Elemental composition and nutritional value of *Araucaria angustifolia* seeds from subtropical Brazil

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Abstract Consumed by populations in South America, *Araucaria angustifolia* seeds have received little study regarding elemental composition and nutritional value. Thirty-five seed sites from subtropical Brazil were sampled and seed concentrations of C, N, K, Ca, Mg, P, Fe, Zn, Mn, Cu, Mo, Ni, Co, Cr, Ba, and Cd were determined. The highest concentration of N was observed in samples from regions with Cfa climate (humid subtropical, oceanic climate, without dry season with hot summer) and igneous rock, which was superior to regions with Cfb climate (humid subtropical, oceanic climate, without dry season with temperate summer) and metamorphic rock. Seeds can be a source of nutrients: K (11.8 g kg⁻¹), P (4.1 g kg⁻¹), Mn (9.1 mg kg⁻¹), Cu (7.2 mg kg⁻¹), Mo (0.93 mg kg⁻¹),

and Cr (0.65 mg kg⁻¹). Values for Ba (0.93 mg kg⁻¹) and Cd (0.19 mg kg⁻¹) indicated no risk to human health. This study expands knowledge regarding the elemental composition of *A. angustifolia*. Results indicate that these seeds have nutritional value, and their consumption can be a good strategy to improve overall human nutrition in this region of South America.

Keywords Recommended dietary allowances · Trace elements · Environmental variation · Conifers

Introduction

Commonly known as Brazilian Pine, Paraná Pine, or Candelabra Tree, *Araucaria angustifolia* (Bert) O. Ktze is a native tree of Brazil. Isolated individuals have also been found in northern Argentina and eastern Paraguay. Currently, *A. angustifolia* is on the list of endangered species since it occupies only 2% of its original range. However, economic, industrial, and cultural factors related to food usage of *A. angustifolia* seeds have contributed to the preservation of this species. Edible seeds of *Araucaria angustifolia* have been part of human diets as far back as pre-Columbian times (Reis et al. 2014; Polet et al. 2017). Cordenunsi et al. (2004) and Schweitzer et al. (2014) demonstrate that *A. angustifolia* seeds can be a source of starch and nutrients (e.g., Fe and Zn) lacking in human diets. In addition, there is current relevance to food technology investigation, especially in bakery products for people with celiac disease (Polet et al. 2017).

Araucaria angustifolia seed are primarily harvested from trees under native conditions in subtropical Brazil (extractivism) since there are few planted forests. In the region of occurrence, there are distinct environmental

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growth conditions (Alvares et al. 2013; Rabel et al. 2018). However, there is a lack of information regarding the nutritional composition of *A. angustifolia* seeds since past studies have only investigated isolated samples (Cordenunsi et al. 2004; Schweitzer et al. 2014). Thus, this study aimed to analyze the elemental composition of *A. angustifolia* seeds from a large area (175,200 km²) of subtropical Brazil to evaluate the level of toxic and beneficial elements and the possible implications for human health.

Materials and methods

Sampling areas and sample preparation

During June and September 2014, 35 seed samples of *A. angustifolia* were obtained from three southern states in Brazil (Paraná, Santa Catarina, and Rio Grande do Sul) (Online Resource 1; Online Resource 2). Seeds from mature fruits were collected from the ground below the tree canopy.

Samples were oven dried for 24 h (65 °C), seed shells were removed, and shelled seeds (pinions) were dried for an additional 48 h (65 °C). Only seeds with no visible damage were selected for analysis. Subsequently, dry pinion mass was calculated by the ratio of seed mass to seed number. Seeds were ground to pass through a 0.5 mm mesh.

Elemental analysis

Concentrations of carbon (C) and nitrogen (N) were determined by dry combustion in a non-metal element analyzer (Elementar, Vario EL III model, Hanau, Germany) using 15 mg per sample (analyzed in duplicate). Samples were weighed into sealed tin capsules and incinerated at a temperature of approximately 900 °C. Acetanilide (Acros Organics; Geel, Belgium) was used for instrument calibration.

Concentrations of other elements were determined by the wet method according to the SW-846 test method 3051A (Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils method; USEPA 2007). Concentrations of potassium (K), calcium (Ca), magnesium (Mg), phosphorous (P), iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), molybdenum (Mo), nickel (Ni), cobalt (Co), chromium (Cr), barium (Ba), and cadmium (Cd) in extracts were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, axial mode; Varian 720-ES model, Mulgrave, Victoria, Australia). For ICP-OES calibration, solutions containing increasing concentrations of analyzed elements were prepared from a

multi-elemental standard solution (QuimLab, Curitiba, Brazil).

Estimating nutritional value

The nutritional value of *A. angustifolia* seeds was estimated by comparing element intake values (established from different indices) using 100 g seed portions (wet basis). Wet basis was used in calculations since *A. angustifolia* seeds are consumed at an average moisture content of 45% (Cordenunsi et al. 2004; Schweitzer et al. 2014). However, to obtain intake values closer to consumption conditions, content of elements in 55 g of seeds (dry basis) was considered to be equivalent to elemental content in a 100 g wet basis portion. The daily intake indices used for adults were as follows: recommended dietary allowances (RDA) for protein, K, Ca, P, Mg, Fe, Zn, Mn, Cu, Mo, and Cr; tolerable upper intake (TUI) for Mo, Co, Ba, Ni, and Cd; and estimated intake (EI) for Cr (WHO 1996; IOM 2001; FSA 2003; SCHER 2012). Protein values were estimated from total tissue N by multiplying by a conversion factor of 6.25.

Statistical analysis

For all data, we present descriptive statistics. In addition, seed dry matter and element concentration results were analyzed considering four sample groups representing different climatic conditions and parent rock (I—Cfa/igneous; ten samples; II—Cfb/igneous, eight samples; III—Cfb/sedimentary, twelve samples; and IV—Cfb/metamorphic, five samples). The data were subjected to the Shapiro–Wilk normality test, and normal data were subjected to the F test, while other data were subjected to the Kruskal–Wallis test. There was significant variation only in the Kruskal–Wallis test ($p < 0.05$), thus the Dunn's test was applied to differentiate treatment effects ($p < 0.05$) for N concentrations. Statistical analyses were performed with the Assistat 7.7 program.

Results and discussion

Elemental composition

Mean C, K, N, and P content indicate that these were the four main nutrients in *A. angustifolia* seeds (Table 1). On average, 95.7% of inorganic constituents (excluding C) of *A. angustifolia* seeds were represented by K, N, and P (primarily soil derived), with K and N representing ~ 80.4%, corroborating results from other studies (Schweitzer et al. 2014; Cordenunsi et al. 2004; Liang et al. 2015).

Table 1 Results of dry matter and elemental composition of Brazilian pine (*Araucaria angustifolia*) seeds from subtropical Brazil

Variable	Unity	Mean	Median	SD	Maximum	Minimum
Dry matter	g seed ⁻¹	3.43	3.33	0.65	5.20	2.52
C	g kg ⁻¹	383	382	9	408	370
N	g kg ⁻¹	10.0	9.9	1.1	12.5	8.1
K	g kg ⁻¹	11.8	11.7	1.1	14.7	9.7
P	g kg ⁻¹	4.18	3.92	0.80	5.99	2.77
Ca	g kg ⁻¹	0.29	0.28	0.08	0.52	0.11
Mg	g kg ⁻¹	0.78	0.79	0.07	0.89	0.62
Fe	mg kg ⁻¹	25.83	23.08	10.42	61.51	15.71
Zn	mg kg ⁻¹	18.86	18.55	3.48	24.18	10.91
Mn	mg kg ⁻¹	9.11	8.72	4.14	19.74	2.40
Cu	mg kg ⁻¹	7.23	7.13	1.56	10.50	4.87
Ni	mg kg ⁻¹	1.30	0.95	0.73	3.42	0.70
Mo	mg kg ⁻¹	0.93	0.89	0.16	1.36	0.69
Ba	mg kg ⁻¹	0.93	0.85	0.39	2.07	0.27
Co	mg kg ⁻¹	0.45	0.39	0.13	0.79	0.32
Cr	mg kg ⁻¹	0.65	0.49	0.36	1.76	0.35
Cd	mg kg ⁻¹	0.19	0.19	0.01	0.23	0.17

Ca and Mg content in *A. angustifolia* seeds from subtropical Brazil (Table 1) were similar to those observed in other studies (same species), but lower than seeds of other species such as Brazil nuts (Naozuka et al. 2011) and walnuts (Rodushkin et al. 2008). A convergent aspect among these species is that Mg concentrations are approximately double that of Ca. Seed Ca and Mg variations may be due to reduced Ca phloem transport aggravated by lower transpiration of fruits compared to leaves. In addition, Ca has less remobilization from leaf and branch tissues since it is predominantly associated with cell walls (White 2012) and oxalate crystals (Barbosa et al. 2017).

Micronutrients with the highest concentrations were Fe and Zn, and Mo and Ni were the lowest (Table 1). While there was wide variation in micronutrient in seeds or nuts of various species, the highest concentrations occur for Fe, Zn, or Mn (Anderson and Smith 2005; Naozuka et al. 2011; Vanhanen and Savage 2013; Souza et al. 2014). Concentrations of Fe and Zn ranged from 15.7 to 61.5 mg kg⁻¹ and 10.9 to 24.1 mg kg⁻¹ (Table 1), suggesting *A. angustifolia* may have genetic potential for genotype selections for higher concentrations of these nutrients.

The mean Ba content in *A. angustifolia* seed (Table 1) was similar to or lower than reported for other nuts and seeds (Rodushkin et al. 2008). In general, Co and Cr concentrations in seeds and nuts varied between 0.07 and 1.9 and 0.01 and 5.9 mg kg⁻¹, respectively (Özkutlu et al. 2011; Vanhanen and Savage 2013; Liang et al. 2015). Thus, concentrations of these elements in *A. angustifolia* seeds (Table 1) were similar to concentrations recorded in other species. The average Cd content in *A. angustifolia*

seeds was 0.19 mg kg⁻¹ (Table 1) below the maximum level allowed for polished rice (0.4 mg kg⁻¹) and wheat (0.2 mg kg⁻¹) (CAC 2015).

Nitrogen was the only element with varying concentration among the classification groups (Fig. 1). The average N concentration was 10.8 g kg⁻¹ in Group I, which was higher than the 9.2 g kg⁻¹ observed in Group IV (Cfb/metamorphic rock). Group II (Cfb/igneous rock) and Group III (Cfb/sedimentary rock) did not differ among groups, with mean concentrations of 9.9 and 10.1 g kg⁻¹, respectively. In general, soils originating from basalt material in Group I (Cfa/igneous rock) are clayey or very

Fig. 1 Nitrogen concentration of *Araucaria angustifolia* seeds. The lower boundary of the box indicates the 25th percentile and the upper boundary, the 75th. Whiskers above and below the box indicate the 95th and 5th percentiles. Lines within the box mark the median (solid line) and mean (dash line). Group I: Cfa/igneous rock; Group II Cfb/igneous rock; Group III: Cfb/sedimentary rock; Group IV: Cfb/metamorphic rock. Different lowercase letters (a, b) inside boxes indicate that groups differ by Dunn's test ($p < 0.05$)

clayey and generally have high organic matter content. During summers in Brazil (December to March), the hot (average temperature ≥ 22 °C) Cfa climate (Alvares et al. 2013) may have favored organic matter decomposition. It is important to note that summer environmental variations can influence *A. angustifolia* trees since this is the period of most intense growth and seed filling. However, seed N concentrations observed in Groups II and III do not seem to be solely influenced by climate, indicating that other factors such as genetic variation, atmospheric N, and edaphic conditions may have influenced results. Studies with more intensive sampling are required to confirm these results and to explore the effects on other elements.

Nutritional value

Protein contribution from seed intake ranged from 5.0 to 7.7% of recommended dietary allowance (Table 2). In comparison, *A. angustifolia* seeds contribute less to protein intake than legume seeds, nuts, amaranth, maize, wheat and barley, but approach that of white rice (Young and Pellett 1994; King et al. 2008). However, it is important to emphasize that these protein contribution values are only approximate indicators of dietary contributions since amino acid composition, antinutritional factors (tannins, amylase inhibitors, cyanogen), and food preparation

techniques can influence overall protein utilization (Young and Pellett 1994). In the case of *A. angustifolia* seeds, the most traditional form of preparation is by cooking in water, which has an inexpressive effect on protein concentration, raises total phenolics and quercetin concentrations (probably from the seed coat), and decreases amylose, glucose, fructose, and sucrose (Cordenunsi et al. 2004). Although *A. angustifolia* seeds (Table 2) contribute less to protein intake compared to other seeds (Young and Pellett 1994; King et al. 2008), the amino acid composition resembles that of cereals such as wheat and corn (Leite et al. 2008). Additionally, these authors reported that lysine was present in higher quantities than observed in wheat, corn, and rice flours, and that methionine and valine were higher in comparison to soybean.

A. angustifolia seeds contributed more than 18% of RDA values for K, P, Mn, Cu, Mo, and Cr (Table 2). Evaluating the nutritional value of *A. angustifolia* seeds, Cordenunsi et al. (2004) observed that only Mg and Cu were supplied in considerable amounts relative to RDA values. An elemental evaluation of *A. angustifolia* seeds from the state of Santa Catarina (Brazil) found that these seeds were a great source of P, Mg, Fe, Mn, and Cu for human diets (Schveitzer et al. 2014). While *A. angustifolia* seeds are not high in protein, they are low in sodium (Na), a vitamin C source (28 mg 100 g⁻¹) (NEPA 2011), and their

Table 2 Contribution to the recommended dietary allowances (RDA), tolerable upper intake (TUI), and estimated intake (EI) indices with the consumption of 100 g of *Araucaria angustifolia* seeds from southern Brazil

Element	Index	Value	RDA, TUI or EI contribution (%)				
			Mean	Median	SD	Maximum	Minimum
Protein ^a	RDA	51 g	6.2	6.1	0.7	7.7	5.0
K ^b	RDA	3500 mg	18.5	18.4	1.6	23.2	15.2
P ^a	RDA	700 mg	32.8	30.6	6.3	47.1	21.8
Ca ^a	RDA	1000 mg	1.6	1.6	0.5	2.9	0.7
Mg ^a	RDA	370 mg	11.7	11.8	1.0	13.3	9.2
Fe ^a	RDA	14 mg	9.7	9.0	3.2	20.9	6.2
Mn ^a	RDA	2.0 mg	25.0	23.1	11.2	54.3	6.7
Zn ^a	RDA	9 mg	11.4	11.8	2.0	14.8	6.7
Cu ^a	RDA	0.90 mg	43.6	43.4	8.3	64.2	29.2
Mo ^a	RDA	45 µg	115	93	20.7	165	84.6
Mo ^a	TUI	2000 µg	2.6	2.5	0.5	3.7	1.9
Cr ^a	RDA	30 µg	121	115	64.9	321	64.6
Cr ^b	EI	770 µg	4.7	3.6	2.5	12.5	2.5
Ni ^d	TUI	1000 µg	7.2	6.1	3.9	18.8	3.8
Ba ^c	TUI	1300 µg	4.0	3.6	1.7	8.7	1.1
Co ^b	TUI	1400 µg	1.8	1.6	0.5	3.1	1.3
Cd ^d	TUI	65 µg	16.3	16.3	0.9	19.2	14.3

The portion of 100 g is on a wet basis, and the raw or prepared seeds have ~ 45% moisture

^aIOM (2001)

^bFSA (2003)

^cSCHER (2012)

^dWHO (1996)

consumption can help meet recommended intake values for several nutrients (Table 2).

Despite the average contribution of Mo and Cr exceeding 100% of RDA, the values are within the maximum tolerated limit (TUI) for Mo and the estimated mean intake (EI) for Cr. With stone pine cultivated in New Zealand, Vanhanen and Savage (2013) reported that the consumption of 50 g of seeds provides a contribution above RDA critical levels for Cr, Cu, Mg, Mn, and Zn.

Conclusion

C, N, K, P, Ca, Mg, Fe, Mn, Zn, Cu, Ni, Mo, Ba, Cr, Co, and Cd content in *A. angustifolia* seeds were generally similar to those reported for other seeds. The lithology and climate of southern Brazil affected only the N concentration of *A. angustifolia* seeds from subtropical Brazil. Based on the estimated contributions to RDA, *A. angustifolia* seeds can be a source of beneficial nutrients (primarily K, P, Mn, Cu, Mo, and Cr), while values for Ba and Cd do not indicate health risks. Thus, consumption of *A. angustifolia* seeds can be a good strategy to improve overall human health.

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References

- Alvares CA, Stape JL, Sentelhas PC, Gonçalves JLM, Sparovek G (2013) Köppen's climate classification map for Brazil. *Meteorol Z*. <https://doi.org/10.1127/0941-2948/2013/0507>
- Anderson KA, Smith BW (2005) Use of chemical profiling to differentiate geographic growing origin of raw pistachios. *J Agric Food Chem* 53:410–418. <https://doi.org/10.1021/jf048907u>
- Barbosa JZ, Constantino V, Zanette F, Motta ACV, Prior SA (2017) Soil fertility affects elemental distribution in needles of the conifer *Araucaria angustifolia*: a microanalytical study. *Cerne* 23:257–266. <https://doi.org/10.1590/0104776020172302313>
- CAC (2015) General standard for contaminants and toxins in food and feed. Food and Agriculture Organization/World Health Organization, Rome
- Cordenunsi BR, Menezes EW, Genovese MI, Colli C, Souza AG, Lajolo F (2004) Chemical composition and glycemic index of Brazilian pine (*Araucaria angustifolia*) seeds. *J Agric Food Chem* 52:3412–3416. <https://doi.org/10.1021/jf0348141>
- FSA (2003) Safe upper levels for vitamins and minerals. Food Standards Agency, York
- IOM (2001) Dietary reference intakes for vitamin A, vitamin K, arsenic, boron, chromium, copper, iodine, iron, manganese, molybdenum, nickel, silicon, vanadium, and zinc. National Academy Press, Washington
- King JC, Blumberg J, Ingwersen L, Jenab M, Tucker KL (2008) Tree nuts and peanuts as components of a healthy diet. *J Nutr* 138:1736–1740. <https://doi.org/10.1093/jn/138.9.1736S>
- Leite DM, Jong EV, Noreña CP, Brandelli A (2008) Nutritional evaluation of *Araucaria angustifolia* seed flour as a protein complement for growing rats. *J Sci Food Agric* 88:1166–1171. <https://doi.org/10.1002/jsfa.3192>
- Liang Y, Qing T, Zhang SX, Yin KX, Qin JY (2015) Determination of trace elements in edible nuts in the Beijing market by ICP-MS. *Biomed Environ Sci* 28:449–454. <https://doi.org/10.3967/bes2015.063>
- Naozuka J, Vieira EC, Nascimento NA, Oliveira PV (2011) Elemental analysis of nuts and seeds by axially viewed ICP OES. *Food Chem* 124:1667–1672. <https://doi.org/10.1016/j.foodchem.2010.07.051>
- NEPA (2011) Tabela brasileira de composição de alimentos. NEPA-UNICAMP, Campinas
- Özkutlu F, Dogru YZ, Özenç N, Yazici G, Turan M, Akçay F (2011) The importance of Turkish hazelnut trace and heavy metal contents for human nutrition. *J Soil Sci Environ Manag* 2:25–33
- Polet JP, Oliveira VR, Rios ADO, Souza CGD (2017) Physico-chemical and sensory characteristics of gluten-free breads made with pine nuts (*Araucaria angustifolia*) associated to other flours. *J Culin Sci Technol*. <https://doi.org/10.1080/15428052.2017.1405861>
- Rabel DO, Motta ACV, Barbosa JZ, Melo VF, Prior SA (2018) Depth distribution of exchangeable aluminum in acid soils: a study from subtropical Brazil. *Acta Sci Agron* 40:e39320. <https://doi.org/10.4025/actasciagron.v40i1.39320>
- Reis MS, Ladio A, Peroni N (2014) Landscapes with *Araucaria* in South America: evidence for a cultural dimension. *Ecol Soc*. <https://doi.org/10.5751/es-06163-190243>
- Rodushkin I, Engström E, Sörlin D, Baxter D (2008) Levels of inorganic constituents in raw nuts and seeds on the Swedish market. *Sci Total Environ* 392:290–304. <https://doi.org/10.1016/j.scitotenv.2007.11.024>
- SCHER (2012) Assessment of the tolerable daily intake of barium. European Commission, Brussels
- Schweitzer B, Rosa AM, Granemann P, Klock AL, Rizzatti IM, Foppa T (2014) Caracterização química de pinhões – sementes de *Araucaria angustifolia* – em diferentes formas de preparo. *Rev Interdiscip Estud Saúde* 3:93–104
- Souza NE, Rodrigues AC, Souza AHP, Matsushita M, Pedrão MR, Dias LF (2014) Quantification of minerals and topopherols isomers in chestnuts approach chemometrics. *Semina Ciênc Agrár* 35:2427–2436. <https://doi.org/10.5433/1679-0359.2014v35n5p2427>
- USEPA (2007) SW-846 Test method 3051A: microwave assisted acid digestion of sediments, sludges, soils, and oils. Office of Solid Waste/USEPA, Washington
- Vanhanen LP, Savage GP (2013) Mineral analysis of pine nuts (*Pinus* spp.) grown in New Zealand. *Foods* 2:143–150. <https://doi.org/10.3390/foods2020143>
- White PJ (2012) Ion uptake mechanisms of individual cells and roots: short-distance transport. In: Marschner P (ed) Marschner's mineral nutrition of higher plants. Academic Press/Elsevier, Amsterdam, pp 7–47
- WHO (1996) Trace elements in human nutrition and health. WHO Library, Geneva
- Young VR, Pellett PL (1994) Plant proteins in relation to human protein and amino acid nutrition. *Am J Clin Nutr* 59:1203–1212

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