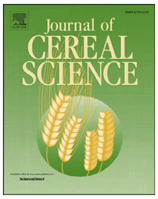
Journal of Cereal Science 71 (2016) 217–223

Contents lists available at ScienceDirect

Journal of Cereal Science

journal homepage: www.elsevier.com/locate/jcs



Whole meal and white flour from Argentine wheat genotypes: Mineral and arabinoxylan differences

María Belén Vignola [a], Malena Moiraghi [a], Emiliano Salvucci [a], Verónica Baroni [b], Gabriela T. Pérez [a], *

[a] *Instituto de Ciencia y Tecnología de Alimentos Córdoba (ICYTAC-CONICET-UNC), Facultad de Ciencias Agropecuarias, Universidad Nacional de Córdoba, 5000 Córdoba, Argentina*

[b] *Instituto de Ciencia y Tecnología de Alimentos Córdoba (ICYTAC-CONICET-UNC), ISIDSA–Universidad Nacional de Córdoba, Córdoba, Argentina*

ARTICLE INFO

Article history:
Received 10 April 2015
Received in revised form
14 June 2016
Accepted 4 September 2016
Available online 7 September 2016

Keywords:
Wheat
Protein
Arabinoxylan
Mineral

ABSTRACT

The aim of this study was to compare mineral and arabinoxylan contents in whole meal and white wheat flour, as well as delineate the influence of genotype and climatic conditions on the variation of these components. Eleven commercial bread wheat cultivars from Argentina obtained in two consecutive harvests were analyzed. Protein, arabinoxylan, mineral concentration and localization were determined. For T-AX variation, year was the main factor accounting for the variability found both in whole meal and in white flour, while WE-AX content was more influenced by genotype on both fractions. There was an average reduction of 56% of T-AX after milling. Mineral content was significantly influenced by genotype and harvest years. Milling significantly reduced the concentration of all the elements ($p < 0.05$). Fe and Zn concentrations in white flour were highly variable. Milling loss had a wide variation from 10 to 74% for Fe, and from 19 to 68% for Zn. Genotypes with lower T-AX, Fe and Zn milling losses than the average were found in this study. This together with the total contents of these components in the grain should be taken into account when the purpose is to improve Zn, Fe, AX content in white flour.

1. Introduction

Wheat (*Triticum aestivum* L.) is one of the primary grains consumed by humans and it is grown around the world in diverse environments, from cool rain-fed to hot dry-land areas. This grain is mainly composed of starch (approximately 60–70% of grain, 70–80% of flour), proteins (approximately 8–20%) and non-protein compounds as cellulose, hemicelluloses, polyphenols, minerals, among others, whose concentrations are distributed differently within the grain. One important constituent is a group of nonstarch polysaccharides referred to as arabinoxylans (AX). AX are not distributed uniformly in the wheat kernel and they constitute 20–27% of the aleurone, 23–32% of the bran, and 2–4% of the endosperm. Considering solubility, they may be classified into water-extractable (WE-AX) and water-unextractable (WU-AX), differing in the physicochemical properties (Li et al., 2009). Although the content of AX in wheat flour is relatively low, this polymer plays an important role in flour functionality, with WE-AX and WU-AX having different effects on breadmaking. Besides, as part of dietary fiber, they also have a major impact on the nutritional quality of cereal foods. The environment can play an important role in the variation of AX content in wheat, often affecting in higher magnitude than genotype (Li et al., 2009).

Among other minor wheat components, minerals, vitamins and antioxidant (micronutrients) have an important role in human nutrition. Micronutrient deficiency is one of the most important challenges facing humanity. The lack of adequate levels of essential vitamins and minerals (iron [Fe], zinc [Zn] and vitamin A, among others) affects more than 2 billion people (Guzmán et al., 2014). Micronutrient deficiency is common in developing countries, where staple cereals (wheat, maize or rice) provide most of the calories (Bouis et al., 2011). It has been indicated that micronutrient levels in wheat grain were controlled to a large extent by environmental factors (temperature, rainfall and evaporation), as well as by interactions between the genotype and the environment

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Abbreviations: AX, Arabinoxylans; EDS, Energy Dispersive Spectrometer; GV, Genotype Variance; T-AX, Total Arabinoxylans; WE-AX, water-extractable arabinoxylans; WF, White Flour; WM, Whole Meal; WU-AX, Water-unextractable arabinoxylans; YV, Year Variance.

* Corresponding author. Av. Valparaiso S/N, Córdoba, Argentina.

E-mail address: gaperez@agro.unc.edu.ar (G.T. Pérez).

http://dx.doi.org/10.1016/j.jcs.2016.09.002
0733-5210/

(Morgonuov et al., 2007).

As consumers become more aware of the numerous health benefits of eating whole grain foods, such as reduced risk of obesity, type 2 diabetes, cardiovascular disease, and cancer, demand for whole grain foods have increased (Parker et al., 2013). Besides having a higher fiber content affecting sensory properties of baked products negatively, whole wheat also have more minerals, enzymatic activity, lipids, and antioxidants than white flour (Adom et al., 2005).

Consumption of products based on white flour in Argentina in 2012 was 94 kg per capita. This is a considerable number to which we must pay attention, since, during grain milling to produce white flour, most bran and germ fractions are significantly lost, thus reducing flour nutritional value.

Although the impact of such minor components as mineral and AX is very important for human nutrition and end use quality (Zhao et al., 2009), micronutrients of Argentine wheat genotypes have not been extensively studied until now. Therefore, the aim of this study was to compare the mineral and arabinoxylan contents in whole meal and white flour obtained from commercial Argentine wheat, as well as to delineate the influence of genotype and climatic conditions on the variation of these components in both wheat fractions.

2. Materials and methods

2.1. Plant material

Eleven commercial bread wheat cultivars from Argentina (ACA 303, ACA 315, ACA 320, Baguette Premiun 11, Biointa 3004, Buck 75 Aniversario, Cronox, Klein Capricornio, Klein Guerrero, Klein Yarara, LE 2330) were grown in Marcos Juarez (S32°42, W 62°6) (subregion II), Córdoba, Argentina. They were provided by the Comparative Trials Network for Wheat Varieties (RET) from two consecutive harvests (2009 and 2010). A random block design with three replicates was used. Nitrogen fertilization was applied to both harvests according to local practice. The annual average precipitation on 2009 was 937 mm while on 2010 was 861 mm and the annual average temperature was 21.47 °C for 2009 and 23.4 °C for 2010.

2.2. Grain hardness and milling

Grain hardness was determined using a NIT Infratec 1241(Foss, Denmark) calibrated according SKCS method according to AACC Method 39-25 (AACC, 2010).

Grains were milled using two different mills. Whole meal was obtained by milling grains with a blade mill (Decalab, Buenos Aires, Argentina) without discarding any grain component; while white flour was obtained by milling grain with a four-roller laboratory mill (Agromatic AG AQC 109, Laupen, Switzerland) provided with a 250 μm sieve which allowed removed all bran content. Only one white flour fraction was obtained.

2.3. Chemical analyses

2.3.1. Protein content

Moisture content was determined using Approved Method 44–19.01 (AACC International 200). Grain protein concentration, on whole meal, was determined by NIR using an Infratec 1241 (Foss, Denmark) according to AACC method 39–70A (AACC, 2010).

The nitrogen content on white flour was determined by means of a micro Kjeldahl method modified with boric acid (Approved Method 46-13, AACC, 2010). Protein was calculated as N × 5.7.

2.3.2. Arabinoxylans determination

Water-Extractable Arabinoxylans (WE-AX) and Total Arabinoxylans (T-AX) were determinated on whole meal and white flour following the method of Hashimoto et al. (1987).

2.3.3. Mineral concentration

Concentrations of major and trace elements including Al, Zn, Cu, Mn, Fe, Ca, Pb, K, Li, Mg, Cr, Co, Ni, Se, Rb, Sr, Mo, Cd, Ba, As were determined on whole meal and white flour with HNO_3 and H_2O_2on heat for 24 h and analyzed by a Thermo-Elemental X7 series ICP-MS (Thermo Fisher Scientific, Bremen, Germany), following the method of Podio et al. (2013).

2.3.4. Localization and distribution of mineral elements

For element distribution, a wheat seed was cut in cross section with a knife cutter, dried overnight and set on a stub, fixed with a commercial doble-sided adhesive carbon tape.

Topographic micrographs of the samples were obtained with FE-SEM (Field emission - scanning electron microscope) Σigma (Carl Zeiss, Jena, Germany), with an Schottky electron gun. Mineral components were detected by an energy dispersive spectrometer (EDS) and for the creation of chemical contrast maps analysis, backscattered electron images were taken. The accelerating voltage was 20 kV and a magnification of 40.000x was chosen. Point analyses and x-ray maps were carried out at the Laboratory of Electron Microscopy and X-ray analysis (LAMARX, Cordoba, Argentina).

2.4. Statistical analysis

Results were expressed as the mean of two replicates. The data were analyzed by ANOVA and results were compared by Fisher's test at a significance level of 0.05; the relationship between measured parameters was assessed by Pearson's test ($p < 0.05$). Cluster analysis was performed on the basis of Euclidean distances using average linkage sorting with maximum cluster number arbitrarily set to three. The clusters were made using mineral content as variables. The magnitude of the effect of year in relation to genotype can be shown through the use of the variance component ratio. Each variance was calculated with INFOSTAT statistical software and a ratio between Year and Genotype variance (YV/GV) larger than 1.0 indicates a greater influence of year relative to the variability associated with the genotype. All analyses were performed using the INFOSTAT statistical software (Di Rienzo et al., 2012).

3. Results and discussion

3.1. Arabinoxylan content

Table 1 shows the T-AX and WE-AX content on whole meal and white flour of the 11 wheat varieties. In relation to whole grain flour results, WE-AX values were in agreement with Finnie et al. (2006) and Dornez et al. (2008), but we found higher contents of T-AX. A significant difference was observed between harvest years for T-AX fraction which presented an average value of 7.59% in 2009 and 11.37% in 2010. On both AX fractions, there were significant differences among cultivars. Considering white flour, similar results in T-AX and WE-AX were found by other authors (Finnie et al., 2006; Dornez et al., 2008). T-AX average content on white flour in 2009 was significantly higher (5.28%) than in 2010 (4.82%). Differences among the 11 cultivars were found (Table 1). Very little is known about genotype and environmental effects on AX content in Argentine wheat. For T-AX variation, the year was the principal responsible for the variability found in whole meal as well as in white flour while WE-AX content was more influenced by genotype

Table 1
Mineral (mg/Kg), T-AX (%), WE-AX (%) and Protein (%) content on whole meal and white flour of 11 cultivars[a].

		Zn	Cu	Mn	Fe	Ba	K	Ca	Mg	Cr	Ni	Rb	Sr	Protein	WE-AX	T-AX
Whole meal flour	ACA 303	15.44b	2.56a	40.58b	24.62c	8.04b	3181.81b	350.04b	895.63a	0.07b	0.27a	1.30b	4.66a	12.23a	0.46b	9.29a
	ACA 315	17.19b	2.67a	49.95c	20.55b	8.69b	3395.27b	372.5b	1052.23a	0.04a	0.27a	1.40b	5.28a	13.47a	0.41a	10.69a
	ACA 320	15.82b	2.76a	44.85b	12.6a	9.73b	3412.04b	368.2b	1017.92a	0.01a	0.40a	1.34b	5.24a	13.27a	0.46b	8.77a
	Bag P 11	8.88a	2.01a	37.19a	16.83b	5.68a	2635.44a	277.11a	910.93a	0.04a	0.46a	1.14a	3.81a	13.12a	0.38a	8.18a
	Biointa 3004	15.36b	2.75a	35.25a	24.40c	6.73a	2812.22a	286.56a	842.2a	0.02a	0.55a	1.25b	3.98a	13.12a	0.33a	8.20a
	Buck 75 Aniv	17.48b	3.16a	42.18b	30.04d	6.13a	3404.81b	375.33b	925.22a	0.03a	0.37a	1.45b	4.36a	13.92a	0.48b	8.81a
	Cronox	13.71b	3.08a	33.13a	23.87c	5.04a	2640.03a	323.93b	840.11a	0.02a	0.33a	1.05a	3.45a	13.28a	0.50b	12.8b
	Klein Capricornio	16.35b	2.78a	43.38b	26.32c	6.82a	2973.31a	361.42b	861.43a	0.02a	0.44a	1.37b	4.72a	13.33a	0.45b	8.38a
	Klein Guerrero	27.28c	2.49a	44.00b	27.63c	7.31a	3382.73b	354.54b	898.21a	0.03a	0.81b	1.43b	4.82a	13.22a	0.35a	10.78a
	Klein Yarara	15.63b	2.30a	38.91b	26.53c	7.16a	3132.23b	338.19b	950.99a	0.04a	0.23a	1.39b	4.65a	12.93a	0.75c	8.91a
	LE 2330	15.34b	2.84a	42.35b	22.88c	11.87c	3730.71b	353.92b	1194.79b	0.02a	0.51a	1.55b	5.58a	13.08a	0.47b	9.50a
	2009 Average	18.60 b	3.20 b	44.75 b	21.94 a	8.72 b	3512.62 b	359.79 b	1086.49 b	0.03 a	0.64 b	1.48 b	5.63 b	13.21 a	0.46 a	7.59 a
	2010 Average	13.85 a	2.15 a	37.38 a	24.65 a	6.41 a	2796.58 a	324.12 a	802.53 a	0.03 a	0.20 a	1.19 a	3.56 a	13.14 a	0.46 a	11.37 b
White flour	ACA 303	8.45a	1.36a	9.89b	8.71a	1.95b	1176.34b	127.27a	257.3b	0.01a	0.18a	0.51a	1.38a	9.54a	0.61b	4.43a
	ACA 315	6.90a	1.47a	7.48a	9.08a	1.43a	900.17a	125.26a	202.55b	0.02a	0.2a	0.45a	1.28a	11.1b	0.6b	5.26b
	ACA 320	9.61a	1.74a	9.25b	11.28a	2.54c	1172.97b	172.86b	263.81b	0.01a	0.07a	0.56b	1.55a	10.91b	0.72b	5.44b
	Bag P 11	6.08a	4.66b	8.77b	9.03a	1.34a	1010.17a	140.38a	218.89b	0.02a	0.22a	0.48a	1.22a	10.36a	0.52a	5.12b
	Biointa 3004	12.5b	1.85a	6.74a	9.08a	1.54a	1038.79a	138.39a	203.42b	0.00a	0.43b	0.51a	1.14a	9.67a	0.35a	5.18b
	Buck 75 Aniv	6.93a	1.49a	8.66b	10.02a	1.24a	1180.97b	138.45a	232.94b	0.00a	0.16a	0.52a	1.24a	11.76b	0.41a	4.63a
	Cronox	6.06a	1.78a	6.64a	7.82a	1.34a	963.27a	182.96b	193.78b	0.02a	0.28a	0.39a	1.05a	9.83a	0.62b	5.65b
	Klein Capricornio	6.61a	5.69b	5.04a	7.91a	1.53a	1042.03a	148.65a	224.33b	0.05b	0.07a	0.41a	0.91a	11.68b	0.61b	5.37b
	Klein Guerrero	9.98a	1.68a	12.78c	15.67b	1.83b	1231.55b	188.65b	247.14b	0.06b	0.45b	0.58b	1.51a	10.99b	0.60b	5.62b
	Klein Yarara	6.01a	1.60a	8.20b	6.93a	1.25a	1056.32a	109.23a	202.43b	0.11c	0.16a	0.48a	1.17a	10.12a	0.67b	5.18b
	LE 2330	4.88a	1.76a	5.12a	9.61a	2.14b	937.68a	122.01a	159.37a	0.01a	0.74c	0.45a	1.28a	9.87a	0.46a	5.10b
	2009 Average	10.79 b	2.95 b	9.40 b	12.01 b	1.54 a	1204.57 b	143.79 a	259.50 b	0.02 a	0.37 b	0.56 b	1.53 b	10.38 a	0.55 a	5.36 b
	2010 Average	4.48 a	1.61 a	6.70 a	7.11 a	1.75 a	924.57 a	146.05 a	177.95 a	0.03 a	0.17 a	0.41 a	0.96 a	10.68 a	0.57 a	4.99 a

[a] Values followed by different letters are significantly different ($P < 0.05$).

on both flours (Fig. 1) in concordance with the results found by Finnie et al. (2006) who found that wheat cultivar played an important role in WE-AX content. Comparing the results of whole meal and white flour, we found significant differences in the T-AX values, observing an average reduction of 56% of this component on white flour after aleurone and pericarp layers were removed. Cronox was the cultivar that presented the highest T-AX reduction (56.25%) while Klein Capricornio presented the lowest percentage loss (35.92%) on both years. WE-AX content was higher on white flour than whole meal probably due to reduced accessibility of the bran fraction to water. There were not found a significant correlation in AX content (total and water soluble) between whole meal and white flour.

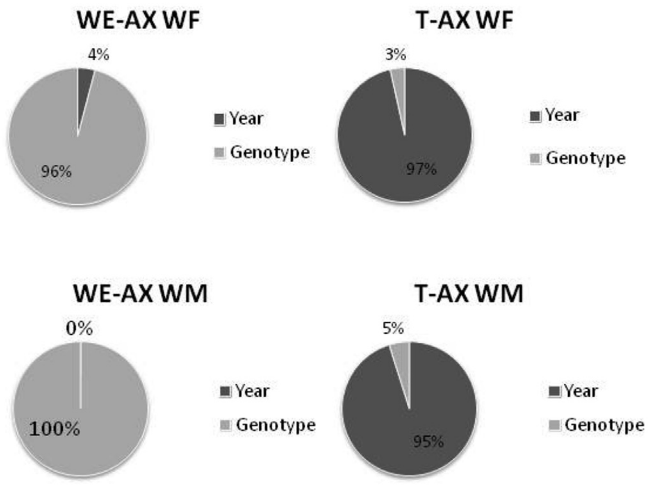


Fig. 1. Variance components of arabinoxylan content in the 11 wheat lines in both flours. WF: White Flour, WM: Whole Meal, WE-AX: Water Extractable Arabinoxylans, T-AX: Total Arabinoxylans.

3.2. *Protein content and grain hardness*

Protein values in whole meal ranged from 12.13 to 14.22% (Table 1). Similar values have been obtained for different wheat varieties in other Argentine wheats (Lerner et al., 2004). In white flour, protein values varied between 8.74 and 13.69% (Table 1) similar to other studies (Colombo et al., 2008). There was a positive correlation between grain hardness and protein content (r: 0.36, $p < 0.05$), as found Swanston et al. (2012). In general, the mean protein content lost during milling was 19.08%. Cultivar Klein Capricornio lost less amount of protein during milling (12.38%), while Biointa 3004 presented the highest loss (26.30%).

During milling, grain texture is an important characteristic for this process. Grain hardness varied between 61.9 and 78.13% and it was affected by genotype and harvest years (data not shown). In 2009 grain hardness was higher (71.53%) than in 2010 (68.02%). No correlations between AX fractions and grain hardness were found, in agreement with Bettge and Morris (2000) who suggested a minimal role of arabinoxylans in modifying wheat grain hardness.

3.3. *Mineral concentrations*

Twenty elements were determined in whole meal and white flour (Zn, Cu, Mn, Fe, Ca, K, Mg, Cr, Ni, Rb, Sr, Mo, Cd, Ba, Li, Al, Se, As, Pb, Co) (Table 1). In relation to whole meal results, eight out of the twenty elements analyzed, showed values below the detection limit: As, Pb, Li, Al, Se, Co, Mo, Cd (data no shown). Potassium (K) was the most abundant element in the cultivars studied, followed by Mg, Ca, Mn, and Fe. The concentrations of elements in kernel as a whole were significantly influenced by harvest years and genotype ($p < 0.001$). Whole meal mineral content was significantly higher in 2009 than in 2010 except for Fe and Cr. That is because temperatures before flowering in 2009 were higher than those recorded in 2010 and it is known that high temperature before flowering contributes to proper development of the embryo, where a large proportion of the micro-elements reside (Joshi et al., 2010).

The same elements analyzed on whole meal showed values below the detection limit on white flour determination (Table 1). K was the most abundant element, as well as on whole meal, followed by Mg, Ca, Fe, and Mn. All elements were significantly different among genotypes and harvest years ($p < 0.05$). There was a significant decrease in the concentration of all minerals from year 2009–2010, suggesting a strong influence of environmental factors such as rainfall and temperature, except for Ca, Ba and Cr content where no significant differences were found ($p > 0.05$). Concerning cultivars, we observed variation among genotypes in each mineral content (Table 1).

Cluster analysis was performed on whole meal and white flour to assess wheat cultivar grouping according to their mineral composition. Zn, Cu, Mn, Ca, Fe, Mg and K contents were used as clustering variables. The cluster number was arbitrarily set in three. The dendrogram for the classification analysis on whole meal is shown in Fig. 2 A. Analysis of variance indicated that cluster 1 was typified by high values of Zn, Cu, Fe and low values of Mn, Ca, Mg and K. Cluster 2 only had one genotype, Baguette Premium 11, which showed the lowest values for all minerals. Cluster 3 possessed the highest content of all minerals.

Cluster analysis was also performed on white flour and the dendrogram is shown in Fig. 2 B. Cluster 1 only had one genotype, Klein Guerrero, which showed the highest mineral content. Cluster 2 possessed the lowest mineral content values while Cluster 3 was typified by high values of Zn, Mn, K and low values of Ca, Fe and Mg. There was no difference on Cu content between the tree clusters. There were differences in genotype grouping for whole meal and white flour indicating that each mineral does not follow the same accumulation pattern in each grain tissue and that genotype influences mineral distribution.

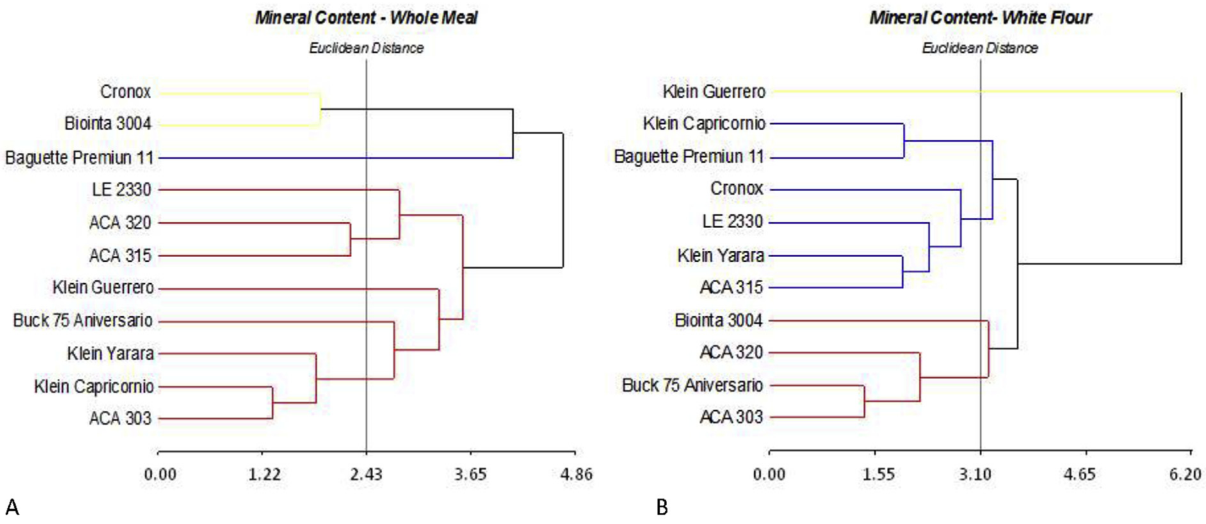
3.4. *Zn and Fe concentration*

Considering that Zn and Fe deficiency have a strong impact on human health, the results of those minerals were analyzed in detail. The total grain Zn concentration across genotypes and harvest years was 7.22–39.51 mg/kg with an average of 16.22 mg/kg. The amount of Fe in the grain also showed a large variation ranging from 5.67 to 31.84 mg/kg with an average of 23.29 mg/kg. Different authors found Fe and Zn concentration values similar to our results (Morgonuov et al., 2007; Zhao et al., 2009). Other studies have shown even greater variation; analyses of lines grown in France showed variation of 19–58 and 14–35 mg/kg for Fe and Zn, respectively (Oury et al., 2006), while in Argentine wheat cultivars Zn content varied between 20 and 30 mg/kg (Podio et al., 2013). For Zn, Baguette Premiun 11 and Klein Guerrero presented the lowest and highest contents, respectively, while for Fe, ACA 320 and Buck 75 Aniversario presented the lowest and the highest contents, respectively (Table 1). These results were in agreement with Zhao et al., (2009) who also showed significant differences in Fe and Zn contents among different wheat genotypes.

The average Zn concentration, on white flour, across genotypes and harvest years was 2.73–20.27 mg/kg with an average of 7.64 mg/kg. The amount of Fe in the endosperm fraction also showed a large variation ranging from 2.77 to 22.31 mg/kg with an average of 9.56 mg/kg. Different authors found Fe and Zn concentration values more similar to our results (Shi et al., 2010; Eagling et al., 2014).

The Fe and Zn concentrations on white flour were highly variable. Their performance varied across genotypes and years ($p < 0.001$), as reported by Gomez-Becerra et al. (2010). LE 2330 and Biointa 3004 cultivars along with Klein Guerrero were those with the lowest and the highest Zn contents, respectively, whereas Klein Yarara and Klein Guerrero were the cultivars with lowest and the highest Fe contents, respectively (Table 1).

We observed correlation between Zn, Fe (r: 0.61, $p < 0.05$) but not between proteins. These results, in concordance with Liu et al. (2014), imply that the alleles for Zn and Fe deposition in the grain



	Zn	Mn	Ca	Fe	K	Mg	Cu
C1	14.53b	34.19a	277.11a	24.13b	2726.13a	887.68a	2.92b
C2	8.88a	37.19a	305.25a	16.83a	2635.44a	910.93a	2.01a
C3	17.57b	43.27b	359.27b	23.89b	3326.61b	1088.31b	2.7b

	Zn	Mn	Ca	Fe	K	Mg	Cu
C1	9.98b	12.78c	188.65b	15.67b	1231.55b	188.65b	1.61a
C2	6.09a	6.87a	138.08a	8.4a	984.94a	138.08a	1.68a
C3	9.37b	8.64b	144.24a	9.77a	1142.27b	144.24a	2.82a

Fig. 2. Dendrogram classification of cultivar by average linkage's method using mineral content as variable and cluster analysis of whole meal and white flour minerals content from 11 wheat cultivars [a,b]. **A**. Cluster 1, n = 2 (Cronox, Biointa 3004); cluster 2, n = 1 (Baguette Premium 11); cluster 3, n = 8 (LE 2330, ACA 320, ACA 315, Klein Guerrero, Buck 75 Aniversario, Klein Yarara, Klein Capricornio, ACA 303). **B**. Cluster 1, n = 1 (Klein Guerrero); cluster 2, n = 6 (Klein Capricornio, Baguette Premiun 11, Cronox, LE 2330, Klein Yarara, ACA 315); cluster 3, n = 4 (Biointa 3004, ACA 320, Buck 75 Aniversario, ACA 303). [a]Values followed by different letters are significantly different ($P < 0.05$). [b]Mean quality parameters of each cluster analyzed by analysis of variance.

co-segregate and therefore Zn and Fe can be improved simultaneously.

3.5. Mineral distribution

Considering grain mineral distribution, external grain layers presented a higher content of all minerals than endosperm fraction; therefore, variation in the proportion of bran-aleurone/endosperm may influence grain mineral composition. As expected, milling significantly reduced the concentration of all the elements ($p < 0.05$), with an average loss ranging from 26.2% for Cu to 81% for Mn. Overall, retention of elements on white flour after milling followed this order: Cu > Ni > Cr > Zn > Ca > Fe > Rb > K > Sr > Mg > Ba > Mn. Since in general, Klein Guerrero presented the lowest average loss, taking into account all minerals (41.49%), and Klein Capricornio presented the highest average loss (67.34%), we conclude that after the same milling process mineral content varies considerably according to the cultivar. The average losses for Zn and Fe were 54.2% and 59.1%, respectively, as described by Brinch-Pedersen et al. (2007). These authors concluded that Fe and Zn losses are typically about 50% or more, with a tendency to greater losses for Fe than for Zn, which indicates a more peripheral localization of Fe. Therefore, milled wheat grain into white flour further results in reduced concentrations of Fe and Zn. However, for Mn, Mg and K percentage losses were higher: 81% for Mn, 77.3% for Mg and 66.4% for K, indicating that a great amount of these minerals were present in the outer layers of the grain.

Mapping of Zn and Fe could not be displayed in this study because of their lower contents. However, the tissular localization and distribution of other important nutritional minerals as Mg, K and Ca in bran, aleurone, embryo and endosperm of wheat grains were assessed by SEM/EDX microscopy and dot map analysis (Fig. 3). Although P content in whole meal and white flour could not be measured by ICP-MS the distribution of this element in the grain was assessed by SEM/EDX microscopy. Mg plays an important role in the nervous system, muscle function, and strong bones (Stipanuk and Caudill, 2012), while K is a very significant body mineral, important to both cellular and electrical function (Haas, 2000). A well-known health benefit of Ca is the important part it plays in developing strong bones; however, it also prevents and treats a variety of bone-related illnesses, such as osteoporosis (Stipanuk and Caudill, 2012). The P function in metabolism is very wide, together with calcium form bone structure, and play an important role in energy production (ATP), cell membranes conformation (phospholipids), and as buffering agent (maintenance of osmotic pressure) (Xue-ke et al., 2016). The highest contents of Mg, K and P were localized in bran tissues and embryo (Fig. 3) while lower contents were found on endosperm fraction. Calcium was scarcely found in embryonic tissues of wheat seeds but it was localized predominately in bran tissues although this distribution was not as pronounced as on the others analyzed minerals. Similar results were also found by De Brier et al. (2015). Phytic acid (IP6) in wheat grain is principally located in the aleurone layer which remains attached to the pericarp during milling and therefore is concentrated in the bran (Tang et al., 2008). Most of Fe and Zn and other bivalent elements in wheat grain are complexed by phytic acid resulting in insoluble salts responsible of the low bioavailability of these elements (Eagling et al., 2014).

There is evidence that the loading of minerals, such as Fe and Zn, into the starchy endosperm is highly regulated and occurs independently from loading into the outer layers that constitute the bran. Consequently, the concentrations of minerals in white flour may not reflect those in whole grain, which is dominated by the

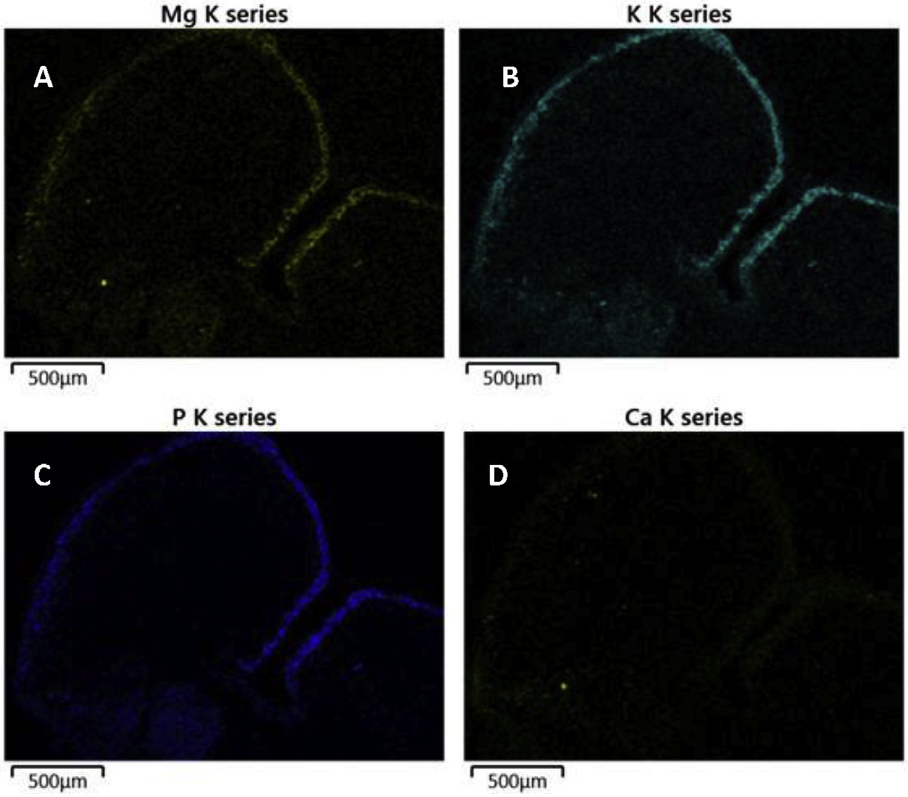


Fig. 3. Longitudinal sectioned wheat grain showing internal structure and localization of mineral elements **A,** Magnesium; **B,** Potassium; **C,** Phosphorus; **D** Calcium. Bar = 500 μm.

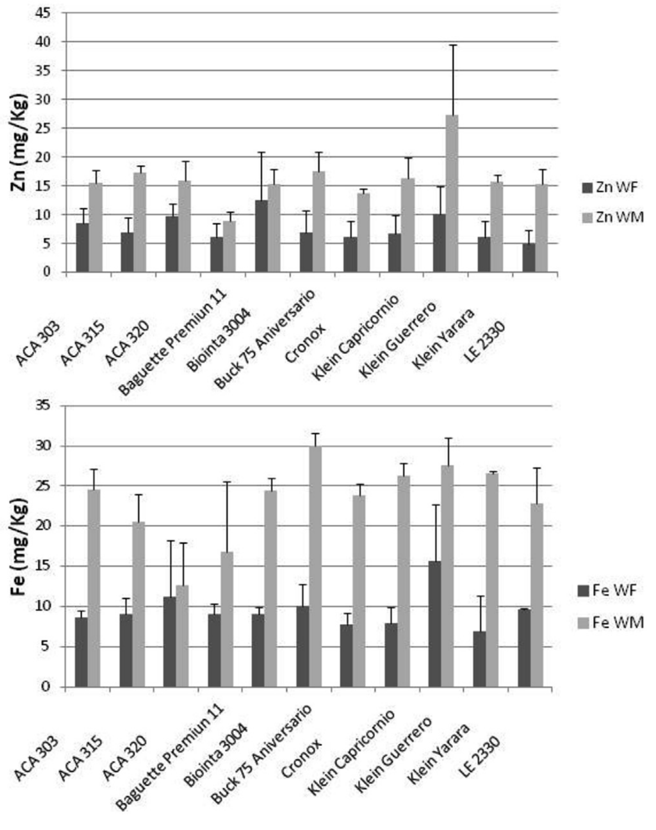


Fig. 4. The concentrations of Fe and Zn in whole meal and white flour fractions of eleven wheat cultivars. Data are means (mg/Kg) of materials grown at one site and two consecutive years. WF: White Flour, WM: Whole Meal.

minerals stored in the outer layers (especially the aleurone) and the embryo (Eagling et al., 2014). However, a positive correlation for Zn (r: 0.54; p: 0.01), K (r: 0.56; p: 0.01) and Mg (r: 0.45; p: 0.03) grain and endosperm content was found. This correlation indicates that cultivars with higher contents of Zn, K and Mg in whole meal should probably produce white flour with higher content of these minerals suggesting that mineral accumulation increase or decrease in the same level in all grain (bran and endosperm).

In regard to genotypes, our results showed that some cultivars with higher concentrations of Fe and Zn in whole meal also tend to have higher concentrations of these minerals in white flour, for example Klein Guerrero, although the concentrations in white flour were much lower than those in whole meal. In other cultivars, like Biointa 3004 and Baguette Premiun 11, the difference on Zn concentration on both flours was not as large as others. The same behavior was also seen on other genotypes for Fe concentration, where cultivar ACA 320 presented a minimal difference (10.48%), while Klein Yarara presented a higher one (Fig. 4).

The differences in element distribution may to some extent reflect that of chelating ligands such as phytate and proteins (Gomez-Becerra et al., 2010) which also can affect the nutritional quality of wheat flour. Besides during grain development minerals are differently accumulated on protein storage vacuoles, which are a primary depository for diverse minerals like Fe, Zn, Mg, Mn, Ca and K (Tanaka et al., 1974), in alleurone and embryo cells. Soil mineral content along with climatic conditions of each particular crop also significantly affects mineral deposition on each grain fraction. Furthermore, grain hardness in another important key which determinates mineral grain content on each grain fraction. The harder the grain, the higher whole meal content of Mn, K and Ca and the higher Fe, K and Mg white flour content (r:0.42–0.67, $p < 0,05$).

3.6. *Effect of climatic conditions and genotypes on mineral concentration*

Whole meal and white flour mineral components tended to be influenced, to different extents, by environmental and genetic factors. The magnitude of the effect of climatic factors in relation to genotype can be shown through the use of the variance component ratio. A ratio larger than 1.0 indicates a greater influence of climatic factors relative to the variability associated with the genotype (Table 2). In relation to whole meal, crop year was mostly responsible for Zn, Mn, Fe, Ba, Ca, and Cr variation content, while genetic factors influence more Cu, K, Mg, Ni, Rb and Sr contents. Considering white flour results, the relative influence of climatic factors on most minerals was more pronounced than genetic variation for Cu, Mn, Ba, Ca, Cr, Ni and Rb contents, and genetic effects were stronger for Fe, Zn, K, Mg and Sr.

4. Conclusion

There was a significant variation in concentration and composition of proteins, arabinoxylan and minerals content not only in whole meal but also in white flour, among Argentine wheat genotypes. For T-AX variation, year was the main factor accounting for the variability found in whole meal as well as in white flour, while WE-AX content was more influenced by genotype on both fractions. Mineral content was significantly influenced by genotype and harvest years. The extent of the influence of climatic conditions related to genetic factors depended on mineral and flour types, where Fe and Zn contents were more affected by crop year in whole grain and by genetic factors in white flour. There were differences in the grouping of different genotypes in each cluster analysis on both whole meal and white flour, indicating that mineral accumulation and deposition depends on the grain fractions and cultivars. There was a severe reduction of T-AX and mineral content after milling because they are mostly presented on the pericarp and the aleurone layer. While in general, genotypes with higher mineral content in whole meal also had higher values in white flour, loss level of each mineral depended on each genotype and there was a wide variation between minerals. The average loss of Zn and Fe were 54.2% and 59.1%, respectively; however the loss percentage had a wide variation for these minerals, from 10% to 74% for Fe, and from 19 to 68% for Zn. In the case of T-AX, milling losses average was 45%. Genotypes with lower T-AX, Fe and Zn milling losses than the average were found in this study, and this fact should be taken into

Table 2
Mineral ratios on both whole meal and white flour and loss percentage after milling.

	Zn	Cu	Mn	Fe	Ba	K	Ca	Mg	Cr	Ni	Rb	Sr
YV/GV WF	0.61	3.59	2.36	0.98	4.77	0.89	2.80	0.69	3.16	2.93	1.13	0.60
YV/GV WM	1.72	0.51	1.27	2.70	2.16	0.93	1.42	0.69	1.53	0.71	0.83	0.47
Lost %	54.19	26.22	81.01	59.17	77.51	66.44	57.36	77.33	0.00	28.57	64.18	73.20

YV: Year Variance, GV: Genotype Variance, WF: White Flour, WM: Whole Meal.

account, along with genotypes with higher contents of these components, when the purpose is to improve Zn, Fe, AX content in white flour. Owing to the high consumption of white flour in Argentina, it was required a deeply study of how milling affects different minerals concentrations on wheat grain and determine which cultivars loss less amount of minerals after milling as such data are of relevance for breeding, production, and milling sectors for Argentina. The next step will be to compare mineral bioavailability from baked goods or other products made with white flour or whole grain flour, in order to assess the efficiency of higher mineral content in both types of products.

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