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Original Research Article

Inter- and intra-variability in the mineral content of rice varieties grown in various microclimatic regions of southern Brazil

Lucilena Rebelo Monteiro[a], Camila Neves Lange[b], Bruna Moreira Freire[b], Tatiana Pedron[b], Júlio José Centeno da Silva[c], Ariano Martins de Magalhães Junior[c], Camila Pegoraro[d], Carlos Busanello[d], Bruno Lemos Batista[b,*]

[a] Centro de Química e Meio Ambiente, Ipen/CNEN-SP Instituto de Pesquisas Energéticas e Nucleares, Sao Paulo, 05508-000, SP, Brazil
[b] Center for Natural and Human Sciences, Federal University of ABC, Santo André, 09210-580, SP, Brazil
[c] Clima Temperado (Embrapa Temperate Agriculture), Brazilian Agricultural Research Corporation, EMBRAPA, Rodovia BR 392, km 78, Pelotas, 96010-971, RS, Brazil
[d] Faculty of Agronomy Eliseu Maciel, Federal University of Pelotas, Capão do Leão, 96160-000, RS, Brazil

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ABSTRACT

The most common goal for rice breeding is to improve the nutritional content and to reduce toxic components. Fourteen varieties of rice were grown for this purpose in six microclimatic regions in southern Brazil. The elemental composition of rice and As-Species were measured by ICP-MS and HPLC-ICP-MS, respectively. Intra- and inter-species variations of essential and non-essential elements in husked grains from an important rice-producing region in Brazil are presented. Arsenic, Cd, Co, Cu, Fe, Mg, Mn, Ni, Se, and Zn were significantly affected by the microclimatic region and the rice varieties. The only exception observed was the effect of Pb variety selection, with 35.4 % associated with random fluctuations. Varieties with both higher levels of Fe/Zn and lower levels of As/Cd were identified in all regions studied. All regions and varieties were able to produce rice with Cd < 10 μg kg^{-1}, but the Santa Vitoria do Palmar region where varieties with Cd < 45 μg kg^{-1} were selected. Well-established varieties result in a higher daily intake of essential elements than the varieties under development. Therefore, our findings may provide information to support the selection procedures for varieties, as well as to encourage improvements in management practices between regions.

1. Introduction

Rice is one of the most consumed foods in developing countries that directly affect the economic and dietary quality (Kennedy et al., 2003; Verma and Srivastav, 2017). Plant breeding is old as human civilization and the selection of better variants often combines old and modern techniques. Often, the aim is to improve yield (Lafitte et al., 2007), milling and cooking characteristics (Verma et al., 2015), the quality of the edible parts, to grow plants faster and easier to cultivate, to harvest and to process. Variants that are more tolerant to environmental stress and resistant to pests are also a constant subject of research. Each plant trait can be individually optimized, but if the others are ignored, no useful variant will be produced (Breseghello and Coelho, 2013). The selection of rice to improve the nutritional content and reduce toxic elements is one of the most frequent research subjects (Garcia-Oliveira et al., 2009; Li et al., 2012; Verma et al., 2015). Several investigations were conducted for high Fe and Zn rice varieties, which could reduce nutritional deficiencies (Kennedy et al., 2003; Alloway, 2008; Garcia-Oliveira et al., 2009; Li et al., 2012; Verma and Srivastav, 2017; Hefferon, 2019; Khan et al., 2019). Iron and zinc deficiencies are the most common nutritional disorders in the world. Approximately 3 billion people have some degree of nutritional deficiency (Khush, 2002) and it is therefore a matter of urgency to identify regions and varieties that produce grains with a high content of these elements.

Covariation of essential and toxic elements such as Cd and Pb in rice varieties has been investigated (Fu et al., 2008; Li et al., 2012; Chung et al., 2018). However, because of the lack of rice selection, crops can go under fortification and still do not respond accordingly. Essential elements and arsenic have been reported in rice grain in many countries (Abtahi et al., 2017; Verma and Srivastav, 2017; Kong et al., 2018), including Brazil (Batista et al., 2010; Kato et al., 2019; Lange et al., 2019; Segura et al., 2020). Rice is known to be a significant dietary source of As and Cd for consumers (Duan et al., 2017; Kumarathilaka et al., 2018). Cadmium safe rice is a priority among hybrid rice farmers (Sun et al., 2016). Therefore, one important step for selecting rice varieties for dietary purposes is the simultaneous identification of

* Corresponding author.
E-mail address: bruno.lemos@ufabc.edu.br (B.L. Batista).

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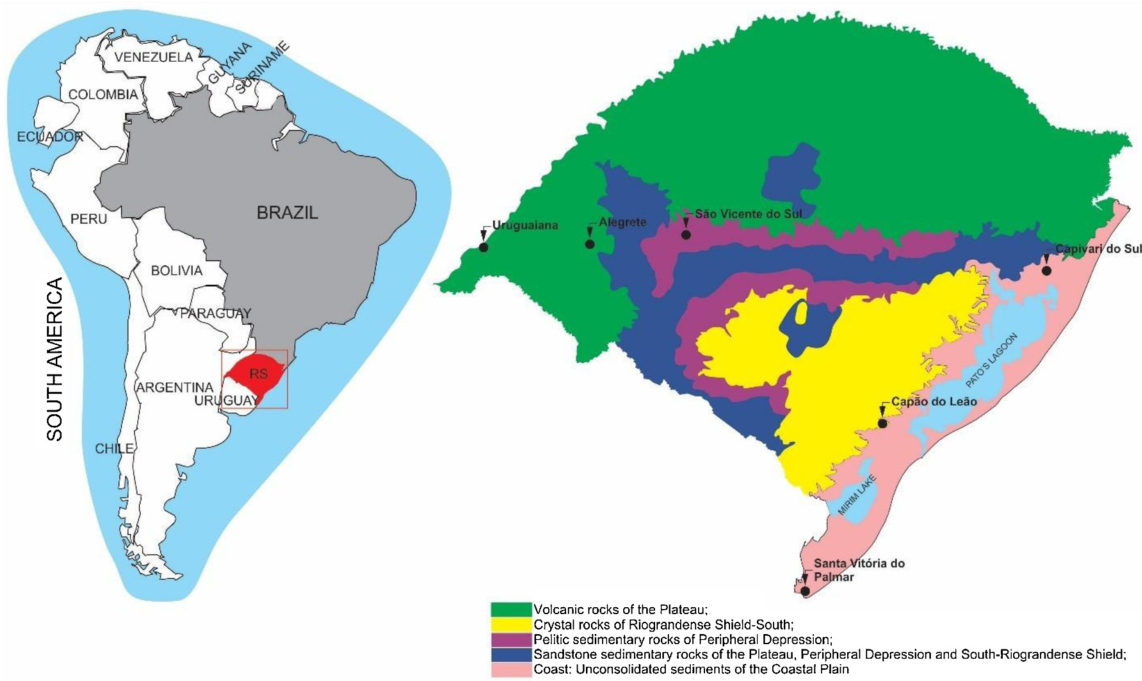

Fig. 1. The location of rice cultivation and the geological profile of the state of Rio Grande do Sul. Green: volcanic rocks of the Plateau; Yellow: crystal rocks of the Riograndense Shield-South; Purple: pelitic sedimentary rocks of the Peripheral Depression; Blue: sandstone sedimentary rocks of the Plateau, Peripheral Depression and South-Riograndense Shield; No-color(coast): unconsolidated sedimentation of the Coastal Plain. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Summary of soil properties used for rice cultivation.

City	OM	pH	P	K^+	Ca^{2+}	Mg^{2+}	CEC	Sand (g kg^{-1})			Clay	Silt	Class
	(g dm^{-3})		(g dm^{-3})	(mmolc dm^{-3})			coarse	fine		total	(g kg^{-1})		
Capão do Leão	12.5 ± 0.7	4.17	29 ± 2.8	2.2 ± 0.1	18.5 ± 0.7	10 ± 0.1	66.5 ± 0.7	263.5	202.5	466	133	401	Loam
Uruguaiana	11 ± 0.1	4.18	7.5 ± 0.7	0.6 ± 0.1	35 ± 1.4	9.5 ± 0.7	81.5 ± 2.1	147	316.5	463.5	196	340.5	Loam
Alegrete	15 ± 0.1	4.16	9.5 ± 0.7	1.9 ± 0.1	17.5 ± 0.7	5 ± 0.1	44.5 ± 0.7	97.5	603.5	701	95	204	Sandy Loam
Santa Vitória do Palmar	11 ± 1.4	4.56	9.5 ± 0.7	0.4 ± 0.1	31 ± 0.1	9.5 ± 0.7	76.5 ± 0.7	181	338.5	519.5	181.5	299	Sandy Loam

OM: organic matter; CEC: cation exchange capacity; Class: soil texture classification.

varieties capable of reducing the accumulation of toxic elements and improving the nutritional content of the seeds.

Under this scenario, the rice breeding program in the Rio Grande do Sul has been developing cultivars with the desired characteristics for irrigated rice since 1972. The quality of the grain of irrigated rice depends on genetic factors and environmental conditions. However, the interactions of genetic mechanisms with environmental conditions are still unclear (Streck et al., 2018).

Considering that in 2013, world rice production amounted to 494 million tons, 82 % of which was destined for human consumption (FAO, 2014). Brazil produced 1178 million tons in the same year. Almost 70 % of this value was produced in the Rio Grande do Sul (RS), the largest producing state (IBGE, 2013). Some of the largest RS producing cities are Uruguaiana, Santa Vitória do Palmar and Alegrete, which account for almost 14 % of total Brazilian production (Althaus et al., 2018). Capivari, São Vicente and Capão do Leão are other highly productive cities. These cities are present in various microclimatic regions of the RS.

In this scenario, 14 varieties of rice (V) were grown in these 6 microclimatic regions (M) to assess the inter-and intra-variability of essential (Fe, Zn, Cu, Mg, Mn, Co and Se) and non-essential (Cd, Ni, Pb and As) elements in husked grains. After the selection of varieties and microclimatic regions producing rice grains with optimized nutritional characteristics, the daily intake of the elements studied was estimated. This information may help farmers to produce rice grains with higher nutritional value.

2. Materials and methods

2.1. Rice cultivation

Rice varieties AB13008, AB12683, AB12625, AB10501, AB10572, AB11551, AB13002, AB13012 and AB12597 developed by the Brazilian Agricultural Research Corporation (Embrapa Temperate Climate, Pelotas, RS, Brazil) were grown during the 2015/16 season (October-March) to assess their value for cultivation and use (VCU). The VCU refers to the potential use of rice in agriculture, industry and trade with a view to increase productivity. The traditional varieties chosen were BRS Pampa, H7CL, BR IRGA 409, IRGA 417 and Avaxi CL (Information Box 1, see Supplementary Material). In terms of rice productivity, the VCU study is presented elsewhere (Magalhaes Junior et al., 2012).

Fig. 1 shows the geographical location and the geological profile of each city where the rice was grown. These microclimatic regions were defined by altitude, soil texture, soil organic matter content, relief, drainage and lowland presence (Althaus et al., 2018; FEPAM, 2017). The Rio Grande do Sul is divided into five geomorphological units: 1-Volcanic Plateau; 2-Crystal rocks of the Riograndense Shield-South; 3-Pelitic sedimentary rocks of the Peripheral Depression; 4-Sandstone

Table 2
Elemental variability observed in 6 cities and 14 rice varieties (ANOVA two-way).

Element	Effect	df	SS	MS	F	p	Var%
Co µg/kg	C	3	506650	168883	4226.84	< 0.0001	82.4 %
	V	9	10339	1149	28.75	< 0.0001	1.7 %
	C*V	60	34541	576	14.41	< 0.0001	5.6 %
	Error	78	3116	40			0.5 %
Se µg/kg	C	3	100792	33597	207.80	< 0.0001	53.8 %
	V	9	4015	446	2.76	0.0074	2.1 %
	C*V	60	33079	551	3.41	< 0.0001	17.7 %
	Error	78	12611	162			6.7 %
Mn mg/kg	C	3	5030	1677	536.60	< 0.0001	68.7 %
	V	9	169	19	6.02	< 0.0001	2.3 %
	C*V	60	874	15	4.66	< 0.0001	11.9 %
	Error	78	244	3			3.3 %
Cu mg/kg	C	3	27	9	166.61	< 0.0001	29.2 %
	V	9	7	1	13.57	< 0.0001	7.1 %
	C*V	60	19	0	5.85	< 0.0001	20.5 %
	Error	78	4	0			4.6 %
Ni µg/kg	C	3	87147	29049	33.03	< 0.0001	3.8 %
	V	9	52581	5842	6.64	< 0.0001	2.3 %
	C*V	60	1241513	20692	23.53	< 0.0001	54.7 %
	Error	78	68589	879			3.0 %
Fe mg/kg	C	3	94	31	15.56	< 0.0001	10.6 %
	V	9	68	8	3.76	0.0006	7.7 %
	C*V	60	410	7	3.38	< 0.0001	46.3 %
	Error	78	158	2			17.8 %
Zn mg/kg	C	3	126	42	36.84	< 0.0001	13.7 %
	V	9	82	9	7.92	< 0.0001	8.9 %
	C*V	60	293	5	4.27	< 0.0001	31.8 %
	Error	78	89	1			9.7 %
Pb µg/kg	C	3	2694	898	45.75	0.0000	35.2 %
	V	9	199	22	1.13	**0.3543**	2.6 %
	C*V	60	2155	36	1.83	0.0061	28.2 %
	Error	78	1531	20			20.0 %
Cd µg/kg	C	3	146258	48753	11881.38	< 0.0001	72.8 %
	V	9	4256	473	115.25	< 0.0001	2.1 %
	C*V	60	32511	542	132.05	< 0.0001	16.2 %
	Error	78	320	4			0.2 %
As µg/kg	C	3	1789672	596557	1082.94	< 0.0001	40.9 %
	V	9	174243	19360	35.15	< 0.0001	4.0 %
	C*V	60	634131	10569	19.19	< 0.0001	14.5 %
	Error	78	42968	551			1.0 %

C: City; V: Variety; df: degrees of freedom; SS: sum of squares; MS: mean squares; F: factor; p: probability; Var (%) = Sum of squares (SS) of each effect by total SS.

sedimentary rocks of the Plateau, Peripheral depression and South-Riograndense Shield; 5-Unconsolidated sedimentation of the Coastal Plain. Rice cultivation and water management followed SOSBAI's technical recommendations (SOSBAI, 2018). The experimental design was a randomized block, with four replicates in portions of 9 rows of 5 m in length, spaced 0.20 m between rows. The plot area consisted of 4 central meters of the five internal rows, with the aim to exclude some incident border effect. The seed density was 100 kg ha^{-1} viable seed using a mechanical seed drill under a conventional seedling system. Plants were cultivated in flooded conditions.

2.2. Sample preparation and chemical analysis

2.2.1. Soils

A representative amount of soil surface samples (0–20 cm) from each microclimate region was collected for soil characterization. Samples were dried at 40 °C, homogenized, quartered and tamed at 2 mm. The soil characteristics (texture, cation exchange capacity, organic matter and pH) and the exchangeable contents of K, P, Ca and Mg were measured according to EMBRAPA (van RAIJ, 2001; Donagema et al., 2011).

2.2.2. Rice grains

Following harvesting, the samples (n = 79) were husked, milled, sieved (< 250 µm) and homogenized. All samples (in triplicate) were weighted (~200 mg) in 50 mL of conical tubes (Falcon Corning, Tamaulipas, Mexico), closed and stored at room temperature for 24 h with 2 mL of concentrated nitric acid (65 % m/m, Synth, Brazil), previously under distilled (DST-1000, Savillex, USA). The tubes were then heated (95 °C) in the graphite-covered digester block (EasyDigest, Analab, France) for 4 h. After cooling, the samples were diluted to 40 mL of ultrapure water (ELGA, Ubstadt-Weiher, Germany) as described by Paniz et al. (2018). Elemental analysis was performed using an inductively coupled plasma mass spectrometer (ICP-MS Agilent 7900, Hachioji, Japan). All conditions and the preparation of standards have been described by Paniz et al. (2018). Table S1 sets out the conditions for analysis.

Standard analytical solutions were used for quantification. For this purpose, a multi-element standard solution (PerkinElmer, Connecticut, USA) containing all analytes (10 mg L^{-1}) was diluted in 5 % HNO_3 for calibration. The internal standards were Germanium and Rh. Rice flour reference material 1568b from the National Institute of Standards and Technology (USA) was used for precision assessment.

2.2.3. Arsenic speciation

Following the elementary analysis, rice from microclimatic regions with a high and low level of As content was selected for the As speciation analysis. Organic As (o-As) and inorganic As (i-As) were measured by high-performance liquid chromatography (1290 Infinity II, Agilent, Germany) hyphenated to ICP-MS (HPLC-ICP-MS) according to Batista et al. (2011). In short, 200 mg of rice flour was placed in a 50 mL plastic tube containing 10 mL of HNO_3 2 %, heated to 90 °C during 2.5 h for extraction of As species. The extract was then filtered and injected into the HPLC-ICP-MS for As speciation.

2.3. Daily intake estimation

Estimated daily intakes (EDI) of the elements studied by rice consumption of low and high accumulating varieties were calculated as Eq. (1):

$$EDI = C_{ce} \text{ x } M_{rdc} \quad (1)$$

Where EDI is the estimated daily intake (µg day^{-1} $person^{-1}$ or mg day^{-1} $person^{-1}$) of each chemical element, C_{ce} is the mean concentration of the element in each rice variety and M_{rdc} represents the daily intake of rice in Brazil. Based on the statistics on rice consumption by the Brazilian Institute of Geography and Statistics (IBGE, 2011), M_{rdc} is expected to be 72.6 g (Freire et al., 2020).

2.4. Statistical evaluation

The data set consisted of 158 cases (2 replicates of 14 rice varieties from 6 microclimatic regions) and 11 variables. These variables had consisted of the essential and non-essential content of mineral elements measured in rice grains. The quantile-quantile (Q-Q) plot was used to check the normal distribution of the data. Two-way ANOVA was used to evaluate differences in the mineral content of the rice varieties (effect 1) and the microclimatic region (effect 2). ANOVA was performed using Statistica version 8.0 from Stat Soft (Tulsa, OK, USA).

3. Results

3.1. Soil characterization

Table 1 presents the results of soil physicochemical characterization by the microclimatic region. Most of the samples consisted of mildly acidic soil (pH = 4.2). Soil organic matter (SOM) ranged from

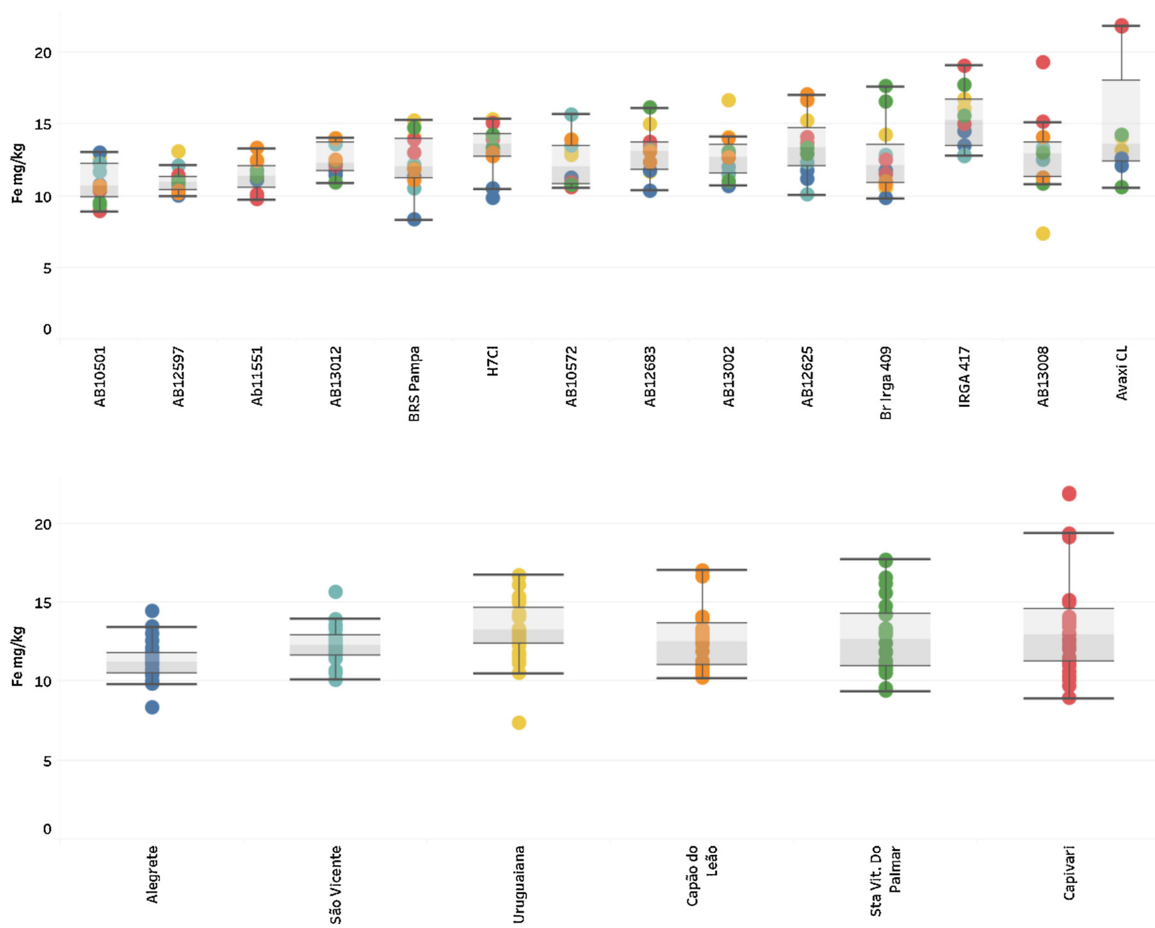

Fig. 2. Concentration of Fe in rice varieties cultivated in the microclimatic regions of Rio Grande do Sul. Microclimatic regions: Alegrete (dark blue); Capão do Leão (orange); Capivari (red); São Vicente (light blue); Santa Vitória do Palmar (green); Uruguayan (yellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

11 mg dm^{-3} in Uruguaiana and Santa Vitória do Palmar to 15 mg dm^{-3} in Alegrete. Phosphorus concentrations varied considerably, with the highest value (29 mg dm^{-3}) observed in Capão do Leão and the lowest in Uruguaiana (7.5 mg dm^{-3}). For potassium, the soils of Uruguaiana and Santa Vitória do Palmar showed the lowest levels (0.6 and 0.4 mmol$_c$ dm^{-3}, respectively) and the highest levels in Capão do Leão and Alegrete (2.2 and 1.9 mmol$_c$ dm^{-3}, respectively). The highest levels of exchangeable calcium were observed in Uruguaiana and Santa Vitória do Palmar, which were approximately twice the levels found in Capão do Leão and Alegrete. The lowest exchangeable magnesium content was detected in Alegrete soil (5 mmol$_c$ dm^{-3}) while in other regions it was approximately 10 mmol$_c$ dm^{-3}.

Cation exchange capacity (CEC), which expresses the capacity of the soil to retain cations, was quite variable between microclimate regions. Alegrete soil presented the lowest CEC (44.5 mmol$_c$ dm^{-3}) and the highest Uruguayan soil (81.5 mmol$_c$ dm^{-3}). The highest sand content (701 g kg^{-1}) was observed in Alegrete, followed by Santa Vitória do Palmar (519.5 g kg^{-1}). Capão do Leão and Uruguaiana had approximately 460 g kg^{-1} of sand. The soil of Alegrete had the lowest content of clay. The highest silt content was found in Capão do Leão (401 g kg^{-1}) and Uruguaiana (340.5 g kg^{-1}) soils (Table 1).

3.2. Elemental content intra- and inter-species variability

Fig. S1 presents the histograms of Fe, Zn, Cu, Mg, Mn and Pb. These elements were considered with a normal distribution by the city and among all evaluated microclimatic regions. Arsenic, Cd, Co, Se and Ni presented normal distributions by microclimatic region but were considered to be non-normal distributions across all microclimatic regions (Fig. S2). Therefore, significant differences between these regions had been observed.

The elemental variability of intra- and inter-species content by microclimatic regions was assessed by two-way ANOVA (Table 2). All the elements were significantly affected by the microclimatic region in which the rice was grown and the rice variety (95% confidence level). The effect of the microclimatic regions was greater than the effect of the variety. The only exception to Pb was that 35.4 % of the variety selection effect was considered to be random. Once both effects were significant, the selection of rice varieties could improve the essential elements in rice (mainly Fe and Zn) and reduce the levels of potentially toxic elements (mainly As and Cd) adjusted by geographical location.

3.2.1. Essential elements

3.2.1.1. Iron and zinc. Concerning Fe nutritional content, the average of all varieties in all microclimatic regions was 12.7 ± 2.3 mg kg^{-1}, n = 310 (Fig. 2). This value is in good agreement with the study reported by Gregorio et al. (2000) which determined the level of Fe in 1138 husked rice samples and the average value calculated by the authors was 12.2 mg kg^{-1}. Previous studies for rice grains reported higher levels of Fe (15 to 17 mg kg^{-1}) (Antoine et al., 2012; Vasconcelos et al., 2003). No rice variety presented Fe content below 5 mg kg^{-1} or over 30 mg kg^{-1}, as reported to Indian aromatic and non-aromatic rice (Verma and Srivastav, 2017) In Alegrete, the mean Fe was 11.3 ± 1.3 mg kg^{-1}, n = 52 (Fig. 2). Alegrete was the only microclimate region with less than 14 mg kg^{-1} of Fe in all varieties. At Alegrete, the lowest and highest levels of Fe were 8.2 mg kg^{-1} and

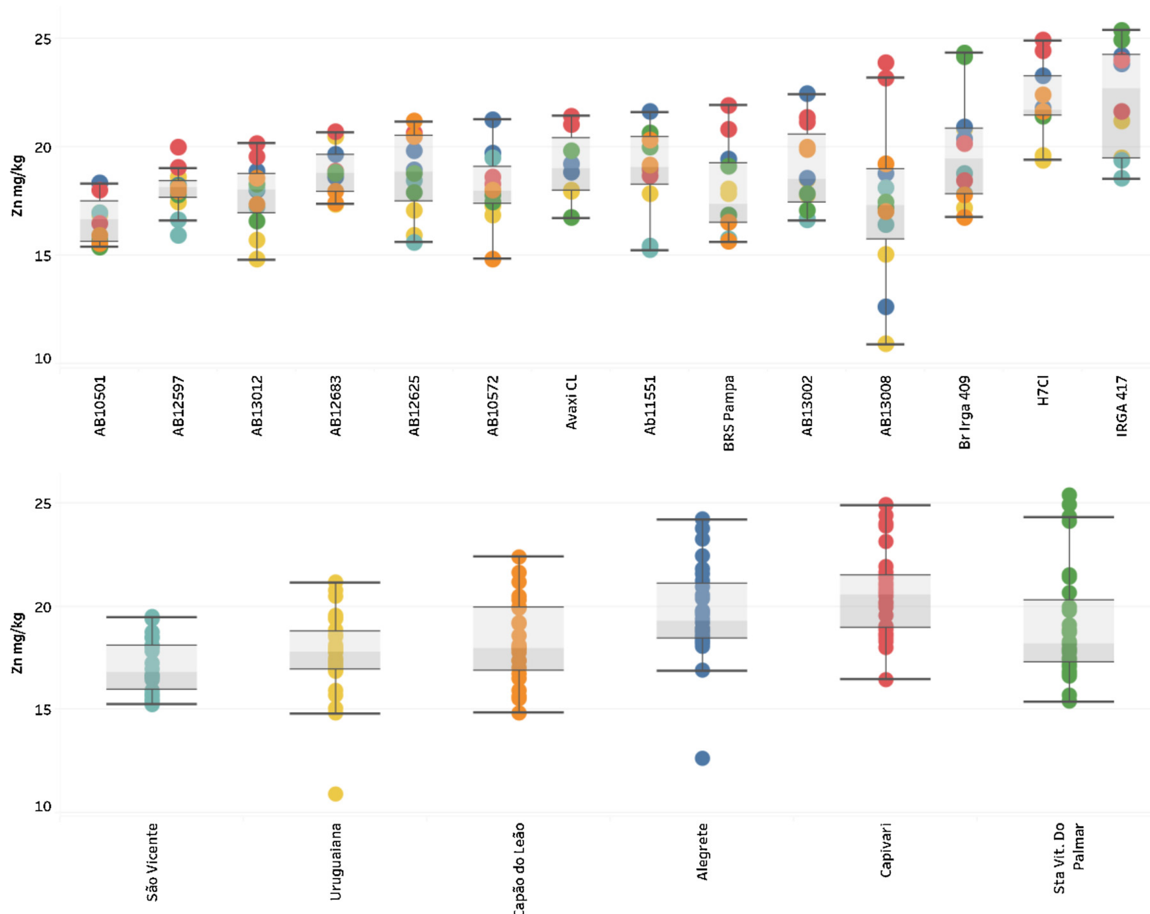

Fig. 3. Concentration of Zn in rice varieties cultivated in the microclimatic regions of Rio Grande do Sul. Microclimatic regions: Alegrete (dark blue); Capão do Leão (orange); Capivari (red); São Vicente (light blue); Santa Vitória do Palmar (green); Uruguayan (yellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

13.9 mg kg^{-1} for the AB13008 and the IRGA 417/AB10572 pairs. Low levels of Fe found in cereal from Alegrete may be related to soil composition or the high yield of rice in the region. The soils of Rio Grande do Sul are slightly acidic and may inhibit the absorption of Fe^{2+}/Fe^{3+}. Althaus et al. (2018) reported that Fe oxide levels are higher in basalt-form soils than in other soils south of Brazil, where Fe can occur in less crystallized forms. In Basalt soils, the high availability of H^+ ions can keep other cations away, reducing the solubility of Fe ions. The soil condition associated with the high productivity of Alegrete could reduce the content of Fe in rice. Other values below 10 mg kg^{-1} Fe in rice grains were observed in Capivari (AB10501 and AB 11551) and Santa Vitória does Palmar (AB10501).

Grains grown on unconsolidated sediment soils of the coastal plains, including Capivari do Sul, Capão do Leão and Santa Vitória do Palmar, generally had the highest content of Fe (Fig. 2). These three microclimatic regions are the southern regions of Brazil with the lowest rice production rate. At Capivari, Avaxi CL was the only one to produce more than 20 mg kg^{-1} of Fe rice. These cities are located in sedimentary soils near tropical lakes, which are rich in amorphous Fe oxides (Fonseca et al., 2011). Under inundated systems of cultivation, these soils are over a reductive environment and this condition facilitates the mobilization of Fe for soil solution (Johnston et al., 2010), favoring the bioavailability of Fe for rice plants.

The average Zn for rice grains in all cities and varieties was 18.8 ± 2.4 mg kg^{-1}, n = 316. According to Trijatmiko et al. (2016), polished grains of popular rice varieties have a concentration of approximately 16 mg kg^{-1} of Zn and a biofortification target of 28 mg kg^{-1} of Zn in rice grains. Four varieties produced rice grains of less than 16 mg kg^{-1} of Zn (Fig. 3) as follows: AB13012 in Uruguaiana, AB13008 in Uruguaiana and Alegrete, AB10501 in Capão do Leão and Santa Vitória do Palmar and AB11551 in São Vicente. Four other varieties of rice produced more than 22 mg kg^{-1} of Zn (Fig. 3), such as IRGA 417 in Santa Vitória do Palmar, Capivari and Alegrete; H7Cl in Capivari, Alegrete and Capão do Leão; IRGA 409 in Santa Vitória do Palmar and AB13008 in Capivari. A strong correlation was observed between the concentrations of Fe and Zn in rice in microclimatic regions (0.98 in Santa Vitoria do Palmar, 0.82 in Sao Vicente, 0.73 in Alegrete, Uruguaiana and Capão do Leão, 0.41 in Capivari) among all varieties (Fig. 4). Bresolin et al. (2019) were probably associated with the Fe-induced activation of bivalent cation transporters, which could favor not only the uptake of Zn but also the uptake of Cu and Cd observed in Santa Vitoria do Palmar. Wissuwa et al. (2008) reported that the concentrations of Zn in rice grains were mainly affected by geogenic Zn levels, followed by genotypes and agronomic practices (water management and fertilization). In addition, the authors noted that it is a challenge to predict which variety could present higher levels of Zn grain when grown in soils with low levels of Zn, such as Brazilian soils (Rehman et al., 2012).

3.2.1.2. Other elements (Co, Cu, Mn, Mg and Se). Copper content in rice grain ranged from 0.39 to 4.44 mg kg^{-1} (average 1.8 ± 0.8 mg kg^{-1}, n = 316). Rice from São Vicente presented Cu levels below 0.9 mg kg^{-1} (Fig. S3). Special attention was given to AB10501, as the sole variety capable of exceeding 0.9 mg kg^{-1} of Cu in São Vicente up to 1.8 mg kg^{-1}. On the other hand, rice grains from Uruguaiana and Santa Vitória do Palmar presented more than 2.5 mg kg^{-1} of Cu, as

Fig. 4. Variety distribution considering Fe vs Zn (mg kg^{-1}) correlation between all microclimatic regions (color indicates As and size indicates Cd) (yellow dotted line corresponds to the elemental average of the city). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3
Rice variety selection in cities with low and high content of As and Cd.

Element	Level of the element at the studied city	City	Variety capable to produce the lowest levels of the toxic element
As	High	*S Vicente*	**AB11551**, IRGA 417, AB13002
	Low	*Capivari*	H7CI, **AB12683**, IRGA 409, IRGA 417
		Sta. Vit Palmar	**H7CI,** AB10572, AB11551
Cd	High	*Sta. Vit Palmar*	**H7CI**, AB130012
	Low	*Capivari*	**AB12683,** AB10572, AB11551
		S Vicente	IRGA 409, AB1572, **AB11551,** AB13012, AB12597

Bold: Varieties identified as capable to produce grains at the same location with low As and low Cd levels.

shown in Fig. S3 (H7Cl, IRGA 417, BR IRGA 409, Avaxi Cl, Ab11551, AB13002). The range found for rice grains in this study was approximately similar to that values (1.19 to 5.57 mg kg^{-1}) found by Batista et al. (2010).

Rice varieties cultivated in Uruguaiana and Alegrete had the highest levels of Co and Se in their grains (Figs. S4 and S5). At Uruguaiana, all varieties exceeded 75 μg kg^{-1} of both elements, while at Alegrete IRGA 417, Avaxi CL, BR IRGA 409, AB12625 and AB11551, they also exceeded this level. Most varieties of Capivari and Santa Vitória do Palmar had less than 20 μg kg^{-1} Co. The lowest Se levels were observed in Capivari, Santa Vitória do Palmar and São Vicente. Se concentrations in Brazilian husked rice cultivars were above the levels found in several provinces of China (14.3 to 34.9 μg kg^{-1}) (Liu et al., 2009) and above the previous Brazilian rice studies (22.8 to 63.2 μg kg^{-1}) (Batista et al., 2010). Cobalt content in rice grains varied widely (8.3 to 267 μg kg^{-1}) and ranged from 4.5 to 104.4 μg kg^{-1} found by Batista et al. (2010).

The smallest mean of Mg was observed in São Vicente (1144 mg kg^{-1}) where the varieties AB12597, AB12625 and BRS Pampa had less than 1000 mg kg^{-1} Mg in grains (Fig. S6). Santa Vitória do Palmar had an average of about 1200 mg kg^{-1}, while the remaining cities had an average of about 1300 mg kg^{-1}. Special attention was given to AB12625, AB12683, BR IRGA 409 and H7Cl with average levels of Mg exceeding 1350 mg kg^{-1}. Batista et al. (2010) found an average of 4.890 ± 1.168 mg kg^{-1} for Brazilian parboiled brown rice grains, our findings were below this value.

The varieties AB10501 cultivated in Capivari do Sul and AB13002 cultivated in Uruguaiana showed 9.6 and 35.4 mg kg^{-1} of Mn, respectively (Fig. S7). Concentrations in traditional rice varieties in this study ranged from 10.6 to 35.8 mg kg^{-1}, the lowest concentration found in BR IRGA 409 grains from Capivari do Sul and the highest in IRGA 417 grains from Alegrete. Our findings were slightly higher than those of 8.2 to 24.2 mg kg^{-1} found in farms in six districts of the Republic of Kazakhstan (Tattibayeva et al., 2016). In rice, these essential elements (Mg and Mn) associated with the total As content were used to trace rice origin in Brazil (Lange et al., 2019).

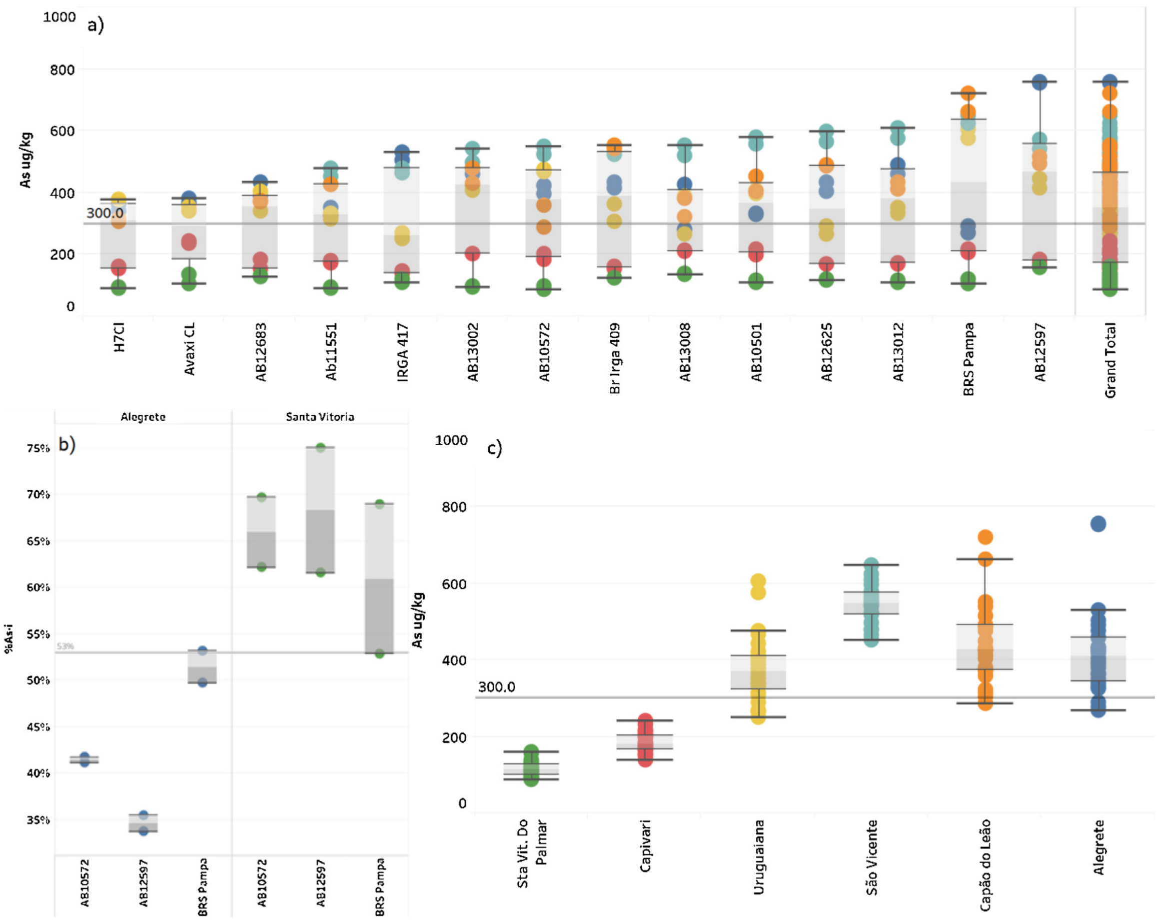

Fig. 5. Concentration of As in rice varieties (a) cultivated in the microclimatic regions (c) of Rio Grande do Sul. Microclimatic regions: Alegrete (dark blue); Capão do Leão (orange); Capivari (red); São Vicente (light blue); Santa Vitória do Palmar (green); Uruguayan (yellow) and Percentage of i-As present in rice, by city and by variety(b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2.2. Non-essential elements

3.2.2.1. Arsenic and cadmium. Table 3 presents a summary of low and high As and Cd levels among cities and varieties. Rice grains from southern Brazil appear to have presented an opposite distribution of As and Cd, particularly in Santa Vitória do Palmar and São Vicente (Figs. 5 and 6). This corresponds to the well-known As and Cd antagonism that occurs in rice grains (Sun et al., 2016). However, there was no statistically inverse correlation between these elements (Fig. S8).

São Vicente presented the highest median (549 μg kg^{-1}) and the lowest Cd median (1.9 μg kg^{-1}). Cadmium was below 4 μg kg^{-1} for all varieties and was not a selection criterion for São Vicente. In this microclimatic region, only three varieties (IRGA 417, AB13002 and AB11551) were able to produce rice of less than 500 μg kg^{-1} (Fig. 5). AB11551 provided the lowest values of As (465.1 μg kg^{-1}) but were also low in Fe and Zn. No rice was able to produce seedlings of less than 300 μg kg^{-1} in Sao Vicente.

Total values reported in Santa Vitoria do Palmar (Segura et al., 2020), ranged from 318 ± 11 μg kg^{-1} to 168 ± 13 μg kg^{-1} for Puitá and IRGA 424 rice varieties. The last value was close to our mean value (115.1 μg kg^{-1}) in the same city. These low As values were associated with the highest Cd values in our study. In Santa Vitoria do Palmar, only two varieties were able to produce rice of less than 45 μg kg^{-1}, AB13002 and H7CL. Between these two, only H7CL had Fe and Zn above the desired nutritional values.

Capivari had the lowest As and Cd medians combined, 181.4 μg kg^{-1} and 4.1 μg kg^{-1}, respectively. Almost all the varieties in Capivari were able to produce low-As and low-Cd rice. However, only two varieties in this microclimatic region were able to produce ideal rice with high Fe and Zn and low As and Cd (IRGA 417 and H7CL). In Capivari and Santa Vitória do Palmar, the varieties AB12683 also produced low-As and high-Fe rice, but the Zn content was below 18 mg kg^{-1}.

Alegrete, Capão do Leão, São Vicente and Uruguaiana produced the highest total As content in rice. All four cities were above the ANVISA limit of 300 μg kg^{-1}) (ANVISA, 2013). Alegrete had the highest total value as found in the AB12957 variety. At Alegrete, BRS Pampa and AB13008 were two varieties less than 300 μg kg^{-1}.

Arsenic speciation was performed in the rice varieties BRS Pampa, AB10572 and AB12597 produced in Alegrete and Santa Vitoria do Palmar. These were the microclimatic regions with the highest and lowest levels of rice, respectively. Differences between microclimatic regions and varieties considered to be from i-As and o-As species were observed as expected. At Alegrete, BRS Pampa had a low percentage of i-As ranging from 49.7 to 53.2 %. At Santa Vitória do Palmar, BRS Pampa had an i-As percentage of 52.9 to 69.9 % (Fig. 5). Thus, even the production of low-as rice, Santa Vitória do Palmar, had a higher percentage of the most toxic As form than Alegrete. Similarly to values reported by Batista et al. (2014) and Segura et al. (2020), rice varieties with the highest values of total As had high levels of o-As.

By international regulations, the variety AB12597 produced in Alegrete (260 ± 5.5 μg kg^{-1}) exceeded the European Commission limit of 350 μg i-As kg^{-1} for husked rice (EU, 2015). Therefore, this sample from Alegrete and all other varieties in all cities agreed with the *Codex Alimentarius Commission* i-As limit of 350 μg kg^{-1} for husked rice and the same limit is adopted by Brazilian regulation (CODEX, 2016; Segura et al., 2020).

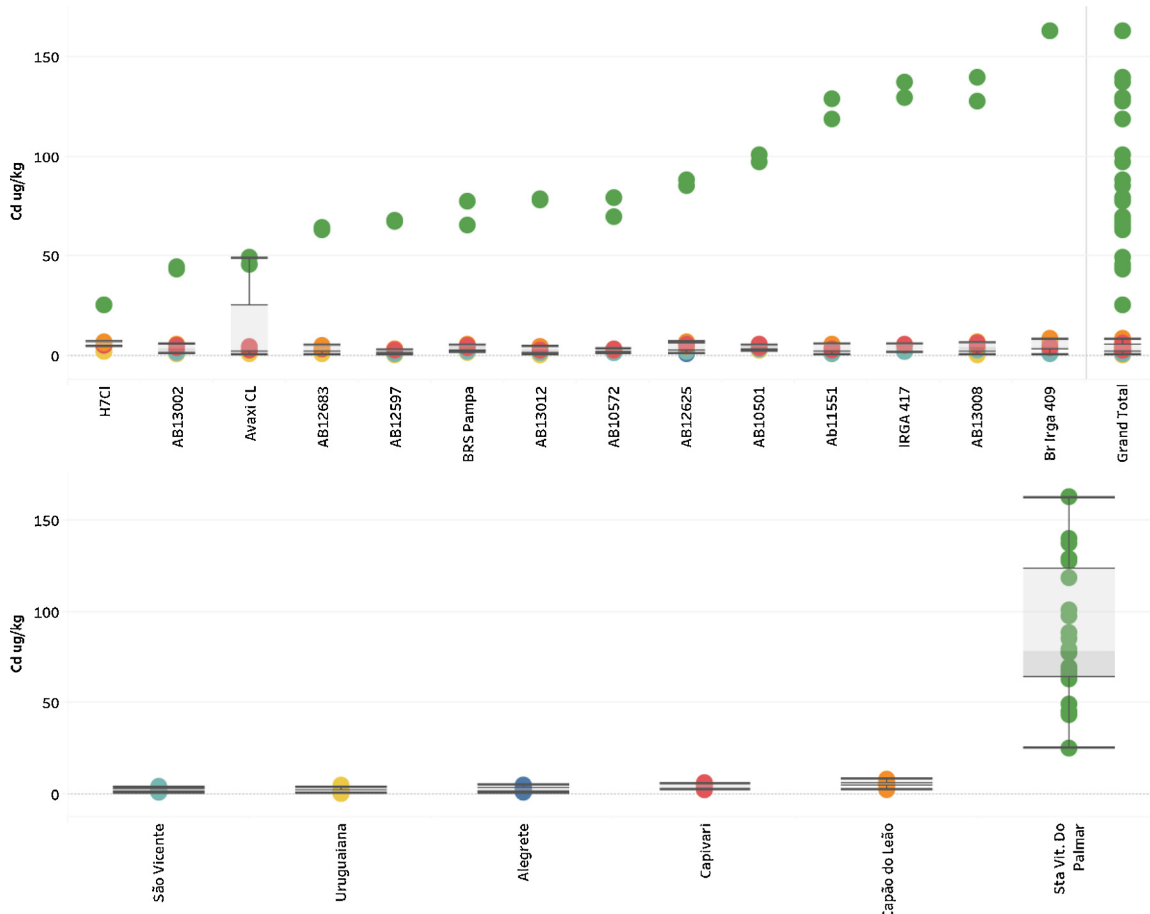

Fig. 6. Concentration of Cd in rice varieties cultivated in the cities of Rio Grande do Sul. Cities: Alegrete (dark blue); Capão do Leão (orange); Capivari (red); SãoVicente (light blue); Santa Vitória do Palmar (green); Uruguayan (yellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

All microclimatic regions produced rice ranging from 0.4 to 8.5 μg kg^{-1} Cd, except for Santa Vitória do Palmar (25.2 to 162.7 μg kg^{-1}) (Fig. 6). Our results were consistent with the observations of Kato et al. (2019) that Cd (2.9 to 44 μg kg^{-1}) varied considerably less than As (< 2.6 to 628 μg kg^{-1}) in Brazilian rice. In Santa Vitoria do Palmar, the criteria for optimization of varieties were associated with Cd and not with As. In this microclimatic region, H7CL, AvaxiCL and AB13002 produced rice less than 50ug kg^{-1}, but only H7CL complied with the Fe and Zn nutritional recommendations In any case, even when Santa Vitoria do Palmar was considered, our study identified rice varieties below the range of 60 to 590 μg kg^{-1} reported in China by Li et al. (2012).

Even rice produced in Santa Vitoria still meets a limit of 200 μg kg^{-1} (EU, 2006) for European Commission Regulations and 400 μg kg^{-1} for ANVISA-the Brazilian regulatory agency (ANVISA, 2013). These relatively elevated Cd values found in Santa Vitoria do Palmar could be attributed to the severe drought in 2015. In which the microclimatic region was under emergency conditions (Zanon et al., 2016), it did not reach the other microclimatic regions studied. Without flooding prior to the rice heading, a water-soluble layer of $CdSO_4$ and/or $CdCl_2$ is formed, increasing the absorption of Cd (Sebastian and Prasad, 2014).

3.2.2.2. Nickel and lead. Considering the Ni levels in rice grains, the lowest levels were observed in Capão do Leão (< 50 μg kg^{-1}) and São Vicente, Capivari and Uruguaiana (< 100 μg kg^{-1}) as shown in Fig. S9. The highest levels of Ni were found in IRGA 417 (458 μg kg^{-1}) and AB1151 (386 μg kg^{-1}). Li et al. (2012) reported a higher range (80–1110 μg kg^{-1}) of Ni in husked rice grains, and Naseri et al. (2015) also reported a higher range (650–900 μg kg^{-1}) than our findings.

Concentrations of Pb in husked rice grains were shown in Fig. S10. Capivari was the microclimatic region with the highest Pb levels in rice (46.17 μg kg^{-1}) and several varieties exceeding 10 μg kg^{-1}. Lead levels among the varieties of rice had a large random component (Table 2). Consequently, no rice selection in this study could produce low Pb levels. In any case, in Capivari, H7Cl and AB12683 were the only varieties with less than 5 μg kg^{-1} Pb in rice grains. The highest concentrations of Pb in grains occurred in microclimatic regions from unconsolidated coastal plain sediments (Santa Vitória do Palmar and Capivari) (FEPAM, 2014) and the lowest was observed in Uruguaiana and Capão do Leão (< 5 μg kg^{-1}). The lead content of rice produced in all microclimatic regions and rice varieties was below the 200 μg kg^{-1} limit of the European Commission Regulation (EU, 2006). In this study, the Pb values were consistent with previous studies of other Brazilian rice samples (Batista et al., 2010, 2012; Maione et al., 2016) and the concentrations are in the same order of magnitude of husked rice from Argentina (8–30 μg kg^{-1}) (Villafañe et al., 2018).

3.3. Daily intake estimation

The estimated daily mineral intake (EDI) of 11 elements using low and high accumulator rice consumption is shown in Table 4. Since rice is a staple food, the desirable levels of the essential elements in rice grains should provide a high percentage of the dietary reference intake (DRI). Therefore, the selection of the rice varieties should be based on

Table 4
Summary of Varieties selected to provide a lower and higher estimated daily intake (EDI) in μg day^{-1} of the elements studied in rice grains by city and element.

Element	Lower values			Higher values			Limit value/DRI[A]
	EDI	City	Variety	EDI	City	Variety	
Fe	319-508	Alegrete	AB13008	1,347 -1,532	Capivari	Avaxi CL	18,000^{w}/8,000^{m}
		Uruguaiana				IRGA 417	
						AB13008	
Zn	770-886	Alegrete	AB13008	1,713-1,822	Sta Vitoria do Palmar	IRGA 417	8,000^{w}/11,000^{m}
					Capivari	BR IRGA409	
		Uruguaiana			Alegrete	H7Cl	
						AB13008	
Co	< 1.02	Capivari	ND	6.97-18.9	Uruguaiana	IRGA 417	–
					Alegrete		
Se	< 0.73	Sao Vicente	ND	7.97-12.9	Alegrete	IRGA 417	55
		Sta Vitoria do Palmar			Uruguaiana	AB12625	
Cu	< 50.8	Sao Vicente	ND	240-319	Sta Vitoria do Palmar	IRGA 417	900
						BR IRGA 409	
Mn	< 946	Capivari	AB10501	up to 2614	Uruguaiana	H7Cl	1,800^{w}/2,300^{m}
					Alegrete	IRGA 417	
Mg	< 65,340	Uruguaiana	AB13008	> 108,900	Capão do Leão	ND	320,000^{w}/420,000^{m}
		Sao Vicente	BRS Pampa		Uruguaiana		
					Santa Vitoria do Palmar		
As	5.08-10.2	Sta Vitoria do Palmar	ND	36.3-53.7	Alegrete		21-560[B]
		Capivari			Capão do Leão	AB12597	
					Sao Vicente	BRSPampa	
Cd	< 0.73	All cities but Santa Vitoria do Palmar	ND	1.45 up to 11.3	Santa Vitoria do Palmar	IRGA 409	58.3[C]
						AB13008	
Pb	< 0.22	Uruguaiana	ND	> 2.2	Capivari	Avaxi CL	1.4 – 210[D]
		Capão do Leão			Sao Vicente	AB11551	
Ni	< 3.6	Capão do Leão	ND	> 21.8	Capivari	Avaxi Cl	770[E]
					Sta Vitoria do Palmar	IRGA 417	

[W] women; [M] male; [A] The Dietary Reference Intakes (DRI) for essential elements are the most recent set of dietary recommendations established by the Food and Nutrition Board of the Institute of Medicine (IOM 2001); [B] EFSA (2009); [C] PTDI = Provisional Tolerable Daily Intake for toxic elements, based on PTMI/30 (EFSA, 2011); [D] JECFA (2011); [E] Tolerable Daily Intake (WHO, 2007).

rice grain varieties with higher levels of Fe and Zn, as well as lower levels of As and Cd, in particular. For example, Freire et al. (2020) have estimated the EDI for 10 Brazilian rice varieties, concluding that the consumption of those varieties could effectively increase the daily intake of Fe as well as decrease the daily consumption of As.

In Capivari, where the content of Fe in rice grains was the highest, varieties that supply 7.48–8.52 % of DRI for women and 16.8–19.2 % for men were selected. The estimated daily intake of Fe by rice in Brazil is 430 μg (Batista et al., 2012). Therefore, the lowest EDI values calculated in our study (319–508 μg day^{-1}) are close to the estimates of these authors.

Zinc deficiency affects 50 % of agricultural land and is recognized as the most critical micronutrient deficiency in plantations (Jena et al., 2018). Tropical soils, such as Brazil, are mostly acidic with high base saturation, high phosphate content and highly weathered, and may cause Zn deficiency in crops in the event of prolonged flooding (Alloway, 2008). The EDI for Zn in rice grains herein corroborates this scenario for the lowest level varieties, although the EDI could be increased by two due to the selection of the variety / microclimate regions proposed in Table 4.

Only through the consumption of the rice varieties H7Cl and IRGA 417 of Uruguaiana and Alegrete could 100 % of the DRI of Mn be achieved. The daily intake of Co, Cu, Mg and Se may be increased from 1.5 to 10 times by the consumption of the selected varieties, which provided the highest levels of these elements (Table 4).

The EDI was also calculated for non-essential elements (Table 4). These values indicated that all varieties of rice produced in all microclimate regions were in agreement with the regulations. For As, the reference dose lower confidence limit (BMDL) was 0.3 to 8 μg day^{-1} kg^{-1} body weight (EFSA, 2009), corresponding to 21 to 560 μg day^{-1} for an average adult of 70 kg. Thus, all the rice produced in Santa Vitória do Palmar and Capivari had EDI values lower than 48.6 % of the BMDL. However, the consumption of varieties such as AB12597 from Alegrete and BRS Pampa from Capão do Leão, São Vicente and Uruguaiana could be twice as high as BMDL. The highest EDI in our study was 53.7 μg. This EDI was similar to those found in contaminated regions of Bangladesh (56.4 μg) (Rahman et al., 2009), which may be a health concern.

The highest EDI for Cd was 11.3 μg day^{-1} found in Santa Vitoria do Palmar. This corresponds to 19.4 % of the Provisional Tolerable Daily Intake (PTDI) (EFSA, 2011). Shahriar et al. (2020) estimated EDI Cd from Bangladesh rice grains and found a range of 0.09 to 0.58 μg kg^{-1} bw^{-1}, corresponding to 6.3 to 40.6 μg day^{-1}. The highest EDI calculated for Ni corresponds to 2.8 % of the Tolerable Daily Intake (770 μg) (WHO, 2007) and 1.5 times the minimum Pb (1.4 μg) (JECFA, 2011). Our findings are above those reported by Nigerian cereals (7.13 μg) (Akinyele and Shokunbi, 2015) for Ni and below for Pb (< 6.34 μg).

4. Conclusion

Several factors have an impact on the accumulation of essential and non-essential elements in rice. In this study, elemental intra- and inter-rice variety variability was identified between 14 rice varieties and 6 microclimatic regions in southern Brazil. Significant differences between the producing cities have been observed for all the elements, as expected. Varieties have significantly changed their elementary content, but not strongly as the environmental effect. The only exception was Pb, which was found to respond randomly to the selection of the variety. We observed that all cities could benefit from the selection of varieties by producing rice with a higher content of Fe and Zn. Furthermore, selected rice can reduce the content of As and Cd, in an optimized process by growing location.

In this study, the microclimatic regions of Alegrete and Santa Vitoria do Palmar were identified as having the highest and lowest total arsenic content. Three varieties (AB12597, AB10572 and BRS Pampa) were found to have higher percentages of o-As than i-As in Santa Vitoria do Palmar. The results of i-As are below the international regulations. Varieties and growing regions have been selected to improve the daily intake of essential and non-essential elements throughout the adult consumption of rice grain. Depending on the rice variety and the microclimate, the intake of essential and non-essential elements may vary dramatically. Varieties of rice and microclimatic regions producing more nutritious and safer rice were identified, which are important information for consumers and market development.

CRediT authorship contribution statement

Lucilena Rebelo Monteiro: Writing - original draft, Writing - review & editing. **Camila Neves Lange:** Writing - original draft, Writing - review & editing. **Bruna Moreira Freire:** Writing - original draft. **Tatiana Pedron:** Writing - original draft. **Júlio José Centeno da Silva:** Conceptualization, Methodology, Writing - review & editing. **Ariano Martins de Magalhães:** Conceptualization, Methodology, Writing - review & editing. **Camila Pegoraro:** Writing - review & editing. **Carlos Busanello:** Writing - review & editing. **Bruno Lemos Batista:** Conceptualization, Methodology, Writing - review & editing.

Declaration of Competing Interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jfca.2020.103535.

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