post-silking period for two flint maize hybrids: Morgan 306 (open symbols) and Cóndor (close symbols) grown at three locations (Balcarce, Pergamino and Paraná) with two different sowing dates (early an late) during two growing seasons (2003-04 and 2004-05). Each symbol corresponded to the mean of three replications for both hybrids. Only data from control treatment for early sowings were including. The vertical bars represent the value of the standard error for the amylose and the amylose/starch ratio. The lines represent the fitted regressions for Cóndor (bold line) and Morgan 306 (dotted line) hybrids. The inserts show details for the corresponding equations.

throughout the kernel growing stage. In fact, a ≈2.7ºC (p<0.0001) increase in T_{oG}, a ≈1.3ºC (p<0.0001) decrease in R_G, a ≈0.2 J/g (n.s.) increase in ΔH_G, and a ≈0.4 J/g.°C (p<0.001) increase for PHI were found when kernels were filled at the warmer location (Paraná) compared to those filled at the cooler one (Balcarce; table 3). Lenihan *et al.* (2005), comparing kernels grown in tropical and temperate environments, found that increases in air temperature during the grain-filling period produced kernels with starch that gelatinized at higher T_{oG}, with narrow R_G and elevated ΔH_G (indicating a taller and narrower endotherm). For the complete data set, a significant association was revealed between the starch composition and the gelatinization onset temperature (T_{oG}); this variable strongly correlated with the others thermal properties (table 4). Increases in Am (%) did not affected ΔH_G but resulted in higher T_{oG} and T_{pG} values. Sandhu *et al.* (2004) and Sandhu and Singh (2007) also reported that the Am (%) in the starch correlated positively with both T_{oG} and T_{pG}, and these variables correlated positively with ΔH_G and PHI. Our findings indicate that the crop environment would affect the behavior of starch during cooking at the industry.

CONCLUSIONS

Variations in the cropping environment by different location and crop management modified the starch composition of flint maize kernels. Amylose/starch ratio decreased as air temperature decreased from the north to the south and by delaying sowing date. The deposition of amylose in the endosperm was increased as growing conditions improved during grain-filling period. Increases amylose deposition resulted in flintier kernels that would perform properly at the dry-milling industry. Starch thermal properties were also modified by these changes in the starch composition.

The results reported herein would contribute to foresee the effect of location and of agricultural practices on kernel quality of flint maize, and to make appropriate management adjustments to obtain a product that meets the market needs. These findings would be of interest for the industry in order to better estimate kernel quality to be expected according to how and where maize was produced.

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