Climatic Thresholds for Concentrations of Minerals and Heavy Metals in Argentinean Soybean

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ABSTRACT

Minerals affect the nutritional, rheological, and safety features of food products. Soybeans represent a good source of minerals. The objective of this study was to evaluate the effect of the environment on the variability of mineral elements in Argentinean soybeans in field experiments. Climatic variables (maximum, mean, and minimum air temperature; solar radiation; precipitation; and potential evapotranspiration) were recorded daily during the seed filling period; soil properties were also reported. Minerals in soybeans were determined by inductively coupled plasma–mass spectrometry. Selenium was determined by hydride generation coupled to an atomic absorption spectrophotometer. Molybdenum and selenium were significantly increased (over 100%) in soybeans grown at higher soil pH with high available molybdenum. Air temperature was the climatic variable that best predicted changes in the soybean seed mineral composition. Optimum weather conditions (OWC) were defined by thresholds of the climatic variables by regression trees for desirable mineral composition. Maximum and minimum daily air temperatures during the seed filling period (30.1 and 17.1°C, respectively) were the OWC for maximizing calcium, magnesium, and manganese contents. A maximum daily air temperature over 28.0°C resulted in higher iron and cobalt levels ($p < 0.001$). Maximum zinc content was observed when solar radiation exceeded 18.1 MJ m^{-2} during seed filling ($p < 0.001$). Results from this study showed variation in the mineral composition of soybeans. Environmental features during the seed filling period should be considered when desired mineral composition is expected in soybean according to the end uses.

MINERALS CONSTITUTE the basis of life on earth (Graham et al., 2007), and their absence in the diet leads to unperceived symptoms and severe health consequences. Mineral undernourishment is of concern throughout the world, and plant-derived foods are considered a mineral source to attain an beginadequate daily mineral intake (Graham et al., 2007). Selenium (Se) is sought for nutraceutical properties because it helps to strengthen the immune system. Geographical areas with Se deficiencies have shown higher incidences of diseases (Rayman, 2012). Soybeans are consumed daily by millions of people and animals. Along with proteins and oil, soybeans provide minerals to the diet (Graham et al., 2007).

Minerals also contribute to the properties of end-food products. Iron (Fe), copper (Cu), and manganese (Mn) affect the oxidative stability and shelf life of edible oils (Knothe and Dunn, 2003). Low Ca, Mn, and boron (Bo) contents in soybeans have been associated with improved visual attributes of a popular Asian food called natto (Yoshikawa et al., 2014).

The uptake of heavy metals, such as lead (Pb), cadmium (Cd), and arsenic (As), occurs at the same time the plant is absorbing mineral nutrients (Lavado, 2006). Some heavy metals, such as Pb, Cd, and As, present in soybeans grown in long-term cultivated areas of the United States (Chen et al., 2009) and Brazil (Corguinha et al., 2015) have been estimated using risk assessment models.

The variability of the concentration of phosphorous (P), B, Zn, and Mn in soybean seeds was observed in soybeans grown in different environments, also affecting the mineral content of tofu (Bhardwaj et al., 2007). Jaureguy et al. (2013) reported that there is significant improvement by sowing date interaction for minerals in soybeans. Late sowing dates associated with lower temperatures during seed fill result in a lower average mineral

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Locations†	Soil	Texture	pH	Salinity	OM‡	CEC§
				dS m^{-1}	%	cmol kg^{-1}
BW (38°19′S; 60°14′W)	Petrocalcic Argiudol	loam	6.4	0.4	2.3	21.5
BO (37°49′S; 63°02′W)	Typic Haplustol	sandy loam	6.8	0.6	1.4	14.9
CE (24°54′S; 65° 29′W)	Udic Ustocrept	loam	6.2	0.5	1.1	10.4
CA (27°38′S; 55°30′W)	Rhodic Kandiudult	loam clay	5.7	0.5	2.4	28.7
FA (27°04′S; 65°25′W)	Typic Hapludol	loam clay	6.0	0.4	1.9	11.3
MA (31°49′S; 63°46′W)	Entic Haplustol	loam silt	6.9	0.4	2.0	19.7
PA (31°44′S; 60°32′W)	Aqcuic Argiudol	loam clay	6.2	0.5	3.2	30.8
RQ (29°40′S; 59°12′W)	Typic Argiudol	loam clay	6.2	0.3	1.5	15.5

† BO, Bordenave; BW, Barrow; CA, Cerro Azul; CE, Cerrillos; FA, Famailla; MA, Manfredi; PA, Parana; RQ, Reconquista.
‡ Organic matter.
§ Cation exchange capacity.

content (Jaureguy et al., 2013). It has been proposed that higher air temperature promotes higher Ca content in seeds (Bellaloui et al., 2011; Gibson and Mullen, 2001).

Heterogeneous farmable land of Argentina (20.2 million ha) contributes to approximately 20% of world soybean production. Several agricultural practices, including crop biofortification, are considered as management tools to enhance mineral composition in staple crops (Graham et al., 2007). For that reason, studying the effect of the environment on mineral composition may help agricultural management efficiency for nutritional purposes. Soybean production is mainly destined for the preparation of food products, and plant foods are the main source of minerals for human and animal nutrition. Addressing the sources of variation in mineral concentration in soybeans may lead to a better understanding of the link between agricultural production and human health (Welch and Graham, 1999). The aim of the present study was to determine the effect of the environmental variables on the variability of mineral elements in Argentinean soybeans evaluated in field experiments. Soil properties and soil minerals were also compared with mineral composition in the soybean seed samples.

MATERIALS AND METHODS
Soybean Materials and Field Experiments

Two soybean [*Glycine max* (L.) Merr.] varieties were use in this study. One of them was ALIM 3.14, which is a breeding line for specialty high-protein and nongenetically modified soybeans developed by the Soybean Breeding Program at Estación Experimental Agropecuaria– Instituto Nacional de Tecnología Agropecuaria. The other one was a commercial transgenic glyphosate-resistant soybean widely used in Argentina (Carrera et al., 2011).

The experimental design and agricultural practices were described in detail by Carrera et al. (2011). Eight locations were selected covering the Argentine soybean cropland from 24°54′ to 38°19′ S and from 55°30′ to 65°25′ W (Table 1): Barrow (BW), Bordenave (BO), Cerrillos (CE), Cerro Azul (CA), Famailla (FA), Manfredi (MA), Parana (PA), and Reconquista (RA). Field experiments were conducted on two sowing dates, classified as early and late, with two in-field replicates in a randomized complete block design during the crop seasons 2006–2007 and 2007–2008. Early sowing dates for lower latitudes were between the end of October and the beginning of November and for higher latitudes between

the end of November and the beginning of December. Late sowing dates for higher latitudes were between the middle of November and the first days of December and for higher latitudes were between the middle of December and the middle of January. Some environments were lost due to adverse conditions, such as extreme drought, hail, floods, or animal damage.

Maximum, mean, and minimum air temperature (°C); precipitation (PP) (mm); potential evapotranspiration (mm); and solar radiation (SR) (MJ m^{-2}) were recorded daily during the seed filling period between the R5 (beginning seed) and R7 (beginning maturity) stages (Fehr and Caviness, 1977). Hydric balance (mm) was calculated as the difference between PP and potential evapotranspiration.

Soil Analysis and Mineral Elements in Soils

Composed soil samples (0–30 cm depth) were analyzed for texture, pH, salinity (dS m^{-1}), organic matter (g kg^{-1}), cation exchange capacity (CEC) (cmol kg^{-1}), and the following available macronutrients: P (ppm), sodium (Na) (cmol kg^{-1}), K (cmol kg^{-1}), Ca (cmol kg^{-1}), and Mg (cmol kg^{-1}) (SAMLA, 2004).

Available micronutrients and trace elements were extracted from 15 g of pulverized soil samples with 30 mL of 0.2 mol L^{-1} EDTA di Na–di H$_2$O (Garrabrants and Kosson, 2000). The concentrations of Fe, Zn, Mn, Cu, Co, and Cd were measured using flame atomic absorption spectrometry (AAnalyst 100; PerkinElmer, Waltham, MA) (USEPA, 2003). Molybdenum was determined with graphite furnace atomic absorption spectrometry (HGA 900 AAnalyst 400; PerkinElmer), and As was determined with hydride atomic absorption spectrometry (FIAS 400 AAnalyst 100; PerkinElmer) (USEPA, 2003).

Mineral Elements Analysis of Soybean Seeds

Calcium, K, Mg, P, Na, Fe, Zn, Mn, Mo, Cu, Co, Se, aluminum (Al), Cd, and As were determined in 2-g soybean samples that were digested with HNO$_3$. The minerals were analyzed by inductively coupled plasma–mass spectrometry (7500c series; Agilent Technologies, Santa Clara, CA) with a H$_2$/He collision cell. National Institute of Standards and Technology standard reference material was used for validation. Detection limits, in mg kg^{-1} seed dry weight basis, were 3.25 Ca, 5.75 P, 86.25 K, 2.18 Mg, 29.75 Na, 0.925 Fe, 0.875 Al, 0.065 Mn, 0.068 Zn,

Table 2. Available minerals in soils from eight locations of the Argentine soybean cropland.

Minerals	Locations†							
	BW	BO	CE	CA	FA	MA	PA	RQ
P, ppm	8.70	66.40	22.40	2.80	21.50	36.80	32.60	13.40
Na, cmol kg^{-1}	0.30	1.30	0.20	0.30	0.30	0.40	0.80	0.30
K, cmol kg^{-1}	1.90	1.60	0.30	0.20	0.70	2.30	1.70	0.50
Ca, cmol kg^{-1}	12.20	6.90	6.50	16.90	5.30	10.60	16.70	7.70
Mg, cmol kg^{-1}	3.60	3.20	2.20	6.40	2.50	2.90	3.60	2.40
Fe, mg kg^{-1}	189.70	134.20	546.30	138.70	246.40	150.40	94.10	193.70
Cu, mg kg^{-1}	1.80	1.50	10.40	1.40	3.00	1.90	2.10	1.30
Zn, mg kg^{-1}	1.50	1.80	71.80	0.90	3.4	125.30	1.40	0.80
Co, mg kg^{-1}	3.20	1.20	46.30	1.10	1.50	2.50	4.50	3.60
Mo, mg kg^{-1}	0.06	0.07	0.09	0.09	0.15	0.48	0.32	0.29
Mn, mg kg^{-1}	196.10	96.00	1773.60	158.60	214.00	284.10	511.60	408.60
As, mg kg^{-1}	0.01	0.02	ND‡	0.17	0.15	0.09	0.15	0.05
Cd, mg kg^{-1}	0.03	0.03	0.02	0.03	0.04	0.35	0.08	0.02

† BO, Bordenave; BW, Barrow; CA, Cerro Azul; CE, Cerrillos; FA, Famailla; MA, Manfredi; PA, Parana; RQ, Reconquista.

‡ Not detected under the established conditions.

Table 3. Seed fill climatic conditions at the environments resulted by combining location, year, and sowing date.

Location†	Sowing date‡	Tmx§	T¶	Tmn#	SR††	pp-pEVT‡‡
		——————————— °C ———————————			MJ m^{-2}	mm
2006						
BW	early	25.0	18.4	11.9	19.7	60.3
	late	23.6	17.6	11.5	17.3	−17.9
BO	early	25.0	18.4	11.9	18.3	66.7
CE	early	26.0	21.4	16.8	16.6	24.2
	late	24.3	20.2	16.0	13.4	5.5
CA	early	30.2	25.1	19.9	22.7	92.2
	late	30.1	25.1	20.1	20.8	91.3
FA	late	26.8	22.0	17.2	11.5	6.4
MA	early	27.0	22.0	16.8	21.0	−27.7
	late	25.6	20.8	16.0	16.1	79.0
PA	early	26.9	22.2	17.5	16.6	337.1
	late	25.1	21.0	16.9	13.4	401.7
RQ	early	30.1	25.0	19.9	20.4	201.3
	late	28.6	23.9	19.2	17.4	−15.7
2007						
BO	late	25.0	17.8	10.6	15.7	−28.6
CE	early	24.7	19.5	16.0	13.3	199.7
	late	24.5	19.4	16.2	14.5	47.6
CA	late	29.7	24.6	19.5	20.1	47.5
FA	early	29.7	24.3	19.0	17.0	158.2
	late	27.6	22.8	18.0	13.5	253.3
MA	early	27.4	22.1	16.7	19.2	8.3
	late	25.6	19.5	13.4	15.3	30.3
PA	late	27.3	21.1	14.9	17.6	−63.0

† BO, Bordenave; BW, Barrow; CA, Cerro Azul; CE, Cerrillos; FA, Famailla; MA, Manfredi; PA, Parana; RQ, Reconquista.

‡ Seed fill occurs from the end of January to the beginning of March for early sowing dates and from the end of February to the middle April for late sowing dates.

§ Maximum air temperature.

¶ Mean air temperature.

Minimum air temperature

†† Solar radiation

‡‡ Precipitation minus potential evapotranspiration.

Table 4. Mean, minimum, and maximum values of mineral concentrations in two soybean genotypes averaged across environments (location, year, and sowing date).

Minerals	Specialty soybean			Commercial GR† soybean		
	Mean	Min.	Max.	Mean	Min.	Max.
			—— g kg^{-1} ——			
Ca	2.99	1.76	4.84	3.93	2.07	6.77
K	19.43	15.14	25.21	15.73	9.60	22.23
Mg	2.34	1.94	2.98	2.72	2.19	3.73
Na	0.51	0.21	0.90	0.66	0.30	1.20
P	8.69	6.34	10.72	7.45	4.98	9.89
			—— mg kg^{-1} ——			
Fe	106.85	74.76	156.94	98.13	77.17	141.16
Al	13.95	2.62	28.38	7.56	2.29	30.94
Zn	43.64	23.82	85.40	48.24	24.74	140.45
Cu	14.32	8.05	23.82	16.24	9.66	24.83
Mn	38.34	21.70	70.05	41.00	17.24	100.51
Mo	7.39	0.65	33.30	5.25	0.68	19.07
Cd	0.04	0.01	0.11	0.04	0.02	0.09
As	ND‡	–	–	ND	–	–
			—— μg kg^{-1} ——			
Co	139.04	39.23	430.20	206.46	60.90	536.00
Se	70.81	1.40	374.40	64.34	ND	413.30

† Glyphosate-resistant.

‡ Not detected.

0.001 Cu, 0.009 Co, 0.055 As, and 0.012 Cd. Selenium was determined by digesting samples with a mixture of nitric acid, hydrochloric acid, and magnesium nitrate (Davis et al., 2001). Hydride generation was performed using an automatic flow injection hydride generator coupled to an atomic absorption spectrophotometer (PinAAcle 900T; PerkinElmer).

Statistical Analysis

Linear mixed models (West et al., 2007) were fitted to estimate the environmental effect on minerals: the "cultivar" (specialty vs. commercial cultivar) effect was considered as fixed, and "environment" (combination of location, sowing date, and year) as well as cultivar × environment interaction effects were regarded as random. The significance of variance components were tested by likelihood ratio tests (Molenberghs and Verbeke, 2007). P values were corrected by Bonferroni criteria ($\alpha = 0.05$). The relative environmental variance (REV) was expressed as the percentage of the environmental standard deviation to the mean mineral concentration. The ratio between mean mineral concentrations of soybean types was calculated. Partial least squares (PLS) regressions (Aastveit and Martens, 1986) were accomplished. The plot suggested by the PLS approach was used to identify the climatic covariables explaining particular trait × environment interactions.

Regression trees (RTs) (Breiman et al., 1984) were fitted to identify climatic thresholds for mineral concentrations in seeds. The response variable (each mineral element) was modeled as a piecewise constant function of the climatic variable. Data were first split into two subsets based on a threshold value of the predictor variable that resulted in the greatest increase/decrease in explained variance of the response variable. Each subset, or node, was then analyzed independently using the same binary partitioning procedure, with a split performed only if the resulting model exceeded predefined criteria of improvement. Environmental variables

splitting early tree nodes were used to define optimum weather conditions (OWC) for each mineral. The predicted response value for that pruned tree was compared with the overall trait mean with a Fisher test at $\alpha = 0.05$. Finally, multiple Pearson correlations between minerals and soil features were calculated at the 5% significance level ($\alpha = 0.05$). InfoGen (Balzarini and Di Rienzo, 2012) software was used to accomplish the statistical analysis.

RESULTS AND DISCUSSION

Environment Effect on Soybean Minerals

The soil properties and soil mineral composition of each location are detailed in Tables 1 and 2. The soils were suitable for agricultural activity with no limitations (Table 1). Zinc, Cd, and As in the used soils were under the maximum allowable concentrations for agricultural production (600, 3, and 20 mg kg^{-1}, respectively) according to Argentinean Law 24051 (Argentinean National Law, 1992). The values of minimum, mean, and maximum air temperatures; solar radiation; precipitation; and hydric balance data for the studied environments defined by the combination of location, crop year, and sowing date are shown in the Table 3. These environmental features are averages of eight sowing locations, 2 yr, and two sowing dates.

The concentration of Se and Mo in soybean seeds showed the greatest variation, followed by Ca, Na, Al, Zn, Cu, Mn, Co, and Cd (Table 4). These mineral concentrations also differed among the analyzed soils (Table 2). The mineral composition in soybeans reflects their content in the soil (Wauchope, 1978), even though soils might not be the unique source of variation because the climatic variables during the growing season may influence the mineral intake from soils (Bennie et al., 1982; Jaureguy et al., 2013). The factor calculated as REV showed the total variance explained by the environmental effect (Table 5). A high and significant contribution of the environment ($p < 0.0036$) occurred in terms of

Table 5. Mineral concentrations averaged across soybean types and environments (locations, year, and date of sowing).

Mineral	Mean	Min.	Max.	REV†	S/C‡
		g kg⁻¹		%	
Ca	3.44	1.76	6.77	24.42*	0.76*
K	17.68	9.60	25.21	6.22	1.24*
Mg	2.52	1.94	3.73	7.54*	0.86*
Na	0.58	0.21	1.20	0.00	0.77*
P	8.10	4.98	10.72	4.94	1.17*
		mg kg⁻¹		%	
Fe	102.73	74.76	156.94	12.04*	1.09
Al	10.93	2.29	30.94	0.01	1.85*
Zn	45.84	23.82	140.45	38.94*	0.90
Cu	15.23	8.05	24.83	13.66*	0.88
Mn	39.59	17.24	100.51	29.30*	0.94
Mo	6.38	0.65	33.30	99.84*	1.41
Cd	0.04	0.01	0.11	25.00	1.00
As	ND§	–	–	–	–
		µg kg⁻¹		%	
Co	170.24	39.20	536.00	58.82*	0.70
Se	67.53	0.00	413.30	131.43*	1.17

* Significant at the 0.05 probability level.
† Environmental variance relative to the mean for each mineral concentration.
‡ Specialty/commercial soybean ratio of averaged values.
§ Not detected.

the total variance for Se and Mo contents, with 131.43 and 99.84% REV, respectively (Table 5). The REVs for Co (59%), Zn (39%), Mn (29%), Ca (24%), Cu (14%), Fe (12%), and Mg (8%) (Table 5) were significantly lower. These low REVs suggested relatively more stable concentrations across environments. Similarly, no variations in Fe content in soybeans from different sowing dates were previously reported by Jaureguy et al. (2013). Iron deficiency is a concern throughout the world. Soybeans represent a good source to address at least an adequate intake (Gibson and Mullen, 2001).

Wiersma and Moraghan (2013) reported minor differences in element concentrations. In this study, the minor differences in Fe, Zn, Cu, Mn, Mo, Co, and Se were primarily attributed to the effect of the location and environment (Table 5). To achieve a better understanding of this variation, PLS regressions were performed. The orthogonal representations are given in Fig. 1, where climatic variables and soil parameters were considered as covariables of the projected regressions of the mineral residues from the linear mixed models. Maximum, mean, and minimum air temperatures were highly correlated (data not shown). Therefore, only mean air temperature was used for the PLS regression (Fig. 1). The effect of the environment on minerals in soybeans was further investigated by RT, which showed climatic thresholds with significant differences in elements concentrations (Table 6; Fig. 2). Also in this study, optimum weather conditions (OWC) were defined as the climatic variables that maximize or minimize the content for each mineral element in soybeans (Table 6).
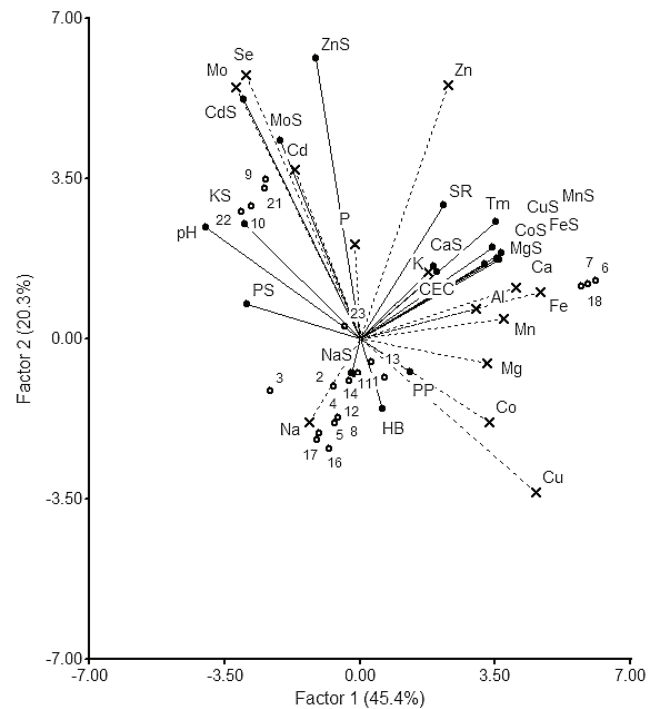

Fig. 1. Orthogonal representation of the projections of climatic and soil variables of partial least squares regressions in mineral concentrations of soybeans. Empty dots represent environments. Predictors are indicated by vectors ended with filled dots: mean daily air temperature (Tm), precipitation (PP), hydric balance (HB), solar radiation (SR), cation exchange capacity (CEC), soil pH, and available minerals in soil (CaS, KS, PS, MgS, NaS, MoS, MnS, FeS, ZnS, CuS, CoS, CdS, and AsS). Predicted response variables (minerals in seeds) are shown with star-ended vectors: K, P, Ca, Mg, Na, Fe, Zn, Al, Mn, Cu, Mo, Co, Se, and Cd. Environments: 1, Barrow 1, 1 (first year, early sowing date); 2, Barrow 1, 2 (late sowing date); 3, Bordenave, 1, 1; 4, Cerrillos, 1, 1; 5, Cerrillos, 1, 2; 6, Cerro Azul, 1, 1; 7, Cerro Azul, 1, 2; 8, Famaillá, 1, 2; 9, Manfredi, 1, 1; 10, Manfredi, 1, 2; 11, Paraná, 1, 1; 12, Paraná, 1, 2; 13, Reconquista 1, 1; 14, Reconquista, 1, 2; 15, Bordenave, 2, 2; 16, Cerrillos, 2, 1; 17 Cerrillos, 2, 2; 18, Cerro Azul, 2, 2; 19, Famaillá, 2, 1; 20, Famaillá, 2, 2; 21, Manfredi, 2, 1; 22 Manfredi, 2, 2; 23, Paraná, 2, 2.

Table 6. Overall mean of mineral concentration and optimum weather conditions for maximizing mineral concentrations in soybean seeds.

Minerals	OWC†					Mineral means	
	Tmx‡	T§	Tmn¶	PP#	SR††	OWC	Overall mean
	————————— °C —————————			mm	Mj m^{-2}	————— g kg^{-1} —————	
Ca	>30.1*		>17.1*			5.10	3.44
K		>20.5*			≤14.8	20.75	17.68
Mg	>30.1*		>17.1*			3.14	2.52
Na	≤26.3*					0.62	0.57
P	>27.1					8.60	8.11
						————— mg kg^{-1} —————	
Fe	>28.0*					122.98	102.73
Al	≤30.1		>16.7*			13.35	10.93
Zn					>18.1*	53.52	45.84
Cu		>22.1*				19.69	15.23
Mn	>30.1*		>17.1*			71.52	39.59
Mo				≤179.4		18.79	6.38
Cd			>17.0*			0.03	0.04
						————— µg kg^{-1} —————	
Co	>28*					309.97	156.10
Se				≤188.8	>18.4*	245.99	63.11

* Significant at the 0.05 probability level.
† Optimum weather conditions.
‡ Maximum air temperature.
§ Mean air temperature.
¶ Minimum air temperature.
# Precipitation.
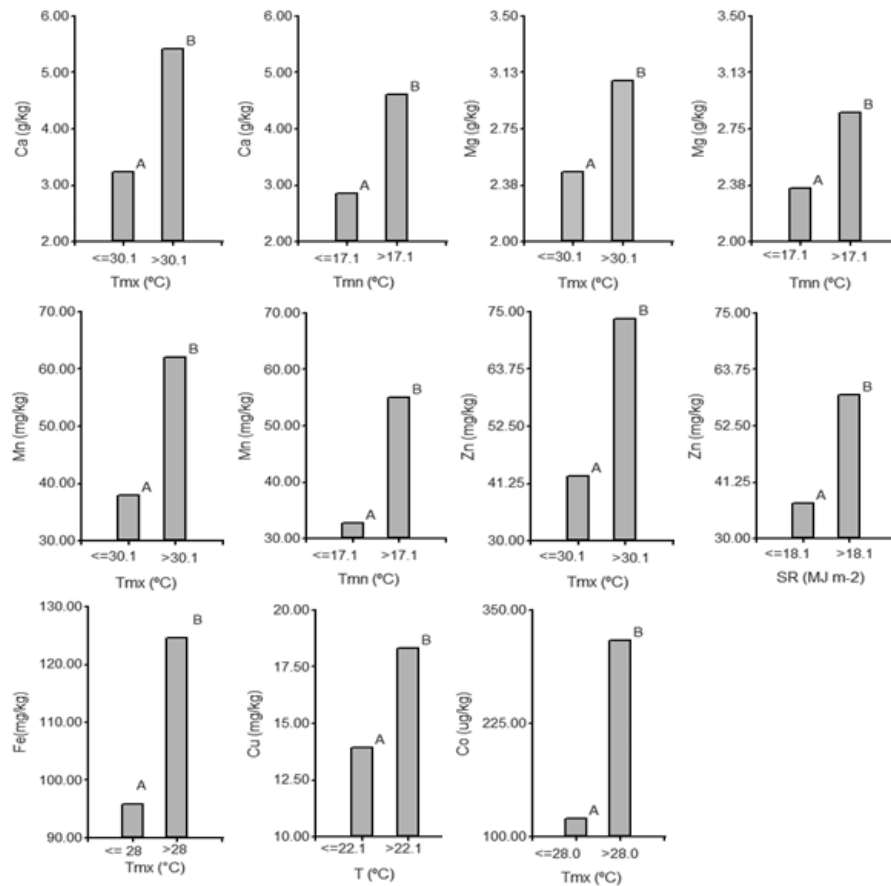†† Solar radiation.

Fig. 2. Differences on mineral concentrations in soybeans ($P \leq 0.001$) after climatic thresholds were applied. Climatic variables were the predictor variables that resulted from splitting data in the regression trees. Climatic variables during the seed filling period (R5–R7): SR, mean daily solar radiation; T, mean daily air temperature; Tmn, mean daily minimum air temperature; and Tmx, mean daily maximum air temperature.

Maximum values were preferred for the nutritionally necessary elements (Ca, Mg, K, P, Fe, Zn, Cu, Mo, Mn, Co, and Al), and minimum values were desired for potentially toxic minerals (Na, As, and Cd) or required under regulation. Some differences emerged between the results of the performed regressions due to deviations of the projections (Arroyo et al., 2005). Therefore, only consistent regressions ($\alpha = 0.05$) with the measured variables were explained.

With few exceptions, air temperature was the most influential factor affecting mineral concentrations of the soybeans. Jaureguy et al. (2013) found higher contents of Ca, K, Mg, Mn, and Fe in soybeans from sowing dates associated with higher air temperature throughout the crop season and during the critical period in the same geographical location. Bellaloui et al. (2011) also observed higher seed Ca concentration in Harosoy isolines affected by increments in the maximum air temperature. Gibson and Mullen (2001) also observed that increments in Ca were accompanied by increments in air temperature to a maximum content at 30°C. In the present study, the average maximum air temperature was 30.5°C (Table 3), and the prediction for higher Ca content was at a maximum air temperature over 30.1°C (Table 6).

The increase in Mg, K, P, Fe, Al, Mn, Cu, and Co was also predicted by high air temperatures (Table 6). Significant increments were observed for Mg ($p < 0.0001$), K ($p = 0.0197$), Mn ($p = 0.0005$), Cu ($p < 0.0001$), and Co ($p < 0.0001$) for higher air temperatures. Greater concentrations of Mg and Mn occurred for maximum air temperatures over 30.1°C. Sodium was the only mineral that increased when the temperature decreased ($p = 0.0043$). Conversely, an increase over 60% in Na content was previously observed with temperatures over 30°C (Gibson and Mullen, 2001). Changes in air temperature had a greater effect on Na, as suggested by the projections in Fig. 1. A 90° angle formed among the projected vectors for Mo, Se, Cd, and Cu with air temperature, indicating that there is low correlation between these minerals and air temperature. Cadmium and Mo were more closely associated with the soil matrix. However, a significant increase in Cu and a decrease in Cd were predicted by air temperature thresholds (Table 6). A higher Fe ($p < 0.0001$) in soybeans resulted from maximum air temperatures over 28°C. Contrarily, Bellaloui et al. (2011) reported higher Fe content in soybeans exposed to lower temperatures.

Solar radiation was closely correlated with air temperature (Fig. 1). Solar radiation was a good variable after air temperature for node formation on splitting data by RT for predicting changes in mineral concentration (Table 6). Significantly higher Zn ($p < 0.0001$) and Se ($p = 0.0088$) contents resulted when SR was over 18.1 and 18.4 MJ m^{-2}, respectively. Assuming no significant differences in the efficiency use of radiation and radiation interception, higher total incoming solar radiation produces a higher biomass; therefore, it was presumed that more nutrients are translocated to the seeds (Bennie et al., 1982). Significant differences ($p < 0.05$) in Ca, Mg, Mn, Fe, and Zn concentration were observed for the SR 18.1 MJ m^{-2} threshold and air temperature thresholds (Table 6). This study confirmed that there was a high correlation between SR and air temperature (Fig. 1).

Bellaloui et al. (2011) demonstrated that soybeans have higher P content when the seeds grow under irrigation conditions. In the present study, P in soybeans was not correlated with hydric balance or PP. Only changes in Mo and Se were predicted by

changes in PP (Table 6). Mineral concentration over the proposed thresholds of PP was not statistically significant ($p > 0.05$).

Soil pH reaction affects the availability of plant nutrients and their likeliness to be absorbed, transported via the xylem, and accumulated in the seed via the phloem (Jensen, 2010). Pearson correlation coefficients were calculated, and significant correlations were found ($p < 0.05$) between the mineral concentration in seeds and the soil's CEC and pH. Significant negative correlations were found between soil pH and the individual mineral concentrations of Ca, Mg, Fe, Al, Cu, Mn, and Co in seeds. Positive significant correlations between soil pH and the concentrations of Mo, Se, and Cd in seeds were also found. Some of these correlations were consistent with the predicted projections of the PLS regressions (Fig. 1); that is, the projections for Cu in seed and soil pH followed opposite directions (an almost 180° angle was formed between their vectors), and Mo in seeds and soil pH followed a similar direction, placed together on the upper left quadrant. A slightly acidic pH soil solution favors the availability of most trace elements to plants except for Mo, whose increased availability is observed in moderately alkaline soils (Jensen, 2010). The levels of Mo in soybeans were also closely correlated with Mo availability in the soil matrix (Fig. 1). Soil from BO had a pH value close to soil from MA (Table 1), but Mo content in the soil differed significantly between the mentioned locations (Table 2). A similar result was observed for Cd. Selenium in seeds was also high and positively correlated with soil pH, in agreement with the projections of Fig. 1. Zhao et al. (2009) extracted a higher content of available Se from soils with higher pH. Potassium and Zn showed no significant correlations with soil pH. Potassium, one of the major plant nutrients that showed the largest concentration in soybeans, appears to be less affected by soil pH. Finally, Zn was significantly correlated with soil CEC.

Genotype Effect on Soybean Minerals

Although cultivar comparison was not the aim of the present study, the mineral element ratio between specialty and commercial soybeans (Table 5) was calculated as a parameter to detect genotype differences. Previous studies suggested that the genotypic background has a stronger effect on seed mineral concentrations than the environment's effect (Bellaloui et al., 2011). Iron content was significantly higher in the specialty soybean than in the commercial transgenic glyphosate-resistant soybeans. Calcium, Mg, and Na concentrations were significantly lower in the specialty soybeans than in the commercial soybeans (specialty/commercial ratio <1 at $\alpha = 0.05$) (Table 5). These traits make specialty soybeans interesting because Fe in seeds is nutritionally important for human diets, and low Ca content is desired for tofu production. Also, it was observed that K, P, and Al were significantly higher on average in the specialty soybeans than in the commercial soybeans. The differences between soybean varieties were consistent across the 20 tested environments.

This is one of the few studies researching changes in the concentrations of soybean minerals affected by the environment during seed fill. Mineral composition in seeds is becoming a concern for breeders and for the food/feed industry because vegetables are the main source of minerals for human and animal nutrition. The concentrations of minerals in soybeans were affected not only by the concentration of minerals in soils and soil pH but also by the climatic conditions (e.g., air temperature and solar radiation) governing during the crop seed filling period. Air

temperature and soil pH have the strongest effect on soybean mineral concentration. Higher air temperature during the seed filling period favored Ca, Mg, P, Fe, Zn, and Co concentrations in soybeans. Molybdenum and Cd in the seeds were correlated with their availability in the soils. Findings from this study bring a better understanding of the variability on mineral concentration in soybeans as affected by climatic and soil variables.

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